Reactive P-Block Cations Stabilized by Weakly Coordinating Anions

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Content

Abstract

The chemistry of the p-block elements is a huge playground for fundamental and applied work. With their bonding from electron deficient to hypercoordinate and formally hypervalent, the p-block elements represent an area to find terra incognita. Often, the formation of cations that contain p-block elements as central ingredient is desired, for example to make a compound more Lewis acidic for an application or simply to prove an idea. This review has collected the reactive p-block cations (rPBC) with a comprehensive focus on those that have been published since the year 2000, but including the milestones and key citations of earlier work. We include an overview on the weakly coordinating anions (WCAs) used to stabilize the rPBC and give an overview to WCA selection, ionization strategies for rPBC-formation and finally list the rPBC ordered in their respective group from 13 to 18. However, typical, often more organic ion classes that constitute for example ionic liquids (imidazolium, ammonium, etc.) were omitted, as were those that do not fulfill the – naturally subjective – “reactive”-criterion of the rPBC. As a rule, we only included rPBC with crystal structure and only rarely refer to important cations published without crystal structure.

This collection is intended for those who are simply interested what has been done or what is possible, as well as those who seek advice on preparative issues, up to people having a certain application in mind, where the knowledge on the existence of a rPBC that might play a role as an intermediate or active center may be useful.

Abbreviations

CN	Coordination number
DFT	Density Functional Theory
ε_r	relative Permittivity of a Solvent (static Dielectric Constant)
FLP	Frustrated Lewis Pairs
IL	Ionic Liquid
n.a.	not available
rPBC	reactive P-Block Cations
WCA	Weakly Coordinating Anion
Ar^{CF3}	$3,5\text{-}(CF_3)_2C_6H_3$
Ar^{Cl}	$3,5\text{-}Cl_2\text{-}C_6H_3$
9BBN	9-bora[3.3.1]bicyclononane
bipy	1,2-Bipyridine
BOX	Bis(oxazoline)
CatBH	Catecholborane/ 1,3,2-Benzodioxaborole
COD	1,5-Cyclooctadiene
Cp	C_5H_5
Cp’	C_5Me_4H
Cp*	C_5Me_5
Cy	Cyclohexyl
DDP	2-(DIPP)amino-4-(Dipp)imino-2-pentene
Dipp	$2,6\text{-}{}^{i}Pr_2\text{-}C_6H_3$
DMAP	4-Dimethylaminopyridine
DMeOPrPE	1,2-(bis(dimethoxypropyl)-phosphino)ethane
DMH	$1,1\text{-}Me_2N_2H_4$
Dmp	2,6-dimethyl-phenyl
dmpe	1,2-Bis(dimethylphosphino)ethane
Do	Donor
DPE	1,2-Diphenylethane
dppe	1,2-Bis(diphenylphosphino)ethane
DTBMP	2,6-Di-*tert*-butyl-4-methylpyridine
dtbpy	4,4’-Di-*tert*-butyl-2,2’-bipyridyl
Et	Ethyl
Fc	Ferrocenyl
FP	$CpFe(CO)_2$
FP’	$Cp'Fe(CO)_2$
FP*	$Cp^{*}Fe(CO)_2$
hppH	1,3,4,6,7,8-hexahydro-2*H*pyrimido-[1,2-a]pyrimidine
IMe	1,3-Bis(methyl)imidazol-2-ylidene
IMes	1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene
^{i}Pr	*iso*-Propyl
$^{i}Pr_2$-ATI	*N,N‘*-Diisopropylaminotroponiminate
IPr	1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene
I^{t}Bu	1,3-Bis(*tert*-butyl)imidazol-2-ylidene
3,5-lutidine	3,5-Dimethylpyridine
Me	Methyl
Me_4-cyclam	*N,N’,N’’,N’’’*-Tetramethyl-1,4,8,11-tetraazacyclotetradecane
Mes	$2,4,6\text{-}Me_3C_6H_2$
$Me_3SiS^{p}Tol$	$1\text{-}SSiMe_3\text{-}4\text{-}Me\text{-}C_6H_4$
Me_3-tacn	*N,N’,N’’*-trimethyl-1,4,7-triaza-cyclononane
nacnac	$(NMesCMe)_2CH$
NBD	2,5-Norbornadiene
NPPh	2,5-Bis(2-pyridyl)-1-phenylphosphole
1-MIM	*N*-Methylimidazole
m-TP	*meta*-Terphenyl
OSSO	*trans*-1,2-cyclooctanediyl-bridged [OSSO]-type bis(phenolate)
OR^{PF}	$\text{-}OC(CF_3)_3$
OR^{HT}	$\text{-}OC(CH_3)(CF_3)_2$
OR^{HF}	$\text{-}OC(H)(CF_3)_2$
OR^{MeF}	$\text{-}OC(CH_3)(CF_3)_2$
Ph	$\text{-}C_6H_5$
Phen	1,10-Phenanthroline
4-Pic	4-Methylpyridine
Pip	Piperidyl
PMAF	Pentamethylazaferrocene
pmdta	*N*,*N*,*N*′,*N*′,*N*′′-pentamethyldiethylenetriamine
PNP	Bis(2-$^{i}Pr_2P\overline{4}$-Me-phenyl)amido
Py	Pyridine
Pytsi	$C(SiMe_3)_2SiMe_2(2\text{-}C_5H_4N)$
p-Xyl	*para*-Xylene
R	typical univalent organic Residue
Salen	*N,N*‘-Ethylenebis(2-hydroxyphenyl)imine
$Salen^{CF3}$	*N,N*‘-Ethylenebis(2-hydroxy-2-$(CF_3)_2$-ethyl)imine
Salomphen	*N,N’*-(4,5-dimethyl)phenylene-bis(2-hydroxyphenyl)imine
Salpen	*N,N*‘-Propylenebis(2-hydroxyphenyl)imine
Sch	tridentate Schiff base
SubPc	Subphthalocyanine
tacn	$1,4\text{-}{}^{i}Pr_2$-1,4,7-triaza-cyclononane
^{t}Bu	*tert*-Butyl
Tf	$\text{-}SO_2CF_3$
THF	Tetrahydrofuran
$timtmb^{tBu}$	1,3,5-{tris(3-tert-butylimidazol-2-ylideno)methyl}-2,4,6-trimethylbenzene
TMM	$\eta^4\text{-}C(CH_2)_3$
Tol	Toluene
Tipp	$2,4,6\text{-}{}^{i}Pr_3\text{-}C_6H_2$
X	Halogen

Introduction

Main Group Chemistry continues to reside at the heart of fundamental as well as applied chemistry. As such, recent years have seen an enormous growth of concepts that shed new light on hitherto undiscovered, or more correctly, underdeveloped areas of main group chemistry. Thus, the availability of stable singlet carbenes[1] as strong donors offered tremendous new perspectives as did the establishment of the frustrated Lewis pairs (FLP) concept[2] or the systematic investigation of (often low valent) cationic mixed main group-transition metal salts.[3–5] In the framework of those approaches, next to other fundamental[6] and applied questions,[7–10] also the stabilization or use of reactive p-block cations (rPBC) with weakly coordinating anions (WCAs) was one focus that led to fascinating new rPBC. This review gives a comprehensive overview on recent rPBC developments since about 2000, but also cites all-time classics in the field. It also includes the fascinating class of transition metal substituted rPBC for which the assignment of the positive charge to one specific moiety is often not clear.

Scope of this Review: Many of the p-block elements have relatively high ionization potentials and electronegativities. Thus, most of the stable examples base on delocalization and other electronic or steric effects. In addition, rPBC are often very electrophilic and/or oxidizing. Therefore, chemically stable and inert weakly coordinating anions (WCAs) and solvents are needed to access their salts. These ingredients allowed the syntheses of a large number of fundamentally interesting rPBC of the groups 13-18 in the condensed phase. We discuss typical synthesis routes, give a brief overview of the WCAs, and describe the rPBC ordered according to their main group as well as cation class. However, typical, often more organic ion classes that constitute for example ionic liquids (imidazolium, ammonium, etc.) were omitted, as were those that do not fulfill the – naturally subjective – “reactive”-criterion of the rPBC. As a rule, we only included rPBC with crystal structure and only rarely refer to important cations published without crystal structure.

Handling of Substance Classes with Recent Reviews: Some of the substance classes, which fit into this review were just recently and sometimes very comprehensively reviewed (cf. our contribution describing the advances in the synthesis of homopolyatomic cations of the non-metals since 2000[11]). To reduce the overlap, we decided to give an overview on general aspects such as WCAs in **Table 1** and include a short table with relevant reviews for each main group at the beginning of each main group chapter and only list the compounds in these cases. Therefore, we only list, but do not describe the cations of this category in the chapters of their corresponding element. Nevertheless, the scope of this review is rather large, which in any case precludes extensive discussions and mainly serves as an overview on what is known.

Reactive p-Block Cations

The rPBC in this article need a WCA as counterion and, therefore, we first briefly describe typical WCAs and give some advice on their selection before turning to typical ionization and synthesis procedures for rPBC preparations. Thereafter, the ordering of the cation classes for the individual sections is described, and finally the rPBC are addressed grouped according to the main group of the relevant cationic entry. In addition, first applications emerged for rPBC salts and will be highlighted in the respective cation sections.

WCA Overview

Because of their potential in fundamental and applied chemistry,[12–15] a great variety of different WCA types are currently known (**Figure 2**) and was frequently reviewed (**Table 1**).

Table 1. General reviews with focus on WCAs.

Year	Topic	Title	Ref
1993	WCAs	The search for larger and more weakly coordinating anions	15
1998	WCAs	Carboranes: A New Class of Weakly Coordinating Anions for Strong Electrophiles, Oxidants, and Superacids	16
2004	WCAs	Noncoordinating anions—fact or fiction? A survey of likely candidates	13,12
2006	WCAs	Chemistry with weakly-coordinating fluorinated alkoxyaluminate anions: Gas phase cations in condensed phases?	14,15, 17
2006	WCAs	Chemistry of the Carba-*closo*-dodecaborate(−) Anion, $[CB_{11}H_{12}]^-$	18
2008		π-Complexation of Post-Transition Metals by Neutral Aromatic Hydrocarbons: The Road from Observations in the 19th Century to New Aspects of Supramolecular Chemistry	19
2013	WCAs	Weakly Coordinating Anions: Halogenated Borates and Dodecaborates	20
2013	WCAs	Weakly Coordinating Anions: Fluorinated Alkoxyaluminates	21
2013	WCAs	Weakly Coordinating Anions: Highly Fluorinated Borates	22
2015	WCAs	Taming the Cationic Beast: Novel Developments in the Synthesis and Application of Weakly Coordinating Anions (to be submitted by IK et al. in October 2015)	23

But which out of the multitude of published WCAs shown in **Figure 2** should be used for a given problem…? Is there one best WCA that fulfills all needs…?

Clearly holds: The more reactive the rPBC are, the more demanding is the task for the anions, to meet the requirements for a successful stabilization in the condensed phase. Some of this reactivity may be dampened kinetically by the use of suitable bulky ligands, e.g. for the silylium ions. **However, there is not one ultimate WCA that fulfills all requirements** to allow for use with all in here described rPBC. Typically, rPBC follow at least one of the following classifications:

- Being a strong electrophile, thus having a strong tendency to coordinate an anion or solvent. Silylium ions SiR_3^+ are good examples for this. This coordination is often the entrance towards an anion degradation by heterolytic cleavage of a bond in the WCA.
- Being a strong oxidant, thus needing anions and solvents compatible with this need. Halogen

and noble gas cations are typical examples.

- Being a weakly bound complex, in which the interesting main group particle can easily be displaced by anion or solvent, just as in many metal-non-metal clusters. This includes protonated, weakly basic molecules that tend to pass the proton to more basic and more coordinating anions or solvents.

Thus, the demand for very weak coordination behaviour is only medium for several very oxidizing cations, but the necessity of the WCA being stable against oxidation is a prerequisite of highest importance. For example, the typical counterions of group 16 to 18 rPBC are fluorometallates like $[MF_6]^-$ or $[M_2F_{11}]^-$ (M = As, Sb) compatible with i) the oxidizing power of the cation and ii) the typically used super acid solvents. However, despite the fact that fluoroantimonates allow for the synthesis of tremendously oxidizing cations like $[Xe_2]^+$, they fail to stabilize the extreme electrophiles $[SiR_3]^+$ and form F-SiR_3 and antimony pentafluoride. On the other hand, with some steric protection at the silylium ion, already the $[B(C_6F_5)_4]^-$ WCA suffices to stabilize for example the $[Si(Mes)_3]^+$ cation. By contrast, and due to the aromatic system, $[B(C_6F_5)_4]^-$ is not compatible with the only mildly oxidizing NO^+ or NO_2^+ cation. Some thoughts that allow for the selection of a suitable WCA for a given problem may be summarized by the triangle shown in **Figure 1**.

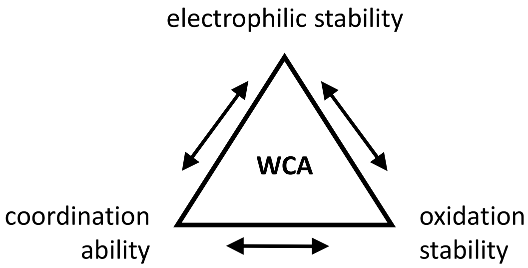


Figure 1. Triangle delineating the independent demands of a rPBC that lead to different mixtures of the WCA properties necessary for its successful stabilization.

With **Figure 1** in mind, a personal selection of the “best WCAs” includes $[1\text{-H-}CB_{11}Me_5Br_6]^-$,[24] $[1\text{-Et-}CB_{11}F_{11}]^-$,[25] $[CB_{11}(CF_3)_{12}]^-$,[26] $[Sb_4F_{21}]^-$,[27] $[Sb(OTeF_5)_6]^-$,[28] $[Al(OR^{PF})_4]^-$ [29–31], $[B(C_6F_5)_4]^-$[32–34] and $[B(CF_3)_4]^-$.[35] A recent noteworthy addition overcoming the frequent disorder of the also towards fluoride abstraction less stable $[B(Ar^{CF3})_4]^-$ anion is the $[B(Ar^{Cl})_4]^-$ WCA.[36]

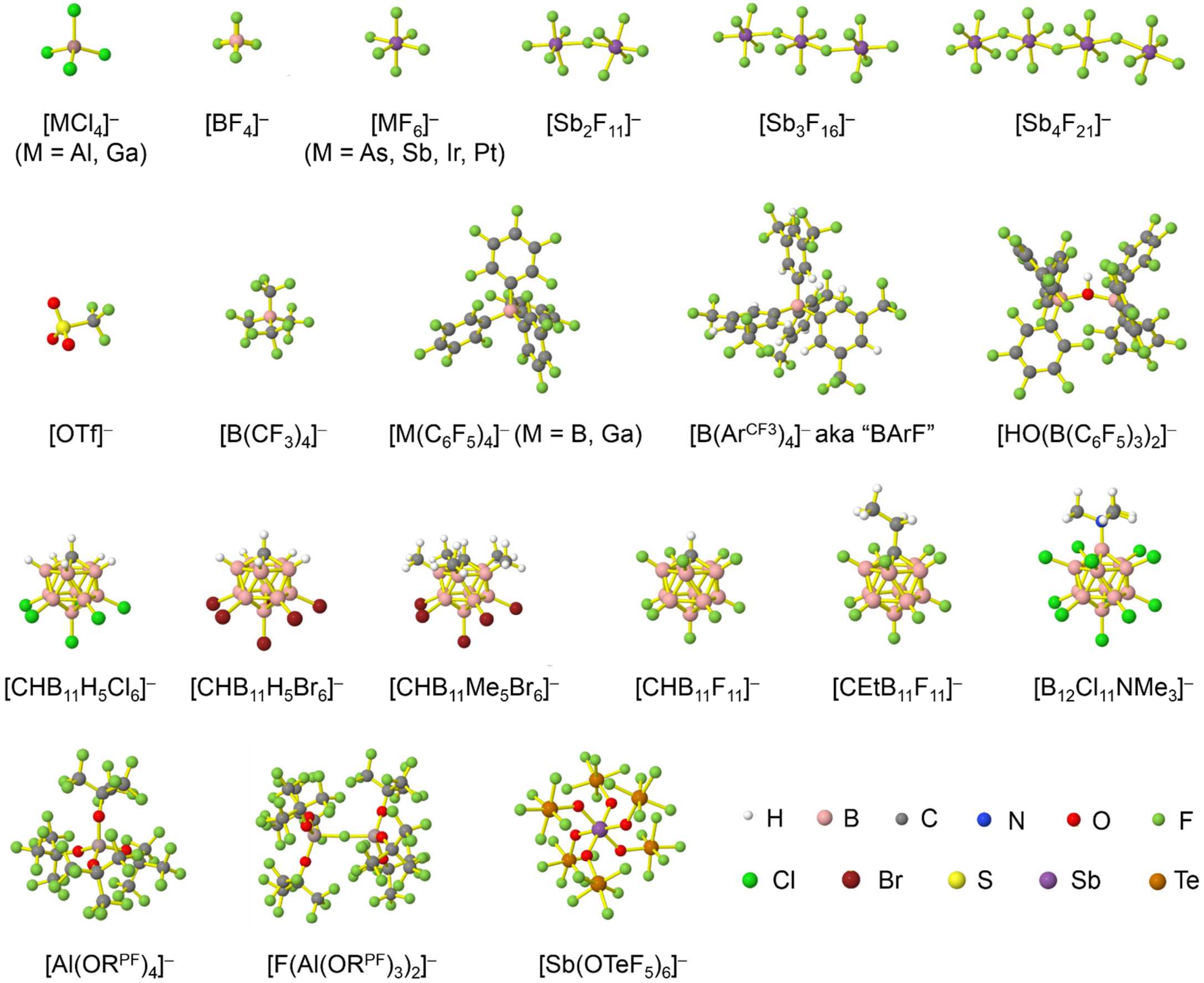


Figure 2. Some of the weakly coordinating anions discussed in this review.

Other aspects that will influence the choice, are the synthetic availability of the entire WCA class, or the specific starting material necessary to ionize the system of interest. In this respect, most of the WCAs known so far also do have disadvantages: The carborates are hard to synthesize and have often low yields. $[CB_{11}(CF_3)_{12}]^-$ is even explosive, as is the LiC_6F_5 intermediate needed for the $[B(C_6F_5)_4]^-$ synthesis. In addition, starting materials such as solvent free Ag^+ salts or NO^+, NO_2^+ are not accessible as salts of $[B(C_6F_5)_4]^-$. Anions with multiple $–CF_3$ groups often tend to disorder in the solid state, which sometimes makes it hard to solve or refine the crystal structure. The problems associated with the refinement of structures with the $[Al(OR^{PF})_4]^-$ WCA even led to the development of the software tool DSR.[37] It allows for the simplified refinement of such disordered structures and is now implemented with standard programs like OLEX2.[38]

Therefore, the search for new useful anions is still in progress. With the amminated chloroborate cluster anion $[1\text{-}Me_3N\text{-}B_{12}Cl_{11}]^-$ another promising candidate that refined earlier ideas by S. Strauss et al.,[39] was just recently presented by Jenne et al. in 2014.[40] The positive charge of the ammonium function leads to an overall –1 charge and makes it possible to use the in 30 g scale accessible $–B_{12}Cl_{11}$ cluster residue. Important starting materials $M^+[1\text{-}Me_3N\text{-}B_{12}Cl_{11}]^-$ ($M^+ = Na^+$, $HNMe_3^+$, $HNOct_3^+$, NO^+, CPh_3^+, $N^nBu_4^+$, Et_3Si^+) have been described facilitating application.[41,40] More details on typical WCA starting materials to introduce a counterion into the given system can be found in the synthesis section below as well in the numerous WCA reviews cited in **Table 1**.

Synthesis Routes to Reactive Main Group Cation Salts

At the beginning, each proposal to prepare a target-rPBC needs to consider the choice of the WCA as delineated in the preceding section, as well as the available starting materials, ionization method and reaction medium.

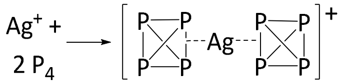
WCA Starting Materials: A suitable starting material, should be accessible in good yields and contain a useful cation that typically acts as either a strong oxidant (e.g. O_2^+ [42], NO^+[29], NO_2^+,[43] $N(arene)_3^+$ [44]) a halide- (e.g. Li^+ [45], Na^+, Ag^+ [46]), hydride- or alkyl-abstractor (CPh_3^+ [47]), a Brønsted acid ($(H(OEt_2)_2^+$ [48], $H(NMe_2Ph)^+$) or a metal cation, if a simple metal complex is desired as product (e.g. Cu^+ [49,50]) (**Table 2**). Neutral Lewis acids for bond heterolysis are available in great variety and include the classical simple halides $M^{III}X_3$ and M^VX_5 (M^{III} = B, Al, Ga; M^V = P, As, Sb, Bi; X = F, Cl, Br, I; not all combinations useful), the rather fine tunable $B(Aryl)_3$ acids (Aryl = fluorinated,[51] chlorinated[52] or fluoroalkylated[53] aromatic residue), or aluminum based systems like $Al(C_6F_5)_3$[54] and $Al(OR^F)_3$.[55] Also the *ion-like* $R_3Si(WCA)$ compounds have frequently been used.[56,57] Recent systematic work analyzed the potency of a given acid versus fluoride, chloride, hydride and methanide as a base. It includes benchmark Lewis acidity values for a smaller set of simple MX_n acids.[58] Neutral Brønsted acids like HF, $HNTf_2$ and derivatives thereof,[59] or combinations of Brønsted and Lewis Acids like $HBr/nAlBr_3$[60,61] are suitable for protonations. Novel, and in large quantity available very strong acids like $R^{HF}OSO_3H$[62] should also be mentioned.

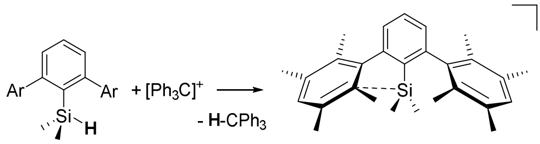
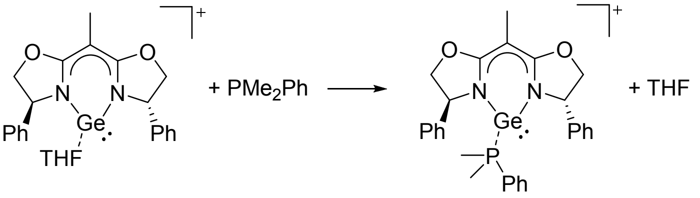
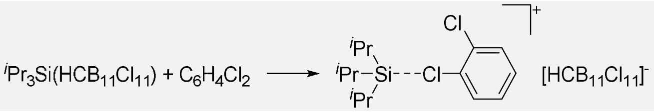
Suitable Media / Solvents: Since the synthesis of reactive ions is aspired, a suitable reaction medium should favorably be polar but not itself be a base or a nucleophile. This often rules out classical polar solvents that are itself good donors such as ethers or nitriles. Often chlorinated solvents CH_2Cl_2 (ε_r = 8.9), 1,2-$Cl_2C_2H_4$ (ε_r = 10.4) or Cl-Ph (ε_r = 5.7) tend to be good choices that nevertheless are incompatible with strong electrophiles like the silylium ions $[SiR_3]^+$. Fluorinated arenes like F-Ph (ε_r = 5.5) and 1,2-$F_2C_6H_4$ (ε_r = 13.4) are good additions that got cheaper (but not cheap) over the last decade. However, they are incompatible with oxidants like $[NO]^+$ or $[NO_2]^+$ due to nitration / nitrosation reactions. Especially for non-metal cations, often superacids or SO_2 (ε_r = 16.3), SO_2ClF (ε_r = n.a.) etc. are the solvents of choice. ILs[63] like acidic BMIM[$AlCl_4$][64,65] and others were shown in recent years to be very promising media for rPBC cation synthesis.[66,67,65] Especially for group 15 cations, solvent free reactions using $Me_3Si\text{-}OSO_2CF_3$ or MX_3 (M = Al, Ga; X = Cl, Br) were shown to provide quantitative yields of the desired salts. By contrast, several of such reactions do work only incomplete or not at all in solution.[68] Similarly, protonations with HBr/n$AlBr_3$ turned out to be best done solvent free.[61,60]

The recently established concepts of absolute acidity,[69] absolute reducity[70] and their two-dimensional combination as the protoelectric potential map[70] can be used to understand protonation and/or redox chemistry over medium / solvent and even phase boundaries. This also includes ILs and therefore a thermodynamically sound pH definition has been introduced for IL media.[61,71]

Ionization Protocols: Overall, we have categorized the rPBC included with the tables in the following sections by an acronym describing the synthetic approach used for their preparation. The synthesis routes are collected, explained and abbreviated in **Table 2**.

Table 2. Acronym (Acr.) and Type of the classified Synthesis Routes leading to rPBC.

Acr.	Type	Example	Ref
Com	Complexation reaction		72
Ox	Oxidation reaction; including 1 e⁻ and 2 e⁻ oxidations.	$Ag^+_{(solv)} + Ga^0_{(s)} \xrightarrow[1\,e^-\,Ox.]{+2\,arene} Ga(arene)_2{}^+_{(solv)} + Ag^0_{(s)}$ $S_8 + 3\,AsF_5 \xrightarrow[2\,e^-\,Ox.]{} S_8{}^{2+}([AsF_6]^-)_2 + AsF_3$	30,31
Lewis	Lewis acid induced halogen bond heterolysis With **neutral** Lewis acids,	$Mes_2B\text{-}\mathbf{F} + Et_3Si(HCB_{11}Cl_{11}) \longrightarrow [Mes_2B]^+[HCB_{11}Cl_{11}]^- + Et_3Si\text{-}\mathbf{F}$	32,33 73

	Including *ion-like* compounds.		
Salt	Salt elimination reaction	$[BCl_3(NHC)] + Na^+ \longrightarrow [BCl_2(NHC)]^+ + NaCl$	74
Hyd	Hydride metathesis reaction With *neutral* or *ionic* H⁻-acceptor	 [1]	76
Alk	Alkyl metathesis reaction With *neutral* or *ionic* R⁻-acceptor	$AlMe_3 + B(C_{12}F_9)_3 \xrightarrow{\text{in } Et_2O} [Me_2Al(OEt_2)_2]^+ [MeB(C_{12}F_9)_3]^-$	77
Ins	Insertion reaction	$P_4 + NO^+ \longrightarrow [P_4NO]^+$	78
Prot	Protonation reaction	$AlCp_3 + [H(OEt_2)_2]^+ [Al(OR^{PF})_4]^- \xrightarrow{-\ 2\ Et_2O} [AlCp_2]^+ [Al(OR^{PF})_4]^- + Cp\text{-}H$	79
Lig	Ligand exchange reaction		80
Ion	Ionization		81
Other	Other reaction not classified as one of the above	–	-

Almost all the early approaches to reactive main group cations used halide abstractors as the Lewis acids AsF_5 or SbF_5, which form the conjugated $[AsF_6]^-$ or $[SbF_6]^-$ WCAs through the reaction. The trityl cation is a hydride abstractor, which is especially in case of silanes as starting materials very useful to produce silylium cations. Most of the metal-non-metal complexes were synthesized by complexation of a non-metal molecule (e.g. P_4, S_8, Cl_2, Xe) with a metal salt of a WCA. The coinage metals Cu^I, Ag^I and Au^I with their d^{10} electron configuration induce positive charge on the main group elements, stabilize the almost undistorted non-metal clusters, and provide insights in their bonding situation. If the cation is a strong oxidant, it is also possible to oxidize neutral substrates directly to give reactive cations, which are in turn stabilized by the corresponding WCA. An interesting recent addition are the transfer oxidation of e.g. the simple diorganodichalcogenides R_2E_2 (E = S, Se) with the combination of XeF_2 (primary oxidant and source of fluoride) and a Lewis acid.[82]

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[1] This type of reaction is sometimes referred to as Bartlett-Condon-Schneider (BCS) type hydride transfer reaction.[75]

On the Representations of the Cation Chemical Structures

Note that the structural diagrams used throughout this review obey a distance criterion for interactions, but not necessarily a 2e2c-understanding of every interaction line. However, at least in the organic residue we attempted to follow an electron precise 2e2c picture. Necessarily, this gets difficult for structures with N-heterocyclic carbenes that formally allow for a neutral dative (imidazolyl) as well as ionic (imidazolium) description (**Figure 3**).

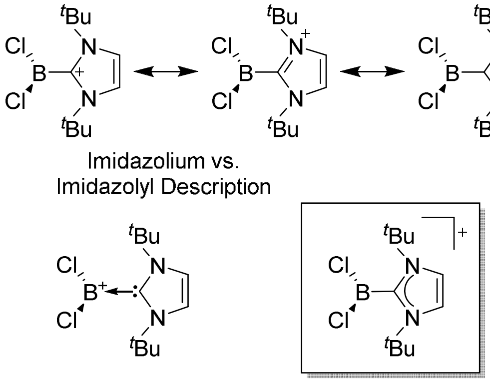


Figure 3. Possible descriptions of NHC-containing structures exemplified for the simple $[Cl_2B\text{-}I^tBu]^+$ cation.

For simplicity, we chose the representation shown in the box in **Figure 3** and adopted similar drawings for related cases throughout. Thus, we only use arrows for relatively weak interactions with the bonding situation in ammine-borane $H_3B\leftarrow:NH_3$ being the prototype as suggested by A. Haaland,[83] and later contributions.[84] For thoughts on these ongoing discussions, see these recent publications: [85]. Only if the positive charge can clearly (and not just formally) be attributed to one atom, we assigned the charge to this atom. More common is the case in the box in **Figure 3**, in which the charge may be delocalized to quite a series of atoms and therefore we placed the charge at the upper right corner.

Ordering of the Cation Classes

The rPBC were as far as possible ordered according to accepted cation classes that may either refer to the number of valence electrons (i.e. the *onium / enium / inium*-series) or to the structure. In each subchapter, we intend to go from homoatomic, to binary and then to more complex cation compositions. The not always consistently used classification according to **onium**- (8 VE), **enium**- (6 VE) and **inium**-cations (4 VE) presents some problems. Note, that the coordination number of a group 14 onium ion may not always be four, as the σ-donation of π-density of a donating double bond may increase the coordination number to 5 as, for example, in the 2-norbornyl cation, a carbonium ion.[86] Similar considerations hold for other donor coordinated onium- und enium-ions. Thus, we typically include the coordination number in the cation classification, for example as **Ligand substituted, (CN = 2)**. By contrast to these cation assignments, the group 15 to 18 cations were in addition classified by the oxidation state of the central atoms. This is often used for such rPBC. In addition, we included *ion-like* compounds that were initially defined for silylium compounds with coordinated counterions that structurally have to be addressed as a tight ion-pair but from the reactivity still bear a considerable amount of reactivity related to the free cation, e.g. see the ion like silylium compounds $R_3Si(WCA)$ in **Figure 4**:

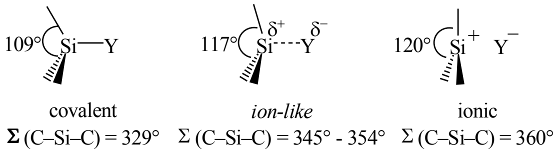


Figure 4. Definition of *ion-like* compounds as exemplified for silylium ions.

Related cases were published for coordinated aluminium cations, e.g. $R_2Al(WCA)$, and were used in a similar manner.[87] For *ion-like* compounds we keep the notation with the anion in parentheses and no charges written, as in $R_3Si(WCA)$ and $R_2Al(WCA)$. Heteropolyatomic clusters were discussed in the group of their most electropositive element (e.g. $[P_3Se_4]^+$ in group 15, but $[S_4N_4]^{2+}$ in group 16).

Group 13 Cations

Traditionally, group 13 chemistry is dominated by compounds in the +III oxidation state.[88] Of those, the simple halides are commonly applied as Lewis acid catalysts and initiators (e.g. BF_3) and usually associated with anion formation (e.g. $[BF_4]^-$). However, discrete trivalent group 13 **cations** have been found to be more reactive, owing to their greater electrophilicity if paired with coordinative unsaturation.[89,10] Except for boron, it has become increasingly possible to stabilize group 13 cations in their +I oxidation state, e.g. by employing bulky substituents and/or **WCAs**[90–92,31] (for thallium, this is the favored oxidation state due to the inert pair effect[93]). Featuring a lone pair of electrons and empty p-orbitals, the +I cations are ambiphilic and can function both as Lewis base or acid, thus offering unique reactivities and selectivities in organometallic chemistry,[94–97] as well as organic[98] and polymer[7,99] syntheses. Overall, different aspects of the chemistry of cationic group 13 compounds were reviewed and these contributions are compiled in **Table 3**. In this context, this sections intends to give a comprehensive overview of reactive group 13 cations of the larger WCAs since about 2000. Due to the large scope of this chapter, we mainly omit rPBC with the simple halometallate based counterions and only include those in special cases of high relevance.

Table 3. Review articles including cationic group 13 compounds.

Year	Group	Title	Ref
1985	13	Arene Complexes of Univalent Gallium, Indium and Thallium	100,101
1998	13	Cationic group 13 complexes	102
2004	13	From group 13–group 13 donor–acceptor bonds to triple-decker cations	94
2005	13	Borinium, Borenium, and Boronium Ions: Synthesis, Reactivity, and Applications	89

2007	13	Development of the Chemistry of Indium in Formal Oxidation States Lower than +III	103
2008	13	Borylene Transfer from Transition Metal Borylene Complexes	3
2008	13	Synthesis, Characterization, and Applications of Group 13 Cationic Compounds	95
2009	13	Highly electrophilic main group compounds: Ether and arene thallium and zinc complexes	90
2009	13	Transition metal borylene complexes: boron analogues of classical organometallic systems	104
2010	13	Electron-Precise Coordination Modes of Boron-Centered Ligands	105
2011	13	Coordination chemistry of group 13 monohalides	96
2011	13	New Light on the Chemistry of the Group 13 Metals	88
2011	13	The Chemistry of the Group 13 Metals in the +I Oxidation State	106
2011	13	Mixed or Intermediate Valence Group 13 Metal Compounds	107
2011	13	Coordination and Solution Chemistry of the Metals: Biological, Medical and Environmental Relevance	108
2012	13	Cationic Tricoordinate Boron Intermediates: Borenium Chemistry from the Organic Perspective	109
2012	13	Cyclopentadiene Based Low-Valent Group 13 Metal Compounds: Ligands in Coordination Chemistry and Link between Metal Rich Molecules and Intermetallic Materials	110
2012	13	Low-Oxidation State Indium-Catalyzed C–C Bond Formation	98
2013	13	1.17 – Low-Coordinate Main Group Compounds – Group 13	97
2013	13	Transition metal borylene complexes	5
2013	13	Boron, aluminum, gallium, indium and thallium	111
2015	13	Discrete Cationic Complexes for Ring-Opening Polymerization Catalysis of Cyclic Esters and Epoxides	10

Boron Cations

For a long time, boron cations have remained a chemical curiosity due to their redox lability. However and partly owing to the developments in the field of WCAs, more and more boron-based cations are being reported. Overall, the cations can be classified according to the coordination number at boron: i.e., di-, tri-, and tetra-coordinated boron cations are referred to as borinium, borenium and boronium cations. To this day, the boron cations have been most notably reviewed by Nöth (1985; a milestone in cationic boron chemistry),[112] Piers (2005; structural and bonding aspects)[89] and Vedejs (2012; reactivties and applications).[109]

Alkyl-/Aryl Substituted (CN = 2): To our knowledge, there is only one contribution to this class of compounds: i.e., the recently reported $[Mes_2B]^+$ borinium cation with the very good $[HCB_{11}Cl_{11}]^-$/$[B(C_6F_5)_4]^-$ WCAs.[113,32] Herein, the boron atom adopts a linear di-coordinated structure and the Mes substituents are aligned orthogonal to each other, allowing for a perfect shielding as well as π-donation into the empty p-orbitals of the highly electrophilic borinium cation (cf. the modelled delocalized molecular orbitals). The $[Mes_2B]^+$ cation is likely to become a textbook compound as it is the first borinium cation that does not rely on strongly π-donating heteroatom substituents (cf. the earlier reported $[({}^tBu_3PN)_2B]^+$ cation[114] in the section **Ligand Substituted (CN = 2)** in **Table 4**).

Ligand Substituted (CN = 3): Tri-coordinated borenium cations are not as electron deficient as the borinium cations and therefore more stable. Nonetheless, the cations can only be isolated in the solid state if chelating (e.g. phthalocyanine[115] and catecholborane[116,117]) or strongly σ-donating ligands (e.g. N-heterocyclic carbene I^tBu[74] or hexaphenylcarbodiphosphorane[118,119]) are applied. For the synthesis and reactivity of the $[BCl_2(I^{t}Bu)]^+$ cation, the nature of the WCA is crucial. Hence and though the cation can be prepared in the presence of $[AlCl_4]^-$, $[OTf]^-$ or $[B(Ar^{Cl})_4]^-$, only the latter allows for a structure with no notable cation-anion contact. This leads to an increased reactivity of the $[BCl_2(I^{t}Bu)]^+[B(Ar^{Cl})_4]^-$ salt.[74]

Ligand Substituted (CN = 4): Some of the tetra-coordinated boronium cations directly derive from the corresponding borenium cations: i.e., the tri-coordinated $[PMAF{-}9BBN)]^+$ cation (only stable in solution, as monitored by ^{11}B NMR spectroscopy) reacts with 1-MIM in a ligand exchange and addition reaction to form the tetra-coordinated $[(1\text{-}MIM)_2(9BBN)]^+$ cation (**Figure 5**).

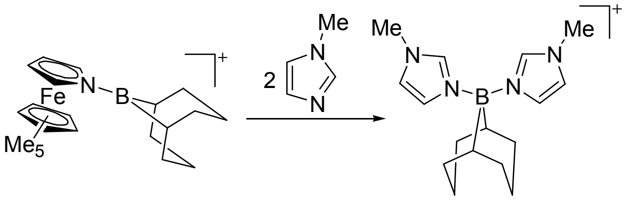


Figure 5. Synthesis of the $[(1\text{-}MIM)_2(9BBN)]^+$ boronium cation via a borenium cation precursor.

For the isolation of the discrete $[BH_2(PR_2H)_2]^+$ cation, the nature of the WCA is again essential: compared to $[OTf]^-$, $[B(Ar^{CF3})_4]^-$ features no hydrogen bond with the cation, thus allowing for increased reactivities.[120]

Transition-Metal Substituted: The number of transition-metal substituted boron cations is much higher than the one of related alkyl-/aryl- or heteroatom substituted compounds. Numerous contributions have been made by Braunschweig and Aldridge and both authors recently reviewed the chemistry of transition-metal borylene complexes.[3,104,5] The d-orbitals of the transition-metals allow for stabilizing σ- and π-interactions with the orbitals of boron (**Figure 6**) and of all the ligands the $FeCp(CO)_2$ / $FeCp'(CO)_2$ / $FeCp^*(CO)_2$ substituents protrude: e.g., various linear borinium cations, such as $[CpFe(CO)_2B(NCy_2)]^+$, and borenium cations derived thereof, such as $[(CpFe(CO)_2)B(NCy_2)(4\text{-}Pic)]^+$, have been isolated.[12]

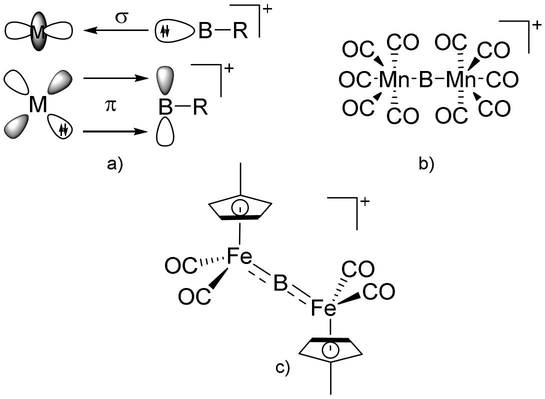


Figure 6. a) Orbital interaction between borylenes and transition-metal fragments; b) and c) exemplarily selected transition-metal substituted borinium cations.

Another notable substance class are the cationic T-shaped platinum boryl complexes that are usually accessible via salt metathesis reactions: e.g., $[(Cy_3P)_2(MeCN)Pt(B{\equiv}O)]^+$ can be synthesized by reacting $(Cy_3P)_2Pt(B{\equiv}O)(Br)$ with the halide abstracting reagent $Ag^+[B(Ar^{CF3})_4]^-$.[121] Employing a ferrocenyl ligand on the other hand, Braunschweig et al. were able to isolate a rare example of a structurally characterized boron dication: $[FcB(Pic)_3]^{2+}$ (**Figure 7**).[122]

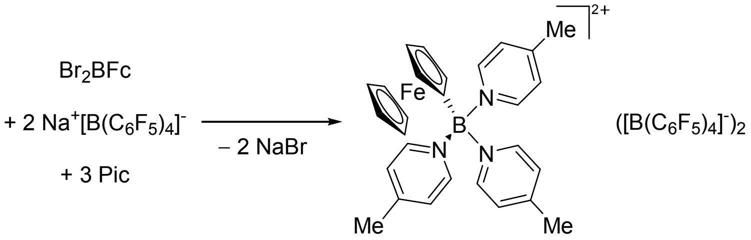


Figure 7. Synthesis of the boron dication $[FcB(Pic)_3]^{2+}$ via bromide abstraction and subsequent complexation.

Multinuclear: Due to the pronounced electron deficiency of boron there are not many contributions to the field of cationic multinuclear boron-based rPBC. The neutral diborane $[HB(\mu\text{-hpp})]_2$ complex however, is an excellent precursor for hydrid abstractions and via unexpected boron−boron coupling reactions the unprecedented tetraborane dication $[B_4H_2(\mu\text{-hpp})_4]^{2+}$ was isolated (**Figure 8**).[123]

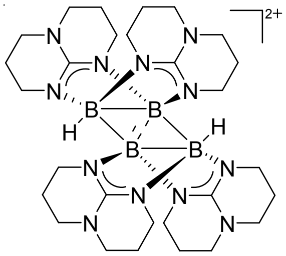


Figure 8. The tetraborane dication $[B_4H_2(\mu\text{-hpp})_4]^{2+}$. The bonding properties in the rhomboid B_4 core of the product can be described as two B–B units connected by 3-c-2-e bonds, sharing a short diagonal.

Multinuclear Transition-Metal Substituted: Compared to their mononuclear congeners, both the ligands and coordination modes in the multinuclear borinium, borenium and boronium cations are very similar: i) linear in the $[(CpFe(CO)\{B(NCy_2)\})_2(\mu\text{-dmpe})]^{2+}$ complex[124], ii) trigonal-planar in the $[(Cy_3P)_2\{Pt(B(Br)\}_2(\mu\text{-Ph})]^{2+}$ dication[125] and iii) tetrahedral in $[\{(bipy)(Me)B\}_2(\mu\text{-Fc})]^{2+}$.[126,127] The aggregation usually occurs via bi-functional ligands like dmpe or via the transition-metal ligand itself (**Figure 9**).

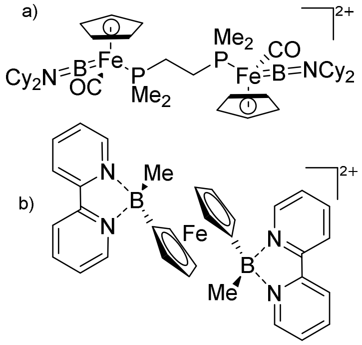


Figure 9. Dicationic a) $[(CpFe(CO)\{B(NCy_2)\})_2(\mu\text{-dmpe})]^{2+124}$ and b) $[\{(bipy)(Me)B\}_2(\mu\text{-Fc})]^{2+126,127}$ complexes.

Aluminum Cations

Among the group 13 cations, the lower- and higher-coordinated derivatives of aluminum have been of significant interest as they feature increased Lewis acidities and ligand labilities, thus allowing for higher catalytic activities compared to their neutral analogs.[95] While Atwood (1998)[102] and Dagorne (2008)[95] have given a good overview on cationic aluminum species from a fundamental perspective, Sarazin and Carpentier (2015)[10] recently reviewed various discrete cationic aluminum complexes that are able to catalyze ring-opening polymerizations.

Alkyl or Aryl Substituted: The synthesis of di-coordinated alkyl complexes of aluminum $[R_2Al]^+$ (R = Me, Et, 2,6-$Mes_2C_6H_3$) is only viable, if extremely weakly coordinating anions (e.g. borate[87] and carboranes[128]) and/or bulky substituents[129] are applied. In the case of "$[Me_2Al]^+$" and "$[Et_2Al]^+$", the Lewis acidity of the aluminum cations is so significant that the latter feature distinct contacts to the corresponding WCAs and should therefore be described as *ion-like* compounds (**Figure 10**). However, preliminary investigations showed that *ion-like* $(Et_2Al)_2B_{12}Cl_{12}$ is a very active initiator for the cationic polymerization of isobutylene.[130]

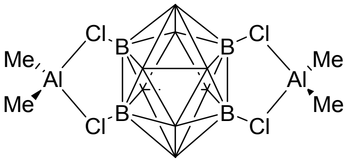


Figure 10. The *ion-like* $(Me_2Al)_2B_{12}Cl_{12}$ salt.[87] For clarity, all BCl moieties of the perchlorinated *closo*-dodecaborate that feature no contact to the "$[Me_2Al]^+$" cation have been omitted.

The $[(2,6\text{-}Mes_2C_6H_3)_2Al]^+$ cation on the other hand, is a discrete and therefore almost linear di-coordinate aluminum cation that features no contact to the WCA $[B(C_6F_5)_4]^-$.[129] The occurrence of the highly Lewis acidic aluminum cation is attributable to the intrinsic stabilization effect of the 2,6-$Mes_2C_6H_3$ ligand: i.e., bending of the flanking Mes-moieties towards the aluminum center.

Cyclopentadienyl Complexed: This class of compounds is to some extent related to the just mentioned alkyl substituted $[(2,6\text{-}Mes_2C_6H_3)_2Al]^+$ complex. Hence, the Cp ligands are η^5- but not σ-bonding, and allow for the synthesis of discrete aluminum cations with different WCAs as counterions: $[(\eta^5\text{-}Cp)_2Al]^+[Al(OR^{PF})_4]^-$[79], $[(\eta^5\text{-}Cp')_2Al]^+[B(C_6F_5)_4]^-$[131] and $[(\eta^5\text{-}Cp^*)_2Al]^+$ $[MeB(C_6F_5)_3]^-$.[132,133] Moreover, the salts offer insights into the relationship between the nucleophilicity of Cp, Cp' and Cp*, the corresponding WCAs and the resultant Lewis acidities and reactivities of the aluminum cations: i.e., with increasing nucleophilicity of the Cp ligands (Cp < Cp' < Cp*) the WCAs can be less coordinating ($[MeB(C_6F_5)_3]^-$ > $[B(C_6F_5)_4]^-$ > $[Al(OR^{PF})_4]^-$). The more interacting anions induce decreased Lewis acidities and lower reactivities of the aluminum cations for the initiation of olefin polymerizations: $[(\eta^5\text{-}Cp)_2Al]^+ > [(\eta^5\text{-}Cp')_2Al]^+ > [(\eta^5\text{-}Cp^*)_2Al]^+$.[79]

Ligand Substituted (CN = 2): The above mentioned σ-coordinated $[R_2Al]^+$ complexes are either stabilized by intermolecular interactions with the corresponding WCAs or intramolecularly by two bulky terphenyl ligands. Within this context, Sekiguchi et al. were able to contribute another cationic di-coordinated, yet differently intramolecularly stabilized aluminum species: the $[^tBu_2MeSi–Al–Si^tBu_2–SiMe^tBu_2]^+$ cation.[134] As supported by the solid-state structure and theoretical calculations, the stabilizing element is a σ-π hyperconjugation of the aluminum cation and the neighboring Si–Si σ bond (**Figure 11**).

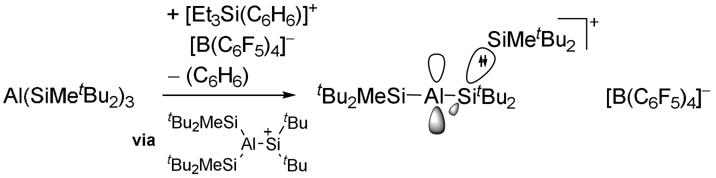


Figure 11. Synthesis of the $[^tBu_2MeSi–Al–Si^tBu_2–MeSi^tBu_2]^+$ cation via demethylation and subsequent migration of a $^tBu_2MeSi$ group.

Ligand Substituted (CN = 3): Tri-coordinated aluminum cations are a bit less electrophilic than their di-coordinated congeners but nevertheless still very reactive. The few examples that have been reported, require chelating and sterically demanding β-diketiminate ligands, thus allowing for the successful synthesis of cationic [(β-diketiminate)Al−H]$^{+}$[135] and [(β-diketiminate)Al−Me]$^{+}$[136] complexes, respectively (**Figure 12**).

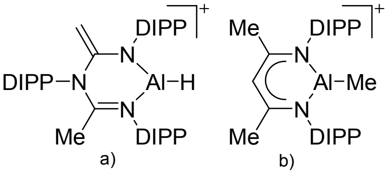


Figure 12. a) The [(β-diketiminate)Al−H]$^+$ cation derives from the reaction of a *N*-imidoylamidine ligand with $AlH_3·NMe_2Et$ and $[Ph_3C]^+[B(C_6F_5)_4]^-$.[135] b) The [(β-diketiminate)Al−Me]$^+$ cation is formed by reacting the neutral precursor (β-diketiminate)Al(Me)$_2$ with the demethylating reactants $[CPh_3]^+[B(C_6F_5)_4]^-$ and $B(C_6F_5)_3$, respectively.[136]

Ligand Substituted (CN = 4): In their recent review on group 13 cations, Dagorne and Atwood state that *"four-coordinate cations are most common … as they incorporate an electronically saturated metal center"*.[95] In all compounds the aluminum cations are coordinated in a tetrahedral fashion with at least one coordination site being occupied by a heteroatom (N, O, P). Moreover, the vast majority of aluminum cations are incorporated into heterocycles, which derive from chelating ligands, such as Pytsi[137], hpp[138], BOX[139], $^iPr_2$-ATI[140,141] and SchNMe$_2$.[142] The usual synthesis routes are alkyl or hydride abstractions. On the other hand, there are a few examples where aluminum is coordinated by four discrete ligands: $[Me_2Al(OEt_2)_2]^+$,[77] $[Me_2Al(THF)_2]^+$,[143] $[Me_2Al(NPhMe_2)_2]^+$ [144] and $[H_2Al(NMe_3)_2]^+$ [145] (cf. **Figure 13** for the complex synthesis of the $[H_2Al(NMe_3)_2]^+$ cation and the in-situ generation of the corresponding WCA).

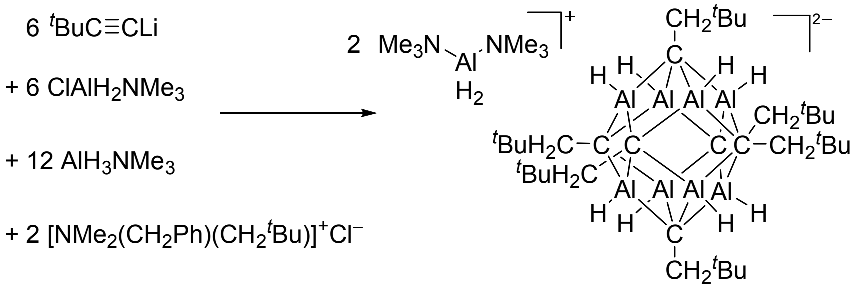


Figure 13. Salt metathesis and hydroalumination reactions lead to the formation of the weakly coordinating carbaalanate cluster that allows for the synthesis of two equivalents of the $[H_2Al(NMe_3)_2]^+$cation.[145]

Ligand Substituted (CN ≥ 5): As mentioned in the previous sub-chapter chelating ligands are of significant importance in terms of stabilizing cationic highly coordinated (CN ≥ 5) aluminum cations. Of all the different chelates, the Salen derivatives[146] protrude, allowing for the synthesis of distorted square pyramidal / octahedral aluminum cations that interact with one[147] or two[148–151] equivalents of Lewis base, such as Et_2O and THF (**Figure 14**).

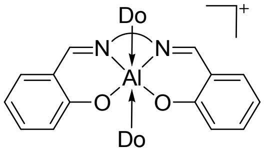


Figure 14. Octahedral or quadratic-pyramidal coordinated $[SalenAl(Do)_n]^+$ cations (Do = Et_2O, THF) with n = 1,2.

Multinuclear: A common structural motif of dicationic and dinuclear aluminum cations are the often centrosymmetric $[Al_2O_2]$-rhomboids[152,141,153,154] as seen in the recently reported $[\{(OSSO)Al\}_2]^{2+}$ cation (**Figure 15**).[155]

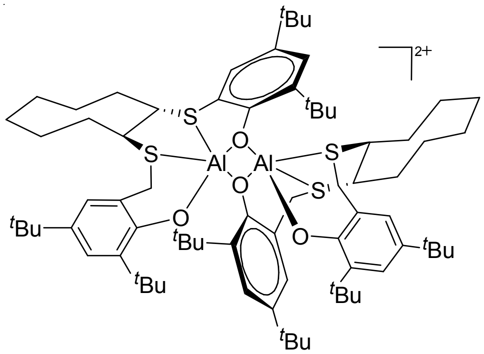


Figure 15. In the $[\{(OSSO)Al\}_2]^{2+}$ cation one aluminum atom is coordinated in a trigonal-bipyramidal and the other in a distorted-square-pyramidal fashion. The cationic species is a potential catalyst for the ring opening polymerization of propylene oxide.[155]

On the other hand, there are various dinuclear, yet singly charged aluminum cations in which the latter usually feature different coordination modes. Notable contributions to this field of research have been made by Jordan et al., such as the cationic aluminum aminotroponiminate[141] and amidinate[156] complexes in **Table 4**.

AlCp* Substituted: The coordination chemistry of low-valent group 13 organyls such as AlCp* to transition-metals is a growing field in inorganic chemistry, though more contributions were reported using the heavier homologue GaCp* (see below). Nonetheless, Fischer et al. were able to isolate the cationic $[Rh(COD)(AlCp^*)_3]^+$ complex by reacting $[Rh(COD)_2]^+$ with three equivalents of AlCp*.[157]

Gallium Cations

As mentioned above, gallium in its +I oxidation state is thermodynamically unstable and usually disproportionates into the metal and the +III ions. Notable contributions to the field of reactive gallium cations therefore allow for the stabilization of the +I oxidation state of gallium.[31]

Alkyl or Aryl Substituted: The isolation of the linear di-coordinated $[(2,6\text{-}Mes_2C_6H_3)_2Ga]^+$ cation[158] was performed by Wehmschulte et al. as a test run for the above mentioned structurally related $[(2,6\text{-}Mes_2C_6H_3)_2Al]^+$ cation.[129] Hence, the bowl-shaped terphenyl substituents are potential ligands in terms of shielding highly electrophilic cations. Moreover, both syntheses were only possible due to the presence of very good WCAs, such as the $[Li\{Al(OR^{HF})_4\}_2]^-$ and $[B(C_6F_5)_4]^-$ anion.

Cyclopentadienyl Complexed: Partial protolysis of GaCp* with $[H(OEt_2)_2]^+[B(Ar^{CF3})_4]^-$ yields the bipyramidal double-cone structured $[Ga_2(\eta^5\text{-}Cp^*)]^+$ cation.[159] The latter can be seen as a GaCp*-substituted “naked” Ga^+ cation, thus reacting as a gallium(I) source with ligands such as DDP (**Figure 16**).

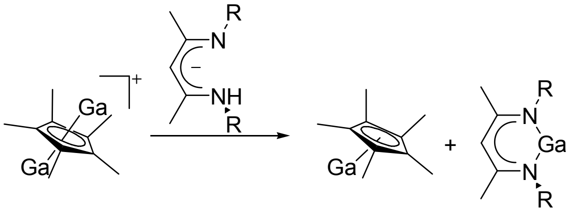


Figure 16. The $[Ga_2(\eta^5\text{-}Cp^*)]^+[B(Ar^{CF3})_4]^-$ salt cleanly reacts as a gallium(I) source with ligands such as DDP.

The coordination mode of the Cp* ligands in the $[(\eta^1\text{-}Cp^*)(\eta^3\text{-}Cp^*)Ga]^+$ cation on the other hand differs.[160] Hence, the originally expected η^5,η^5-ferrocene-like structure that was also observed for the aluminum analogue is likely perturbed by the more interacting $[BF_4]^-$ counterion.

Arene Complexed: Cationic arene complexes of univalent gallium are known for more than 30 years and Schmidbaur et al. have made notable contributions to this field of research.[100,101] Yet, the reported compounds feature strong cation-anion interactions and are labile towards com- and disproportionations. More recently, Krossing et al. developed a simple oxidative route to $[Ga(\eta^6\text{-arene})_n]^+$ complexes of the weakly coordinating $[Al(OR^{PF})_4]^-$ anion with n = 2, 3 (**Figure 17**).[31,91,92] The arene complexes have proven to be a powerful starting material for further gallium(I) chemistry (e.g. various ligand exchange reactions) but also highly efficient catalyst for the polymerization of isobutylene.[7,8,99]

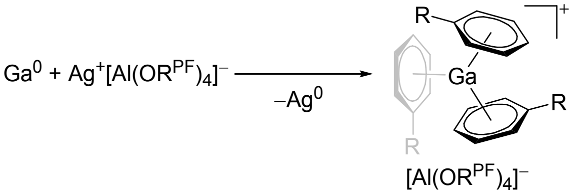


Figure 17. Oxidative access to $[Ga(\eta^6\text{-arene})_n]^+$ complexes with n = 2, 3(R = F, Me).

Ligand Substituted (CN = 2): The arene ligands in the $[Ga(\eta^6\text{-arene})_n]^+$ cations with n = 2, 3 can be substituted by electron-richer analogues. In addition, σ-donating ligands such as carbenes IR (R = Pr, Mes)[161] or phosphines P^tBu_3[162] can also be applied, yielding bent $[Ga(IR)_2]^+$ and $[Ga(P^tBu_3)_2]^+$ complexes (cf. the stereoactive electron lone pair at the gallium(I) cation). Another notable di-coordinated gallium(III) cation is the linear $[^tBu_3Si–Ga–Si^tBu_3]^+$ complex (**Figure 18**), which could be isolated in the presence of the $[Al(OR^{PF})_4]^-$ WCA, but not the simple $[GaCl_4]^-$ anion.[163]

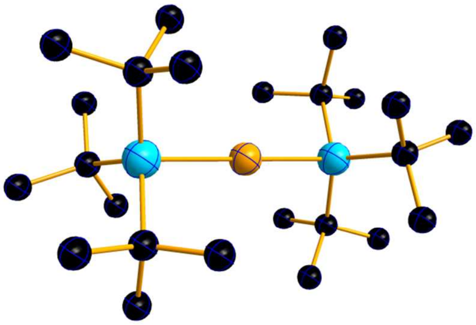


Figure 18. Molecular structure of the $[^tBu_3Si–Ga–Si^tBu_3]^+$ cation. A. Budanow, T. Sinke, J. Tilmann, M. Bolte, M. Wagner, *Two-coordinate gallium ion $[^tBu_3Si\text{-}Ga\text{-}Si^tBu_3]^+$ and the halonium ions $[^tBu_3Si\text{-}X\text{-}Si^tBu_3]^+$ (X = Br, I): sources of the supersilyl cation $[^tBu_3Si]^+$ Organometallics* **2012**, *31*, 7298–7301. Data from this Reference were used to draw this figure and the hydrogen atoms were omitted for clarity.[163]

Ligand Substituted (CN = 3): This class of tri-coordinated gallium(I) cations again derives from the above mentioned $[Ga(\eta^6\text{-arene})_n]^+$ cations with n = 2, 3. The coordination mode for the gallium(I) cations is trigonal-pyramidal due to the stereoactive lone pair electrons. Besides sterically less demanding phosphines, N-heterocylic arenes like pyrazine and DTBMP (a σ-, and not a π-donating ligand, proving its perception of being non-nucleophilic wrong) were also applied as potential ligands.[164] Due to the bifunctionality of pyrazine, both the monomeric $[Ga(pyrazine)_3]^+$ complex and the one-dimensional coordination polymer $[\{Ga(\mu\text{-pyrazine})_2(\eta^1\text{-pyrazine})\}^+]_\infty$ were isolated (**Figure 19**).

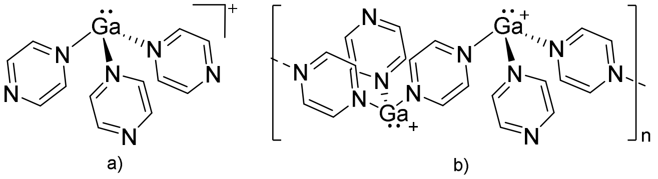

a) b)

Figure 19. a) Monomeric $[Ga(pyrazine)_3]^+$ complex and b) One-dimensional coordination polymer $[\{Ga(\mu\text{-pyrazine})_2(\eta^1\text{-pyrazine})\}^+]_\infty$. The propagation of the polymer into the second dimension was not possible as each cationic strand is surrounded by strands of the corresponding $[Al(OR^{PF})_4]^-$ anions.[164]

Ligand Substituted (CN = 4): Using the BOX ligand, Dagorne et al. isolated tetra-coordinate neutral gallium complexes.[165] The latter were easily ionized by applying $[CPh_3]^+[B(C_6F_5)_4]^-$ or $B(C_6F_5)_3$ in NMe_2Ph. Interestingly, the trityl cation functions as hydride and $B(C_6F_5)_3$ as methyl abstracting reactant (**Figure 20**).

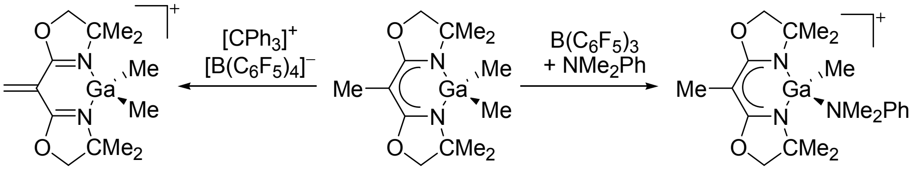


Figure 20. Hydride vs. methyl abstraction of neutral BOX ligated gallium complexes.[165]

Ligand Substituted (CN ≥ 5): Cationic penta- and hexa-coordinated gallium complexes are synthesized via protonation[166,167] or complexation.[168] Within this context, the $[Ga([18]crown\text{-}6)(C_6H_5F)_2]^+$ complex is of special interest as the gallium(I) cation features no contact to the corresponding $[Al(OR^{PF})_4]^-$ anion and the C_6H_5F ligands coordinate in different fashions (**Figure 21**).[168]

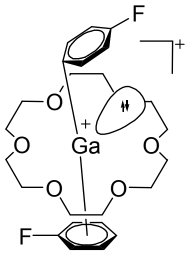


Figure 21. The $[Ga([18]crown\text{-}6)(\eta^6\text{-}/\eta^1\text{-}C_6H_5F)_2]^+$ cation. The η^6- and η^1-coordination modes could be an indication for a stereoactive lone pair on the side of the weaker and only η^1-coordinated C_6H_5F molecule.[168]

As the N-heterocyclic arenes are potential ligands for univalent gallium (see above), Krossing et al. additionally reacted the chelating bipy with the $[Ga(\eta^6\text{-}C_6H_5F)_2]^+$ complex. Instead of witnessing a simple ligand exchange reaction, they isolated the paramagnetic and distorted octahedral $[Ga^{III}\{(bipy)_3\}^\bullet]^{2+}$ complex due to the non-innocence of the bipy ligand.[17] This is reminiscent to transition metal chemistry where for example the $[Ru^{III}\{(bipy)_3\}^\bullet]^{2+}$ complex features similar bonding.

Transition-Metal Substituted: Similar to the transition-metal substituted boron cations, $CpFe(CO)_2$ (FP) and $Cp^*Fe(CO)_2$ (FP*) are the most important ligands in terms of stabilizing di-, tri- and tetra-coordinated gallium cations: cf. the $[(FP^*)_2Ga]^+$ [169], $[(FP^*)_2Ga(4\text{-Pic})]^+$ [170], $[(FP^*)Ga(phen)(Y)]^+$ (Y = Cl, S^pTol)[171] cations (**Figure 22**).

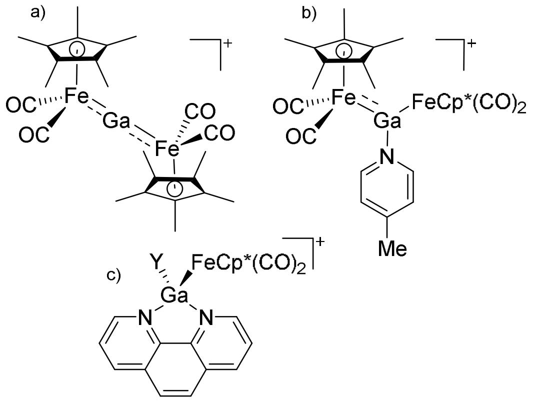


Figure 22. a)The linear di-coordinated cation [(FP*)$_2$(μ-Ga)]$^+$ derives from a salt metathesis of (FP*)$_2$GaCl and Na$^+$[B(Ar^{CF3})$_4$]$^-$. The Fe–Ga–Fe moiety features a significant π bonding component (population analysis).[169] b) The [(FP*)$_2$(μ-Ga)(4-Pic)]$^+$ cation is an addition product of [(FP*)$_2$Ga]$^+$ and 4-Pic and the second structurally characterized complex containing a cationic tri-coordinated gallium centre.[170] c) Applying the chelating phen ligand, Ueno et al. isolated the tetra-coordinated [(FP*)Ga(phen)(Y)]$^+$ (Y = Cl, S^{p}Tol) cations, i.e. the first transition-metal complex with a thiolate group on the gallium atom.[171]

Multinuclear: There are not many contributions to this field of research and some cationic multinuclear gallium complexes are a product of hydrolysis.[172,173] Two remarkable examples however are the dinuclear [(η^6-C$_6$H$_5$F)Ga(μ-η^6-*m*-TP)$_2$-Ga(η^6-C$_6$H$_5$F)]$^{2+}$ complex[8,99] in which the gallium(I) cations are solely π-coordinated by arene ligands as well as the σ-coordinated amidinate-bridging [{^{t}BuC(N^{i}Pr)$_2$}GaMe{^{t}BuC(N^{i}Pr)$_2$}GaMe$_2$]$^+$ cation.[156]

Multinuclear Transition-Metal Substituted: A notable class of contributions are the β-diketiminate/THF coordinated gallium cations that can be bridged by a gold atom[174] or a {ZnClTHF}$_2$-rhomboid.[175] Reaction of Cp*Fe(η^5-P$_5$) with the [Ga(*o*-C$_6$H$_4$F$_2$)$_2$]$^+$ complex on the other hand resulted in aggregation and the formation of a cationic one-dimensional coordination polymer (**Figure 23**).[176]

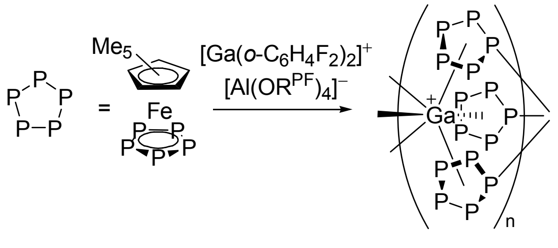


Figure 23. Reaction of [Ga(*o*-C$_6$H$_4$F$_2$)$_2$]$^+$ and Cp*Fe(η^5-P$_5$) results in aggregation and formation of a cationic one-dimensional coordination polymer.

GaCp* Substituted: As of today, GaCp* is a widely used ligand concerning cationic transition-metal complexes, thus leading to an enormous variety of cationic gallium species. This area of research has been intensively reviewed by Fischer et al.[110] and we would like to refer to the multiple entries in **Table 4** of this review. Yet, some of the compounds also include "naked" and bridging gallium atoms: e.g. [(Ga)Ru(PCy$_3$)$_2$(GaCp*)$_2$]$^+$,[177] [(Ga)M(GaCp*)$_4$]$^+$ (M = Ni[178], Pt[179,180]), [(Cp*Ga)$_4$Rh{Ga(Me)}]$^+$,[181] [(Cp*Ga)$_4$Rh{Ga(Me)(py)}]$^+$,[181] [{Ru(GaCp*)$_3$-[(CH$_2$)$_2$C{CH$_2$(μ-Ga)}]}$_2$]$^+$,[177] [{(GaCp*)$_4$Pt}{Pt(H)-

$(GaCp^*)_3\}(\mu\text{-}Ga)]^{2+}$.[180] Contrary to GaCp* (a strong σ-donor and weak π-acceptor, cf. similarity to the boron related compounds in **Figure 6**, the "naked" gallium cations function as pure acceptor ligands, with significant components of σ- and π-symmetry contributing to the M−Ga linkages.[179,180]

Indium Cations

Compared to the lighter homologue gallium, well-defined indium(I) halides exist, though they are practically insoluble in organic solvents. The synthesis of $In^+[OTf]^-$ by Macdonald et al. as a soluble alternative is therefore an important development concerning the indium(I) chemistry.[182]

Cyclopentadienyl Complexed: Using the just mentioned $In^+[OTf]^-$ salt as starting material and reacting it with manganocene, the inverse sandwich complex $[In_2(\eta^5\text{-}Cp)]^+$ was successfully synthesized.[183] Interestingly, the counterion is the complex $[Cp_3In^{III}–Cp–In^{III}Cp_3]^-$ ion, deriving form a partial oxidation of the starting material. The formation of the mixed valence species seems to be preferred over an alternative indium(II) species. Reacting InCp* (a hexamer in the solid state) with a mixture of $B(C_6F_5)_3$ and $H_2O{\cdot}B(C_6F_5)_3$, the first indium-based triple-decker cation $[(\eta^6\text{-}Tol)In(\mu\text{-}\eta^5\text{-}C_5Me_5)In(\eta^6\text{-}Tol)]^+$ was formed.[184] Reducing the size of the counterion from $[(C_6F_5)_3BO(H)B(C_6F_5)_3]^-$ to $[B(C_6F_5)_4]^-$ on the other hand, results in the formation of the inverse sandwich complex $[In_2(\eta^5\text{-}Cp^*)]^+$ in which the indium(I) cations are not capped by toluene molecules but rather interact with the $[B(C_6F_5)_4]^-$ anions (**Figure 24**).[185]

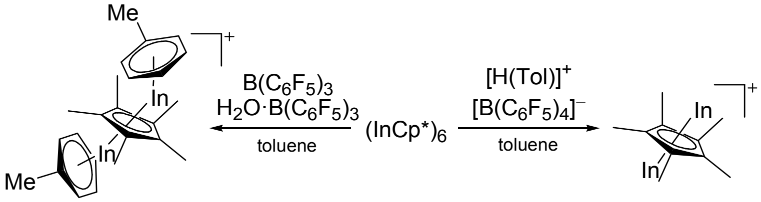


Figure 24. Reducing the size of the counterion from $[(C_6F_5)_3BO(H)B(C_6F_5)_3]^-$ to $[B(C_6F_5)_4]^-$ "squeezes" the toluene molecules from the triple-decker cation, yielding the inverse sandwich complex $[In_2(\eta^5\text{-}Cp^*)]^+$.

Arene Complexed: By reacting elemental indium with $Ag^+[Al(OR^{PF})_4]^-$, Krossing et al. expanded the above mentioned oxidative route to gallium(I) salts towards the synthesis of $[In(arene)_n]^+$ complexes with n = 2, 3.[162] Identical compounds can also be synthesized by using the salt metathesis reactions of Scheer et al., with insoluble InCl as starting material.[186]

Ligand Substituted (CN = 2): These $[In(arene)_n]^+$ complexes with n = 2, 3 are an ideal starting material for further indium(I) chemistry: e.g. the arene ligands can be substituted for N-heterocyclic carbenes such as IPr.[161] Salt metathesis reactions on the other hand are still very important: i.e., using the isosteric and isoelectronic terphenyl Mes_2py ligand, Aldridge et al. were able to isolate mixed-leptic $[In(Mes_2py)(\eta^6\text{-}C_6H_5F)]^+$ (both σ- and π-coordinated) and homo-leptic $[In(Mes_2py)_2]^+$ complexes (only σ-coordinated, though the flanking mesityl rings of the Mes_2py ligands also partly π-coordinate).[187] The latter features an indium(I) cation wholly encapsulated by two Mes_2py ligands and remarkably long In−N distances, which the authors explain with an energy mismatch between the (low lying) pyridine ligand donor and (high energy) metal acceptor orbitals.

Ligand Substituted (CN = 3): Besides complexation and ligand exchange reactions of $In^+[OTf]^-$ and $[In(arene)_n]^+$ (n = 2, 3) with ligands such as bis(imino)pyridines[188,189] and PPh_3,[162] tri-coordinated indium cations can also be isolated by thermolysis of $[\{^iPr_2\text{-ATI}(CPh_3)\}InMe_2]^+$, a cationic tetra-coordinated indium precursor (**Figure 25**, conversion of a) to b)).[190]

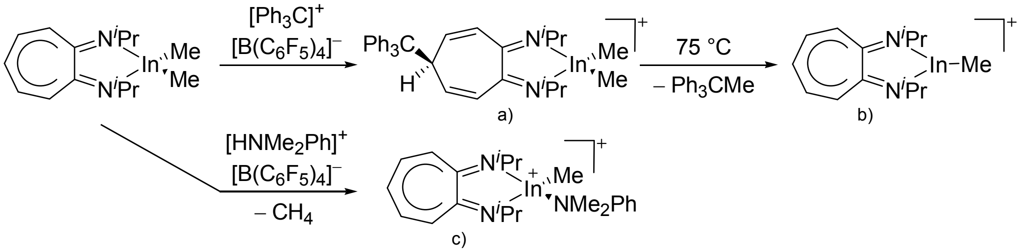


Figure 25. Formation of tetra- and tri-coordinated cationic diimine substituted indium complexes: a) $[\{^iPr_2\text{-ATI}(CPh_3)\}InMe_2]^+$, b) $[(^iPr_2\text{-ATI})InMe]^+$ and c) $[(^iPr_2\text{-ATI})In(Me)(NMe_2Ph)]^+$. For each complex, the counterion is $[B(C_6F_5)_4]^-$.

Ligand Substituted (CN = 4): The cationic diimine $[\{^iPr_2\text{-ATI}(CPh_3)\}InMe_2]^+$ complex was synthesized by reacting the neutral $(^iPr_2\text{-ATI})InMe_2$ precursor with the ionizing $[Ph_3C]^+[B(C_6F_5)_4]^-$ salt (**Figure 25**).[190] Surprisingly, the latter does not function as methyl abstracting reactant but rather adds to the C5 carbon of $(^iPr_2\text{-ATI})InMe_2$. Reacting $(^iPr_2\text{-ATI})InMe_2$ with the protonating $[HNMe_2Ph]^+[B(C_6F_5)_4]^-$ on the other hand, results in CH_4 formation and the labile adduct $[(^iPr_2\text{-ATI})In(Me)(NMe_2Ph)]^+$ (**Figure 25**).[190]

Ligand Substituted (CN ≥ 5): Compared with the lighter homologues aluminum and gallium, indium shows a tendency to expand its coordination sphere.[102,95] Protonolysis of the neutral $In(CH_2SiMe_3)_3$ complex in THF therefore yields a penta-coordinated indium cation: $[In(CH_2SiMe_3)_2(THF)_3]^+$.[191] Moreover, $In^+[OTf]^-$ [192,193] and $[In(arene)_n]^+$ [168] (n = 2, 3) can be reacted with the crown ether [18]crown-6, yielding cationic indium complexes with similar structures to the gallium congener (cf. **Figure 21**) and strong anion-cation interactions in the case of the $[OTf]^-$ anion. Reacting $In^+[OTf]^-$ with [15]crown-5 on the other hand, the sandwich complex $[In([15]crown\text{-}5)_2]^+$ was isolated.[194]

Transition-Metal Substituted: The class of cationic transition-metal substituted indium compounds very much relates to the related gallium structures: i.e., the $[InPt(PPh_3)_3]^+$ complex with a “naked” Pt-substituted indium cation[179,180] as well as the di- and tri-coordinated $[(FP^*)_2In]^+$ and $[(FP^*)_2In(THF)]^+$ complexes.[195] Reacting the chelating phen ligand with the $[In(C_6H_5F)_2]^+$ complex in the presence of silver salt, Krossing et al. isolated the silver bound indium dication[17] $[(phen)_2In{-}Ag(\eta^3\text{-}C_6H_5F)]^{2+}$ that is related to the $[InPt(PPh_3)_3]^+$ complex.[179,180] In this complex the tetragonal-pyramidal $[In(phen)_2]^+$ cation reacts as a Lewis basic donor (cf. the stereoactive 5s lone pair at indium), while the $[Ag(\eta^3\text{-}C_6H_5F)]^+$ complex is the corresponding Lewis acidic acceptor.

Multinuclear: For the synthesis of multinuclear indium cations, the $[In(arene)_n]^+$ [168] complexes with n = 2, 3 are a powerful starting material. Hence a dicationic $[\{(PPh_3)_3In\}_2(\mu\text{-}PPh_3)]^{2+}$ complex in which one PPh_3 ligand bridges both indium(I) cations was isolated.[162] Applying the non-innocent and chelating bipy and phen ligands on the other hand, Krossing et al. surprisingly isolated the first cationic tri- and tetra-nuclear indium clusters: $[In_3(bipy)_{5\text{-}6}]^{3+}$ and $[In_4(Do)_6]^{4+}$ (Do = phen, bipy) (**Figure 26**).[17] This result very much differs from the above mentioned synthesis of the paramagnetic $[Ga^{III}\{(bipy)_3\}^{\bullet}]^{2+}$ complex and can be attributed to the higher redox-stability of indium compared to gallium. In addition and to our knowledge, these are the first higher charged clusters that have been reported to this day: i.e., for cluster formations usually reductive syntheses are applied, yielding neutral and anionic clusters.

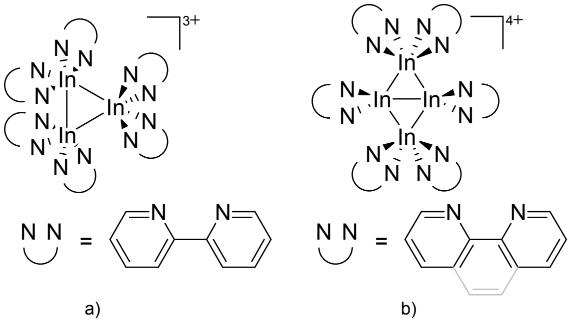


Figure 26. Cationic a) $[In_3(bipy)_{5\text{-}6}]^{3+}$ and b) $[In_4(Do)_6]^{4+}$ (Do = bipy, phen) complexes synthesized via ligand exchange reactions and aggregations.

Thallium Cations

In contrast to the lighter homologues, thallium's thermodynamic most stable oxidation state is +I. Hence, various syntheses of unsubstituted thallium(I) cations of different WCAs have been reported: i.e., the protonation of TlOEt using $[H(OEt_2)_2]^+[B(Ar^{CF3})_4]^-$ / $[B(C_6F_5)_4]^-$ [196,197], the Lewis acid base reaction of $Tl^+[OTeF_5]^-$ and $B(OTeF_5)_3$[198] and the salt metathesis of TlF and $Li^+[Al(OR^{HF/PF})_4]^-$.[199,200] The thallium(I) salts are relatively stable (cf. the silver congeners decompose upon exposure to light) and mainly used as reactant to introduce WCAs (e.g. salt metathesis reactions). $Tl^+[Al(OR^{HF})_4]^-$ could only be isolated, if the precursors were applied in an exact 1:1 stoichiometry. An excess of TlF however, led to the formation of the cationic multinuclear $[Tl_3F_2Al(OR^{HF})_3]^+$ complex.[200]

Arene Complexed: Various cationic thallium(I) arene complexes have been reported. While the di- and tri-coordinated $[Tl(\eta^6\text{-arene})_n]^+$ complexes (arene = C_6H_5Me, n = 2, 3;[201] Mes, n = 2;[202] C_6Me_6, n = 2[203]) are structurally related to the lighter homologues, C_6Me_6 additionally allows for the first mono-coordinated $[Tl(\eta^6\text{-}C_6Me_6)]^+$ complex (DFT calculations gave a remarkable Tl–C_6Me_6 π-bonding energy of 163 kJ mol^{-1}).[204]

Ligand Substituted (CN = 2): Reacting $Tl^+[OTeF_5]^-$ with $B(OTeF_5)_3$ in 1,2-dichloroethane, the solvent functions as chelating ligand, thus forming the five-membered $TlCl_2C_2$-ring in $[Tl(1,2\text{-}Cl_2C_2H_4)]^+$ (after silver and ruthenium, thallium was at that time the third reported metal atom coordinated by a simple chlorocarbon).[198] By contrast, from CH_2Cl_2 the "naked" $Tl^+[B(OTeF_5)_4]^-$ salt was isolated.

Ligand Substituted (CN = 3): Similar to the lighter homologues gallium and indium, the $[Tl(\eta^6\text{-}C_6H_5R)_2]^+$ (R = F, Me) bent-sandwich complexes can interact with N-heterocyclic ligands such as Mes_2Py, thus forming tri-coordinated $[Tl(Mes_2py)(\eta^6\text{-}C_6H_5R)_2]^+$ complexes.[187] On the other hand tri-dentate chelating ligands like timtmb^{tBu}[205] and bis(imino)pyridines[206] can be applied to isolate tri-coordinated thallium(I) cations (**Figure 27**).

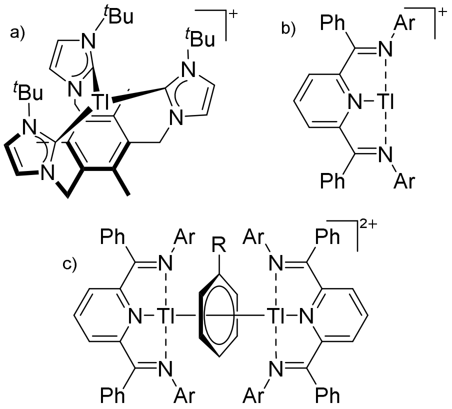


Figure 27. Both the a) $[Tl(timtmb^{tBu})]^+$ and b) $[\{ArN{=}CPh\}_2(NC_5H_3)Tl]^+$ complexes derive from $Tl^+[OTf]^-$ and are synthesized via complexation reactions of the corresponding ligands. In addition, the inverted sandwich structure c) $[\{\{ArN{=}CPh\}_2(NC_5H_3)Tl\}_2(\mu\text{-}\eta^6\text{-}C_6H_5R)]^{2+}$ (Ar = 2,6-$Et_2C_6H_3$, 2,5-$^tBu_2C_6H_3$; R = H, Me) was isolated.

Ligand Substituted (CN = 4): The protonation of TlOEt with $[H(OEt_2)_2]^+[H_2N\{B(C_6F_5)_3\}_2]^-$ in Et_2O yielded the tetrahedral coordinated cationic $[Tl(OEt_2)_4]^+$ complex, which shows no contact to the corresponding WCA.[203]

Ligand Substituted (CN ≥ 5): 2,5-Bis(2-pyridyl)-1-phenylphosphole (NPPh) exhibits a rich coordination chemistry towards thallium(I) cations and dependent on the nature of the solvents and WCAs, different structures were obtained: i.e., reacting $Tl^+[Al(OR^{PF})_4]^-$ with NPPh in CH_2Cl_2 / C_6H_5Me, the tetra-coordinated and C_6H_5Me-capped $[Tl(NPPh)_2(\eta^6\text{-}C_6H_5Me)]^+$ complex formed, whereas in CH_2Cl_2 / *n*-pentane the dinuclear and dicationic $[Tl_2(NPPh)_4]^{2+}$ was isolated (**Figure 28**). If $Tl^+[PF_6]^-$ was applied as starting material a coordination polymer with strong cation-anion interactions was formed.

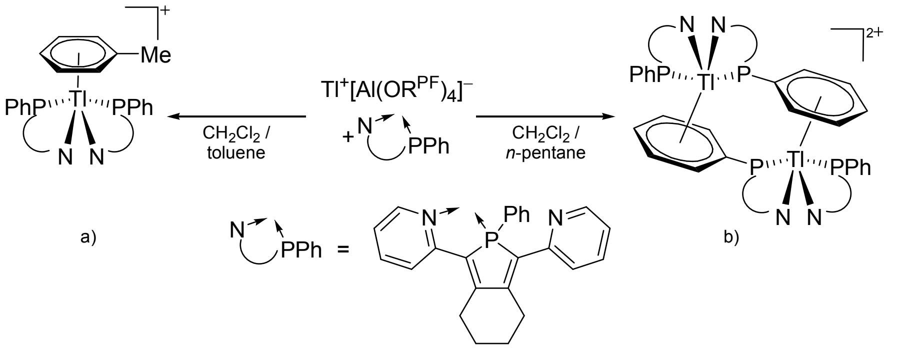


Figure 28. Solvent effects on the formation of cationic thallium(I) complexes of NPPh. a) If toluene is applied, the solvent-stabilized penta-coordinated $[Tl(NPPh)_2(\eta^6\text{-}C_6H_5Me)]^+$ complex forms. b) If non-coordinating *n*-pentane is applied two $[Tl_2(NPPh)_2]^+$ cations aggregate via their phenyl substituents, forming the dinuclear and dicationic $[Tl_2(NPPh)_4]^{2+}$ complex.

An even higher coordinated thallium cation is the $[Tl([18]crown\text{-}6)]^+$ complex, which features a similar structure as the [18]crown-6 complexes of the lighter homologues gallium and indium.[203]

Transition-Metal Substituted: Reacting the above mentioned $[Tl(\eta^6\text{-}C_6H_5Me)_n]^+$ complexes (n = 2, 3) with $FeCp_2$, Sarazin et al. were able to isolate the $[Tl_2(FeCp_2)_3]^+\{[H_2N\{B(C_6F_5)_3\}_2]^-\}_2$ salt that contains the mono- and di-coordinated $[Tl(FeCp_2)_n]^+$ complexes with n = 1, 2 in a 1:1 ratio.[203] Increasing the amount of $FeCp_2$ from 1 to 2.2 equivalents, only the $[Tl(FeCp_2)]^+$ complex was isolated.[204] In contrast to the lighter homologues, the reaction of $Cp^*Fe(\eta^5\text{-}As_5)$ with $Tl^+[PF_6]^-$ and $Li^+[FAl\{OC_6F_{10}(C_6F_5)\}_3]^-$ did not result in aggregation and formation of a cationic one-dimensional coordination polymer, but rather yielded the pseudo-trigonal-planar $[Tl\{(\eta^5\text{-}As_5)FeCp^*\}_3]^+$ complex.[176] Performing a similar chemistry in the presence of the very good WCA $[Al(OR^{PF})_4]^-$ however, one-dimensional polymers were isolated (cf. **Figure 23**), proving the importance of the WCA.[207] Reacting the neutral $Pt(CH_2Ph)Cl(PCH_2\text{-}ox)$ complex with $Tl^+[PF_6]^-$, Braunstein et al. did not isolate any chloride abstraction product but a “trapped” thallium(I) cation: the cationic $[\{P(Ph_2)CH_2ox\}(Cl)(Tl)Pt\text{-}CH_2Ph\}]^+$ complex.[208] Herein, the ligand functions as a chelate and interacts with thallium via a Pt−Tl bond and a η^6-benzyl coordination (**Figure 29**).

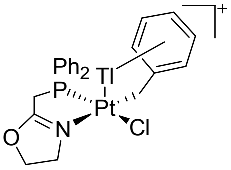


Figure 29. The first fully characterized metal−metal bonded Tl−Pt−Cl complex. If $Ag^+[OTf]^-$ and $Ag^+[BF_4]^-$ is applied, the expected chloride abstraction takes place.[208]

Multinuclear: Some of the cationic multinuclear thallium complexes have already been mentioned in the text above. A further example is the $[Tl(\beta\text{-triketimine})_2]^{2+}$ complex that features Tl−η^6-aryl and weak thallophilic interactions, allowing to overcome the Coulomb repulsion of both cations (cf. **Figure 28**).[14] The reaction of the P_n-ligand $\{CpMo(CO)_2\}_2(P_2)$ with $Tl^+[Al(OR^{PF})_4]^-$, yields the dicationic

$[Tl_2(\{CpMo(CO)_2\}_2)_6]^{2+}$ complex that features a distorted Tl_2P_4 ring (**Figure 30**).[207]

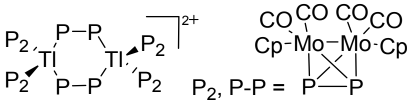
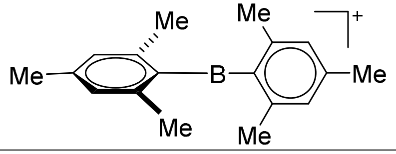
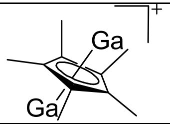
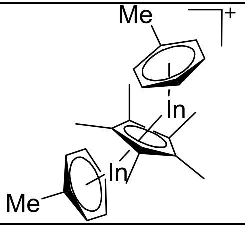
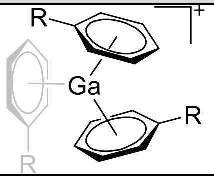
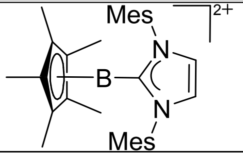


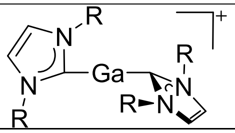
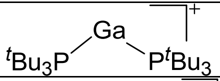
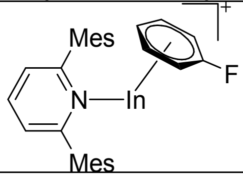
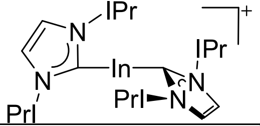
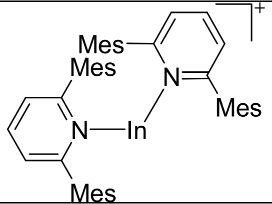
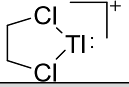
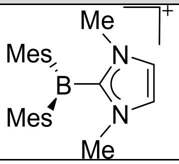
Figure 30. Formation of the $[Tl_2(\{CpMo(CO)_2\}_2)_6]^{2+}$ complex.

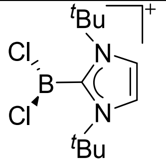
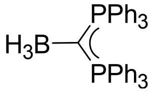
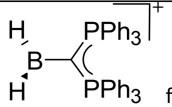
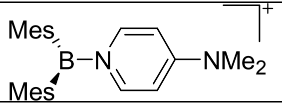
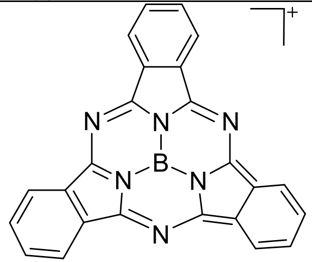
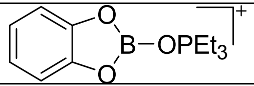
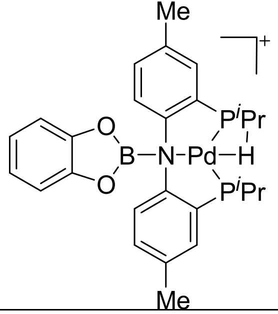
Reacting $RuCl_2(DMeOPrPE)_2$ with $Tl^+[PF_6]^-$ an "arrested" chloride abstraction occurs.[209] In the resultant one-dimensional coordination polymer, the thallium(I) cations are coordinated in an unusual octahedral fashion with a stereoactive $6s^2$ lone pair at thallium.

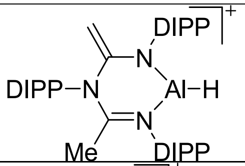
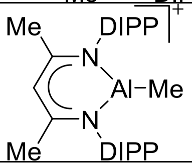
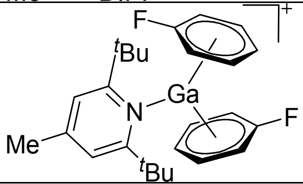
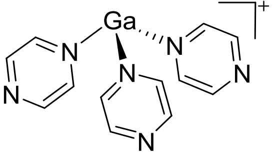
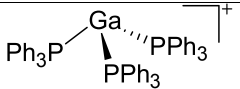
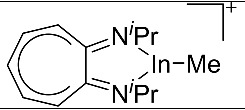
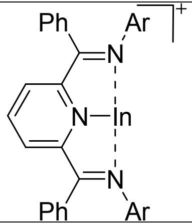
Table 4. Group 13 cations, their counterions (WCA) as well as the synthesis routes. The entries are ordered as follows: i) from boron- to thallium-based cations, ii) from unsubstituted, via alkyl/aryl, Cp, arene and ligand to transition-metal substituted cations, ii) from low to high CNs, iv) from mono- to multinuclear group 13 complexes. Note that the structural diagrams obey a distance criterion for interactions, but not necessarily a 2e2c-understanding of every interaction line. See comment in the Introduction.

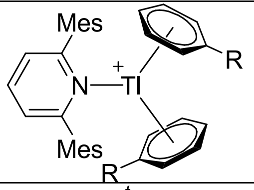
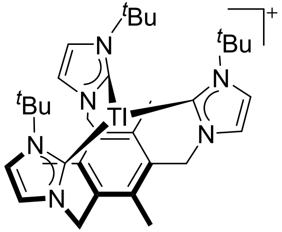
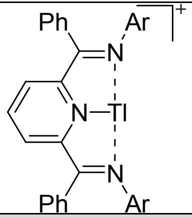
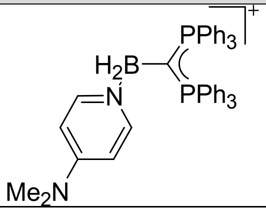
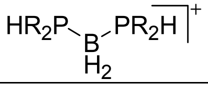
Cation	WCA	Class*	Synthesis	Comment / Structure	Ref
Unsubstituted					
In^{+}	$[\mathrm{OTf}]^{-}$	Prot	$\mathrm{InCp^{*} + H^{+}[WCA]^{-}}$	soluble in organic solvents in contrast to the In(I) halides	182
Tl^{+}	$[\mathrm{B(Ar^{CF3})_4}]^{-}$ / $[\mathrm{B(C_6F_5)_4}]^{-}$	Prot	$\mathrm{TlOEt + [H(OEt_2)_2]^{+}[WCA]^{-}}$	-	196,197
Tl^{+}	$[\mathrm{B(OTeF_5)_4}]^{-}$	Lewis	$\mathrm{Tl^{+}[OTeF_5]^{-} + B(OTeF_5)_3}$ in $\mathrm{CH_2Cl_2}$ / 1,2-$\mathrm{C_2Cl_3F_3}$	-	198
Tl^{+}	$[\mathrm{Al(OR^{PF})_4}]^{-}$ / $[\mathrm{Al(OR^{HF})_4}]^{-}$ / $[\mathrm{Al(OR^{MeF})_4}]^{-}$	Salt	$\mathrm{TlF + Li^{+}[WCA]^{-}}$	-	199,200
Alkyl/Aryl Substituted					
$[\mathrm{Mes_2B}]^{+}$	$[\mathrm{HCB_{11}Cl_{11}}]^{-}$ / $[\mathrm{B(C_6F_5)_4}]^{-}$	Salt	$\mathrm{Mes_2BF + Et_3Si(HCB_{11}Cl_{11})}$ / $\mathrm{[Et_3Si(Mes)]^{+}[WCA]^{-}}$		113,32
$(\mathrm{R_2Al})$ (R = Me, Et)	$[\mathrm{B_{12}Cl_{12}}]^{2-}$	Alk	$\mathrm{R_3Al + \{[CPh_3]^{+}\}_2[B_{12}Cl_{12}]^{2-}}$	*ion-like* compound	87
$(\mathrm{Et_2Al})$	$[\mathrm{CB_{11}H_6X_6}]^{-}$ (X = Cl, Br)	Alk	$\mathrm{Et_3Al + [CPh_3]^{+}[CB_{11}H_6X_6]^{-}}$	*ion-like* compound	128
$[\mathrm{(2,6\text{-}Mes_2C_6H_3)_2Al}]^{+}$	$[\mathrm{B(C_6F_5)_4}]^{-}$	Hyd	$\mathrm{(2,6\text{-}Mes_2C_6H_3)_2AlH + [CPh_3]^{+}[WCA]^{-}}$	related structure to the $[\mathrm{Mes_2B}]^{+}$ cation, though the Mes moieties of the 2,6-$\mathrm{Mes_2C_6H_3}$ substituent additionally shield the aluminum cation	129
$[\mathrm{(2,6\text{-}Mes_2C_6H_3)_2Ga}]^{+}$	$[\mathrm{Li\{Al(OR^{HF})_4\}_2}]^{-}$	Salt	$\mathrm{(2,6\text{-}Mes_2C_6H_3)_2GaCl + 2\ Li^{+}[WCA]^{-}}$	similar structure as the $[\mathrm{(2,6\text{-}Mes_2C_6H_3)_2Al}]^{+}$ cation	158
Cyclopentadienyl Complexed					
$[(\eta^{5}\text{-Cp})_2\mathrm{Al}]^{+}$	$[\mathrm{Al(OR^{PF})_4}]^{-}$	Prot	$\mathrm{AlCp_3 + [H(OEt_2)_2]^{+}[WCA]^{-}}$	-	79
$[(\eta^{5}\text{-Cp'})_2\mathrm{Al}]^{+}$	$[\mathrm{B(C_6F_5)_4}]^{-}$	Alk	$\mathrm{Cp'_3Al + [CPh_3]^{+}[WCA]^{-}}$	-	131
$[(\eta^{5}\text{-Cp*})_2\mathrm{Al}]^{+}$	$[\{\mathrm{Ph(Me)B}(\eta^{5}\text{-}\mathrm{C_5H_4})_2\}\mathrm{ZrCl_2}]^{-}$	Alk	$\mathrm{Cp^{*}{}_2AlMe} + \{\mathrm{Ph(SMe_2)B}\text{-}(\eta^{5}\text{-}\mathrm{C_5H_4})_2\}\mathrm{ZrCl_2} + [\mathrm{Ph_3P{=}N{=}PPh_3}]^{+}\mathrm{Cl}^{-}$	-	132
$[(\eta^{5}\text{-Cp*})_2\mathrm{Al}]^{+}$	$[\mathrm{MeB(C_6F_5)_3}]^{-}$	Alk	$\mathrm{Cp^{*}{}_2AlMe + B(C_6F_5)_3}$	-	133
$[(\eta^{5}\text{-Cp})_2(\mathrm{Et_2O})_2\mathrm{Al}]^{+}$	$[\mathrm{Al(OR^{PF})_4}]^{-}$	Prot	$\mathrm{AlCp_3 + [H(OEt_2)_2]^{+}[WCA]^{-}}$	$\mathrm{Et_2O}$ can coordinate the $[(\eta^{5}\text{-Cp})_2\mathrm{Al}]^{+}$ cation.	79
$[\mathrm{Ga_2}(\eta^{5}\text{-Cp*})]^{+}$	$[\mathrm{B(Ar^{CF3})_4}]^{-}$	Prot	$\mathrm{[H(OEt_2)_2]^{+}[WCA]^{-} + GaCp^{*}}$		159
$[(\eta^{1}\text{-Cp*})(\eta^{3}\text{-Cp*})\mathrm{Ga}]^{+}$	$[\mathrm{BF_4}]^{-}$	Prot	$\mathrm{Cp^{*}{}_3Ga + HBF_4}$	cf. $[\mathrm{B}(\eta^{5}/\eta^{1}\text{-Cp*})_2]^{+}$ and $[\mathrm{Al}(\eta^{5}/\eta^{5}\text{-Cp*})_2]^{+}$	160
$[\mathrm{In_2}(\eta^{5}\text{-Cp})]^{+}$	$[\mathrm{Cp_3In{-}Cp{-}InCp_3}]^{-}$	Com	$\mathrm{In^{+}[OTf]^{-} + Cp_2Mn}$ in $\mathrm{C_6H_5Me}$	inverted sandwich structure (cf. the related $[\mathrm{Ga_2}(\eta^{5}\text{-Cp*})]^{+}$cation)	183

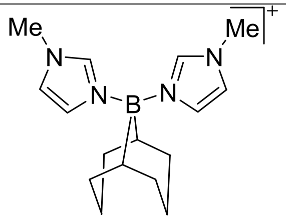
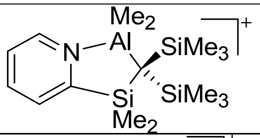
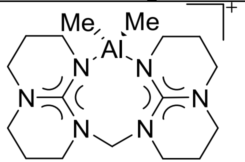
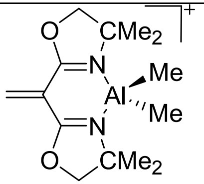
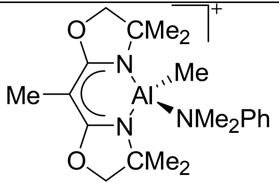
$[In_2(\eta^5\text{-}Cp^*)]^+$	$[B(C_6F_5)_4]^-$	Prot	$[(C_6H_5Me)H]^+[WCA]^- + InCp^*$	similar structure to the $[Ga_2(\eta^5\text{-}Cp^*)]^+$ cation	185
$[(\mu\text{-}\eta^5\text{-}C_5Me_5)In_2(\eta^6\text{-}Tol)_2]^+$	$[(C_6F_5)_3BO(H)B(C_6F_5)_3]^-$	Prot, Com	$(Cp^*In)_6 + B(C_6F_5)_3 + H_2O{\cdot}B(C_6F_5)_3$		184,185
Arene Complexed					
$[Ga(\eta^6\text{-}C_6H_5R)_n]^+$ (R = F, Me; n = 2, 3)	$[Al(OR^{PF})_4]^-$	Ox	$Ga^0 + Ag^+[WCA]^-$ in arene		31,91,92
$[Ga(\eta^6\text{-}arene)_n]^+$ (n = 2, 3)	$[Al(OR^{PF})_4]^-$	Com	$[Ga(C_6H_5F)_{2\text{-}3}]^+[WCA]^-$ + arene (arene = Mes, *p*-Xyl, C_6Me_6)	bent-sandwich (2 ligands) or tubby coordinated complex (3 ligands)	7
$[Ga(\eta^6\text{-}DPE)]^+$	$[Al(OR^{PF})_4]^-$	Com	$[Ga(C_6H_5F)_{2\text{-}3}]^+[WCA]^-$ + DPE	first structurally characterized bent-sandwich *ansa*-arene complex	8,99
$[In(\eta^6\text{-}C_6H_5F)_n]^+$ (n = 2, 3)	$[Al(OR^{PF})_4]^-$	Ox	$In^0 + Ag^+[WCA]^-$ in C_6H_5F	bent-sandwich complex (cf. gallium analogue)	162
$[In(\eta^6\text{-}o\text{-}C_6H_4F_2)_2]^+$	$[Al(OR^{PF})_4]^-$	Salt	$InCl + Li^+[WCA]^-$ in $o\text{-}C_6H_4F_2$	bent-sandwich complex (cf. gallium analogue)	186
$[Tl(\eta^6\text{-}C_6Me_6)]^+$	$[H_2N\{B(C_6F_5)_3\}_2]^-$	Other	$[Tl(C_6Me_6)_2]^+$ in $Et_2O + C_6H_5Me$, vacuum	first example of a mono-η^6-coordinated thallium complex	204
$[Tl(\eta^6\text{-}C_6H_5Me)_2]^+$	$[HCB_{11}H_5Br_6]^-$	Salt	$Cs^+[HCB_{11}H_5Br_6]^- + TlF$	bent-sandwich complex (cf. gallium analogue)	201
$[Tl(\eta^6\text{-}C_6H_5Me)_3]^+$	$[H_2N\{B(C_6F_5)_3\}_2]^-$	Com	$[Tl(OEt_2)_2]^+[WCA]^- + C_6H_5Me$	tubby coordinated complex (cf. gallium analogue)	203
$[Tl(\eta^6\text{-}Mes)_2]^+$	$[B(OTeF_5)_4]^-$	Lewis, Com	$Tl^+[OTeF_5]^- + B(OTeF_5)_3$ in Mes	tubby coordinated complex (cf. gallium analogue)	202
$[Tl(\eta^6\text{-}C_6Me_6)_2]^+$	$[H_2N\{B(C_6F_5)_3\}_2]^-$	Com	$[Tl(OEt_2)_3]^+[WCA]^- + C_6Me_6$	tubby coordinated complex (cf. gallium analogue)	203
Ligand Substituted (CN = 2)					
$[Cp^*B(IMes)]^{2+}$	$[AlCl_4]^-$	Lewis	$Cp^*BCl_2(IMes) + 2\ AlCl_3$		210
$[(^tBu_3PN)_2B]^+$	$[B(C_6F_5)_4]^-$	Hyd	$(^tBu_3PN)_2BH + [Ph_3C]^+[WCA]^-$	$\left[{}^tBu_3P{=}N{-}B{-}N{=}P{}^tBu_3\right]^+$	114
$[^tBu_2MeSi{-}Al{-}Si^tBu_2{-}Si^tBu_2Me]^+$	$[B(C_6F_5)_4]^-$	Alk	$Al(SiMe^tBu_2)_3 + [Et_3Si]^+[WCA]^-$	hyperconjugation with a neighboring Si–Si bond	134

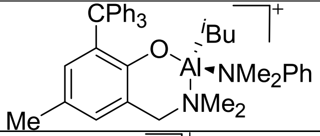
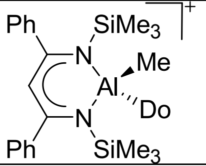
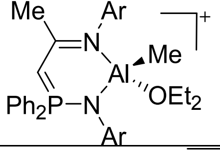
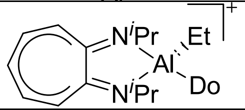
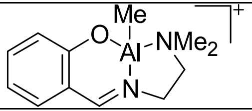
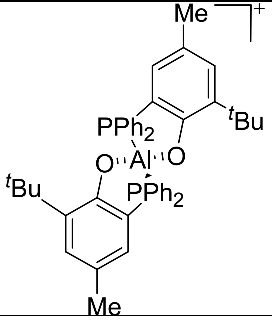
$[Ga(IR)_2]^+$ (R = Pr, Mes)	$[Al(OR^{PF})_4]^-$	Com	$[Ga(C_6H_5F)_2]^+[WCA]^-$ + IR		161
$[{}^tBu_2MeSi–Ga–Si{}^tBu_2–Si\text{-}Me{}^tBu_2]^+$	$[B(C_6F_5)_4]^-$	Alk	$Ga(SiMe{}^tBu_2)_3 + [Et_3Si(C_6H_6)]^+[WCA]^-$	stabilized by hyperconjugation with a neighboring Si–Si bond	134
$[{}^tBu_3Si–Ga–Si{}^tBu_3]^+$	$[Al(OR^{PF})_4]^-$	Salt	$({}^tBu_3Si)_2GaCl + Ag^+[WCA]^-$	linear arrangement	163
$[Ga(P{}^tBu_3)_2]^+$	$[Al(OR^{PF})_4]^-$	Com	$[Ga(C_6H_5F)_2]^+[WCA]^- + P{}^tBu_3$		162
$[In(Mes_2py)(\eta^6\text{-}C_6H_5F)]^+$	$[B(Ar^{CF3})_4]^-$	Salt, Com	$InBr + Na^+[WCA]^- + Mes_2py$		187
$[In(IPr)_2]^+$	$[Al(OR^{PF})_4]^-$	Com	$[In(C_6H_5F)_2]^+$ + IPr		161
$[In(Mes_2py)_2]^+$	$[B(Ar^{CF3})_4]^-$	Salt	$In^+Br^- + Na^+[WCA]^- + 2\ Mes_2py$		187
$[Tl(1,2\text{-}Cl_2C_2H_4)]^+$	$[B(OTeF_5)_4]^-$	Lewis, Com	$Tl^+[OTeF_5]^- + B(OTeF_5)_3$ in $1,2\text{-}C_2H_4Cl_2$		198
Ligand Substituted (CN = 3)					
$[BMes_2(IMe)]^+$	$[OTf]^-$	Salt	$Mes_2BF + [Me_3Si]^+[OTf]^- + [Ag(IMe)_2]^+[Ag_2I_3]^-$		211

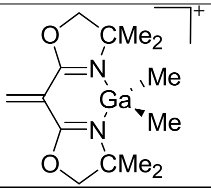
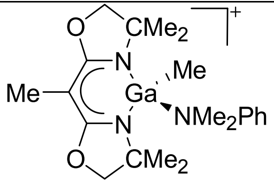
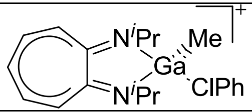
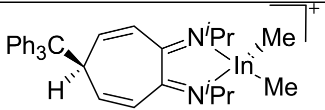
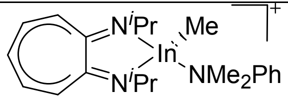
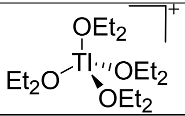
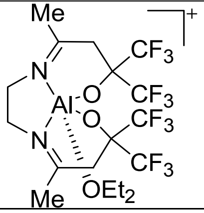
$[BCl_2(I^tBu)]^+$	$[B(Ar^{Cl})_4]^-$	Salt	$BCl_3(I^tBu) + Na^+[WCA]^-$		74
$[\{(PPh_3)_2C\}BH_2]^+$	$[HB(C_6F_5)_3]^-$	Hyd	 $+ B(C_6F_5)_3$	 first dihydroborenium cation	118,119
$[BMes_2(DMAP)]^+$ / $[B(Ar^N)_2(DMAP)]^+$ $Ar^N = 4\text{-}(Me_2N)\text{-}2,6\text{-}Me_2\text{-}C_6H_2)$	$[OTf]^-$	Salt	$Mes_2BF + Me_3Si\text{-}OTf + Ar^N{}_2BF + DMAP$		57
$[B(SubPc)]^+$ $(Sub = C_{24}H_{12}N_6)$	$[HCB_{11}Me_5Br_6]^-$	Salt	$B(SubPc)Cl + Et_3Si(HCB_{11}Me_5Br_6)$		115
$[CatB(O{=}PEt_3)]^+$	$[HCB_{11}H_5Br_6]^-$	Salt, Com	$Ag^+[WCA]^- + CatBBr + OPEt_3$		116
$[(CatB)(PNP)PdH]^+$	$[B(Ar^{CF3})_4]^-$ / $[CB_{11}H_{12}]^-$	Other	$[(PNP)Pd(THF)]^+[WCA]^- + CatBH$		117

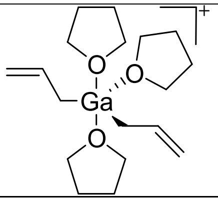
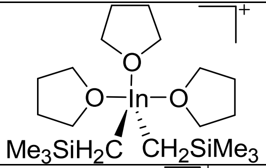
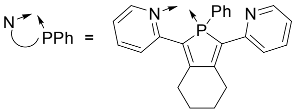
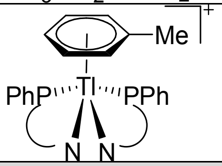
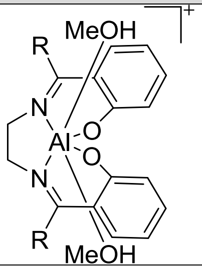
$[ArN(C(=CH_2)NAr)(C(Me)NAr)AlH]^+$ (Ar = DIPP)	$[B(C_6F_5)_4]^-$	Hyd	$ArN(CMeNAr)_2 + AlH_3{\cdot}NMe_2Et + [Ph_3C]^+[WCA]^-$		135
$[\{HC(CMeNAr)_2\}AlMe]^+$ (Ar = DIPP)	$[B(C_6F_5)_4]^-$ / $[MeB(C_6F_5)_3]^-$	Alk	$\{HC(CMeNAr)_2\}AlMe_2 + [CPh_3]^+[WCA]^-$ / $B(C_6F_5)_3$		136
$[Ga(\eta^6\text{-}C_6H_5F)_2(DTBMP)]^+$	$[Al(OR^{PF})_4]^-$	Com	$[Ga(\eta^6\text{-}\mu C_6H_5F)_n]^+[WCA]^- + DTBMP$ (n = 2, 3)		164
$[Ga(pyrazine)_3]^+$ / $[\{Ga(\mu\text{-}pyrazine)_2\text{-}(\eta^1\text{-}pyrazine)\}^+]_\infty$	$[Al(OR^{PF})_4]^-$	Com	$[Ga(C_6H_5F)]^+[WCA]^- + pyrazine$ (n = 2, 3)	 / one-dimensional coordination polymer	164
$[Ga(PPh_3)_3]^+$	$[Al(OR^{PF})_4]^-$	Com	$[Ga(C_6H_5Me)_2]^+[WCA]^- + PPh_3$		31,91,92
$[({}^iPr_2\text{-}ATI)InMe]^+$	$[B(C_6F_5)_4]^-$	other	thermolysis of $[\{{}^iPr_2\text{-}ATI(CPh_3)\}InMe_2]^+[WCA]^-$		190
$[\{ArN{=}CPh\}_2(NC_5H_3)In]^+$ (Ar =2,4-${}^tBu_2C_6H_3$, 2,5-${}^tBu_2C_6H_3$, 2,6-$Et_2C_6H_3$, 2,6-${}^iPr_2C_6H_3$,)	$[OTf]^-$	Com	$In^+[WCA]^-$ + bis(imino)pyridine ligand		188,189

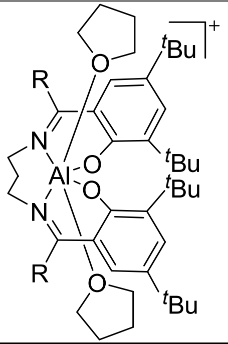
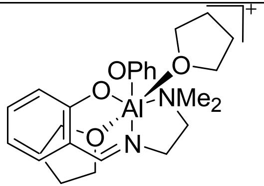
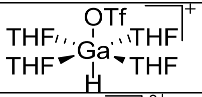
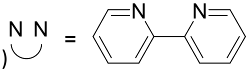
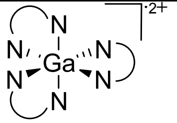
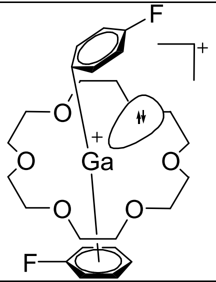
$[In(PPh_3)_3]^+$	$[Al(OR^{PF})_4]^-$	Com	$[In(C_6H_5F)_n]^+[WCA]^-$ + 3 PPh_3 (n = 2, 3)	trigonal pyramidal (cf. gallium analogue)	162
$[Tl(Mes_2py)(\eta^6\text{-}C_6H_5R)_2]^+$ (R = F, Me)	$[B(Ar^{CF3})_4]^-$	Salt, Com	TlCl + $Na^+[WCA]^-$ + Mes_2py in C_6H_5R		187
$[Tl(timtmb^{tBu})]^+$	$[OTf]^-$	Com	$Tl^+[WCA]^-$ + $timtmb^{tBu}$		205
$[\{ArN{=}CPh\}_2(NC_5H_3)Tl]^+$ (Ar = 2,6-$Et_2C_6H_3$, 2,5-$^tBu_2C_6H_3$)	$[OTf]^-$	Com	$Tl^+[WCA]^-$ + bis(imino)pyridine ligand		206
Ligand Substituted (CN = 4)					
$[\{(PPh_3)_2C\}BH_2(DMAP)]^+$	$[HB(C_6F_5)_3]^-$	Com	$[\{(PPh_3)_2C\}BH_2]^+[WCA]^-$ + DMAP		118,119
$[BH_2(PR_2H)_2]^+$ (R = ^{t}Bu, Cy, Ph)	$[B(Ar^{CF3})_4]^-$	Salt	$[BH_2(PR_2H)]^+Br^-$ + $Na^+[WCA]^-$		120

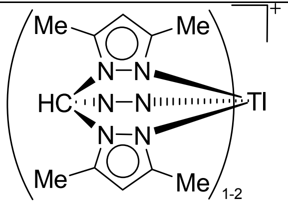
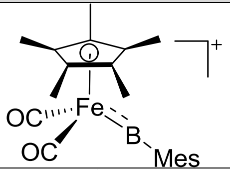
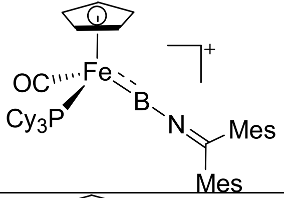
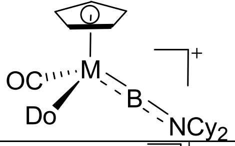
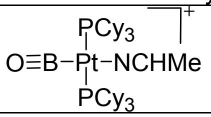
$[(1\text{-MIM})_2(9BBN)]^+$	$[B(Ar^{CF3})_4]^-$	Com	$[PMAF\text{–}9BBN)]^+[WCA]^-$ + 1-MIM		212
$[Me_2Al(OEt_2)_2]^+$	$[MeB(C_{12}F_9)_3]^-$	Alk	$AlMe_3 + B(_{12}F_9)_3$ in Et_2O	-	77
$[Me_2Al(THF)_2]^+$	$[\{Me_2Si(NDIPP)_2\}_2Zr_2Cl_5]^-$	Alk	$Al_2Me_6 + \{Me_2Si(NDIPP)_2\}ZrCl_2(THF)_2$	-	143
$[Me_2Al(NPhMe_2)_2]^+$	$[B(C_6F_5)_4]^-$	Prot, Com	$Al_2Me_6 + [HNMe_2Ph]^+[WCA]^-$	-	144
$[H_2Al(NMe_3)_2]^+$	$[(AlH)_8(CCH_2{}^tBu)_6]^{2-}$	Other	$^tBu{\equiv}CLi + AlH_3{\cdot}NMe_3 + ClAlH_2{\cdot}NMe_3$ $+[^tBuCH_2(Bzl)NMe_2]^+Cl^-$	-	145
$[(Pytsi)AlMe]^+$	$[MeB(C_6F_5)_3]^-$	Alk	$(Pytsi)AlMe_2 + B(C_6F_5)_3$		137
$[H_2C\{hpp\}_2AlMe_2]^+$	$[BPh_4]^-$	Prot	$[\{hpp\}H_2C\{hpp\}H]^+[WCA]^-$ + $AlMe_3$		138
$[\{H_2C{=}C(BOX\text{-}Me_2)_2\}Al\text{-}(Me)_2]^+$	$[B(C_6F_5)_4]^-$	Hyd	$\{BOX\text{-}Me_2\}Al(Me)_2 + [CPh_3]^+[WCA]^-$		139
$[\{BOX\text{-}Me_2\}Al(Me)(NMe_2Ph)]^+$	$[MeB(C_6F_5)_3]^-$	Alk	$\{BOX\text{-}Me_2\}Al(Me)_2 + B(C_6F_5)_3$ in NMe_2Ph		139

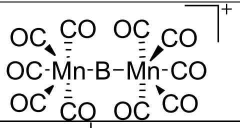
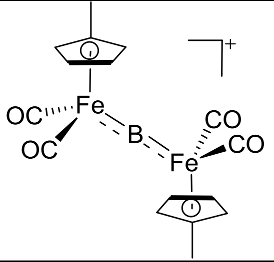
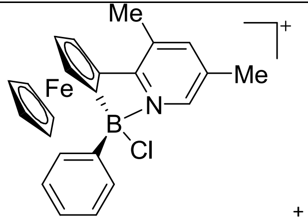
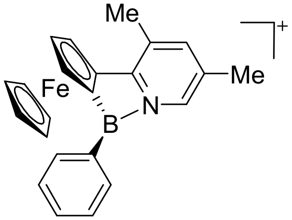
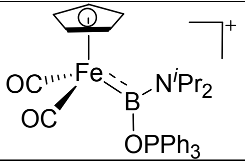
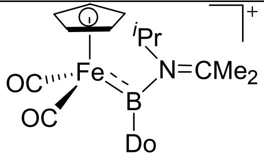
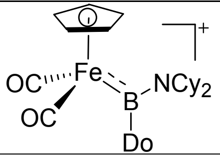
[{6-(CH$_2$NMe$_2$)-2-CPh$_3$-4-Me-C$_6$H$_2$O}Al(^{i}Bu)(NMe$_2$Ph)]$^+$	[HB(C$_6$F$_5$)$_3$]$^-$	Hyd	{6-(CH$_2$NMe$_2$)-2-CPh$_3$-4-Me-C$_6$H$_2$O}Al-(^{i}Bu)$_2$ + B(C$_6$F$_5$)$_3$ + NMe$_2$Ph		213,214
[{HC(CPhNSiMe$_3$)$_2$}-Al(Do)Me]$^+$ (Do = Et$_2$O, THF)	[B(C$_6$F$_5$)$_4$]$^-$ / [MeB(C$_6$F$_5$)$_3$]$^-$	Prot / Alk, Com	{HC(CPhNSiMe$_3$)$_2$}AlMe$_2$ + [HNMe$_2$Ph]$^+$[WCA]$^-$ + Et$_2$O / B(C$_6$F$_5$)$_3$ + THF		215
[(ArN)C(Me)CHPPh$_2$(NAr)AlMe(OEt$_2$)]$^+$ (Ar = DIPP)	[B(C$_6$F$_5$)$_4$]$^-$	Alk, Com	(ArN)C(Me)CHPPh$_2$(NAr)MMe$_2$ + [Ph$_3$C]$^+$[WCA]$^-$ in Et$_2$O		216
[(^{i}Pr$_2$-ATI)Al(Et)(Do)]$^+$ (Do = ClPh, NCMe)	[B(C$_6$F$_5$)$_4$]$^-$	Alk, Com	(^{i}Pr$_2$-ATI)AlEt$_2$ + [CPh$_3$]$^+$[WCA]$^-$ in PhCl / + MeCN		140,141
[(SchNMe$_2$)AlMe]$^+$	[BPh$_4$]$^-$	Salt	(SchNMe$_2$)AlMeCl + Na$^+$[WCA]$^-$		142
[{η^2-O,P-(2-PPh$_2$-4-Me-6-^{t}Bu-C$_6$H$_2$O)}$_2$Al]$^+$	[MeB(C$_6$F$_5$)$_3$]$^-$	Alk	{η^2-O,P-(2-PPh$_2$-4-Me-6-^{t}Bu-C$_6$H$_2$O)}$_2$AlMe + B(C$_6$F$_5$)$_3$		217

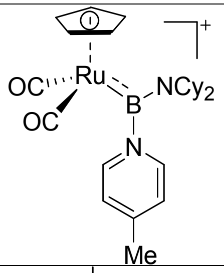
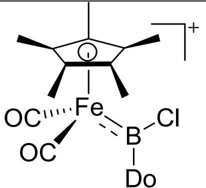
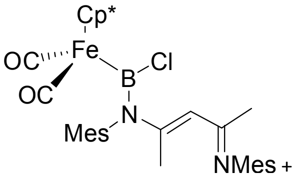
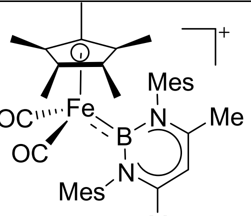
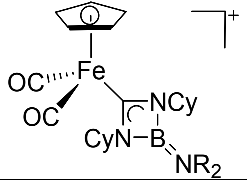
$[\{\mathrm{H_2C{=}C(BOX\text{-}Me_2)_2}\}\mathrm{Ga\text{-}(Me)_2}]^+$	$[\mathrm{B(C_6F_5)_4}]^-$	Hyd	$\{\mathrm{BOX\text{-}Me_2}\}\mathrm{Ga(Me)_2} + [\mathrm{CPh_3}]^+[\mathrm{WCA}]^-$		165
$[\{\mathrm{BOX\text{-}Me_2}\}\mathrm{Ga(Me)}]^+$	$[\mathrm{MeB(C_6F_5)_3}]^-$	Alk	$\{\mathrm{BOX\text{-}Me_2}\}\mathrm{Ga(Me)_2} + \mathrm{B(C_6F_5)_3}$ in $\mathrm{NMe_2Ph}$		165
$[(^i\mathrm{Pr_2\text{-}ATI})\mathrm{Ga(Me)(ClPh)}]^+$	$[\mathrm{B(C_6F_5)_4}]^-$	Alk, Com	$(^i\mathrm{Pr_2\text{-}ATI})\mathrm{GaMe_2} + [\mathrm{CPh_3}]^+[\mathrm{WCA}]^-$ in PhCl		140
$[\{1,2\text{-}(\mathrm{N}^i\mathrm{Pr})_2\text{-}5\text{-}\mathrm{CPh_3}\text{-cyclohepta-3,6-diene}\}\mathrm{InMe_2}]^+$	$[\mathrm{B(C_6F_5)_4}]^-$	Other	$(^i\mathrm{Pr_2\text{-}ATI})\mathrm{InMe_2} + [\mathrm{Ph_3C}]^+[\mathrm{WCA}]^-$		190
$[(^i\mathrm{Pr_2\text{-}ATI})\mathrm{In(Me)(NMe_2Ph)}]^+$	$[\mathrm{B(C_6F_5)_4}]^-$	Prot	$(^i\mathrm{Pr_2\text{-}ATI})\mathrm{InMe_2} + [\mathrm{HNMe_2Ph}]^+[\mathrm{WCA}]^-$		190
$[\mathrm{Tl(OEt_2)_4}]^+$	$[\mathrm{H_2N\{B(C_6F_5)_3\}_2}]^-$	Prot	$\mathrm{TlOEt} + [\mathrm{H(OEt_2)_2}]^+[\mathrm{WCA}]^-$ in $\mathrm{Et_2O}$		203
Ligand Substituted (CN = 5)					
$[\{\mathrm{Salen^{CF3}}\}\mathrm{Al(OEt_2)}]^+$	$[\mathrm{MeB(C_6F_5)_3}]^-$	Alk	$\{\mathrm{Salen^{CF3}}\}\mathrm{AlMe} + \mathrm{B(C_6F_5)_3}$ in $\mathrm{Et_2O}$		147

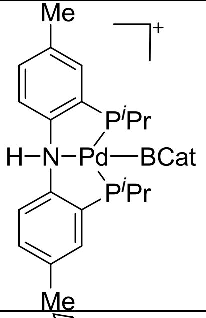
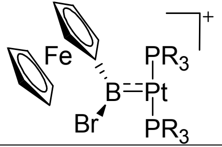
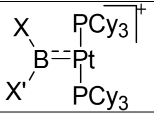
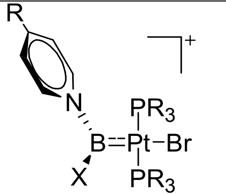
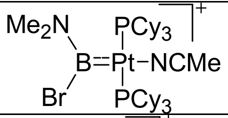
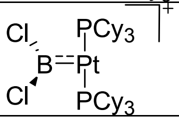
$[Ga(\eta^1\text{-}C_3H_5)_2(THF)_n]^+$ (n = 2, 3)	$[B(C_6F_5)_4]^-$ / $[B(Ar^{Cl})_4]^-$	Prot	$Ga(\eta^1\text{-}C_3H_5)_3(THF) + [HNMe_2Ph]^+[WCA]^-$		166
$[In(CH_2SiMe_3)_2(THF)_3]^+$	$[B(C_6F_5)_4]^-$	Prot	$In(CH_2SiMe_3)_3 + [HNMe_2Ph]^+[WCA]^-$ in THF		191
$[Tl(NPPh)_2(\eta^6\text{-}C_6H_5Me)]^+$ NPPh = 2,5-Bis(2-pyridyl)-1-phenylphosphole	$[Al(OR^{PF})_4]^-$	Com	Tl^+ + NPPh in CH_2Cl_2 / C_6H_5Me 		218
Ligand Substituted (CN ≥ 6)					
$[DoAl(MeOH)_2]^+$ (Do = Salen, Acen)	$[BPh_4]^-$	Salt, Com	$DoAlCl + Na^+[WCA]^- + MeOH$		148,149

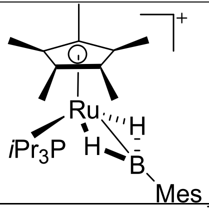
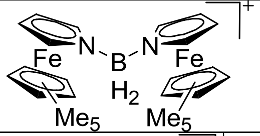
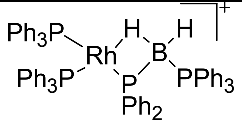
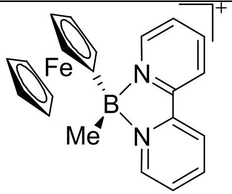
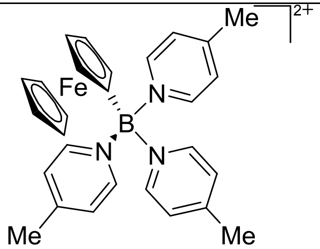
[Salpen(^{t}Bu)Al(THF)$_2$]$^+$	[BPh$_4$]$^-$	Salt, Com	Salpen(^{t}Bu)AlCl + Na$^+$[WCA]$^-$ + THF		150,151
[(SchNMe$_2$)Al(OPh)-(THF)$_2$]$^+$	[BPh$_4$]$^-$	Com	[(SchNMe$_2$)AlPh]$^+$[WCA]$^-$ + O$_2$ in THF		142
[GaH(THF)$_4$(OTf)]$^+$	[Ga(THF)$_4$(OTf)$_2$]$^-$	Prot	GaCp* + HOSO$_2$CF$_3$ in THF		167
[Ga^{III}{(bipy)$_3$}$^{\bullet}$]$^{2+}$	[Al(OR^{PF})$_4$]$^-$	Com	[Ga(C$_6$H$_5$F)]$^+$[WCA]$^-$ + bipy (n = 2, 3) 	 paramagnetic complex featuring non-innocent bipy ligands	17
[Ga([18]crown-6)(η^6-/η^1-C$_6$H$_5$F)$_2$]$^+$	[Al(OR^{PF})$_4$]$^-$	Com	[Ga(η^6-C$_6$H$_5$F)]$^+$[WCA]$^-$ + [18]crown-6 (n = 2, 3)		168

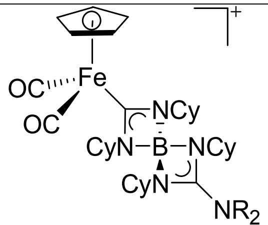
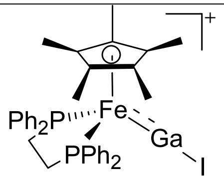
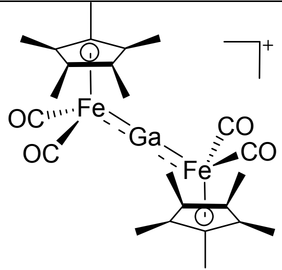
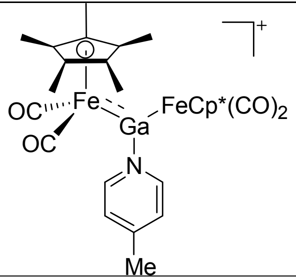
$[In([18]crown\text{-}6)]^+$	$[OTf]^-$	Com	$In^+[WCA]^-$ + [18]crown-6	no coordinated solvent, but a strong anion-cation interaction: cf. In–O = 227.2 pm and 278.5 pm (sum of the van der Waals radii 345 pm)	192,193
$[In([18]crown\text{-}6)(\eta^6\text{-}/\ \eta^1\text{-}C_6H_5F)_2]^+$	$[Al(OR^{PF})_4]^-$	Com	$[In(\eta^6\text{-}C_6H_5F)_n]^+[WCA]^-$ + [18]crown-6 (n = 2, 3)	similar structure to the gallium analogue (see above)	168
$[In([15]crown\text{-}5)_2]^+$	$[OTf]^-$	Com	$In^+[WCA]^-$ + [15]crown-5	sandwich complex	194
$[\{HC(3,5\text{-}Me_2pz)_3\}_nTl]^+$ (n = 1, 2)	$[PF_6]^-$	Com	$Tl^+[WCA]^-$ + $HC(3,5\text{-}Me_2pz)_3$		219
$[Tl([18]crown\text{-}6)]^+$	$[H_2N\{B(C_6F_5)_3\}_2]^-$	Com	$[Tl(C_6H_5Me)_2]^+[WCA]^-$ + [18]crown-6	similar to gallium analogue, yet featuring significant Tl–F interactions to two counteranions	203
Transition-Metal Substituted					
$[(FP^*)(BMes)]^+$	$[B(Ar^{CF3})_4]^-$	Salt	$(FP^*)(BMes)Br$ + $Na^+[WCA]^-$		220
$[CpFe(CO)(PCy_3)\text{-}(BNCMes_2)]^+$	$[B(Ar^{Cl})_4]^-$	Salt	$CpFe(CO)(PCy_3)(B(Cl)\text{-}NCMes_2)$ + $Na^+[WCA]^-$		221
$[CpM(CO)(R)\{B(NCy_2)\}]^+$ (M = Fe, Ru; Do = CO, PMe_3, PPh_3)	$[B(Ar^{CF3})_4]^-$	Salt	$CpM(CO)(R)\{B(NCy_2)Cl\}$ + $Na^+[WCA]^-$		12,124
$[(Cy_3P)_2(MeCN)Pt(B{\equiv}O)]^+$	$[B(Ar^{CF3})_4]^-$	Salt, Com	$(Cy_3P)_2Pt(B{\equiv}O)(Br)$ + $Ag^+[WCA]^-$ + MeCN		121

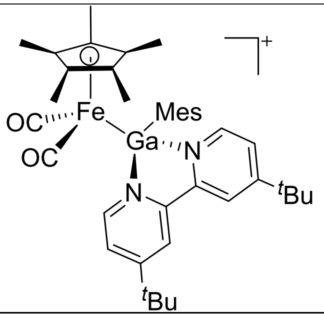
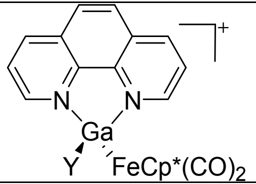
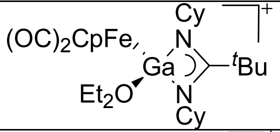
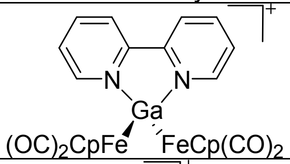
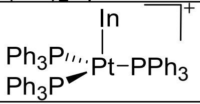
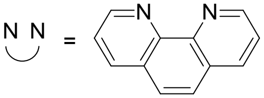
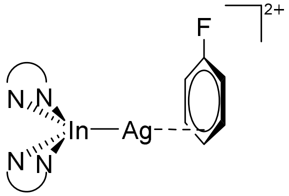
$[\{(OC)_5Mn\}_2(\mu\text{-}B)]^+$	$[B(Ar^{CF3})_4]^-$	Salt	$\{(OC)_5Mn\}_2(\mu\text{-}BBr)$ + Na^+[WCA]$^-$		222
$[(FP')_2(\mu\text{-}B)]^+$	$[B(Ar^{CF3})_4]^-$	Salt	$(FP')_2B(Cl)$ + Na^+[WCA]$^-$		222
$[Fc(NC_5H_2Me_2)BPh]^+$	$[Al(OR^{PF})_4]^-$	Salt	 + Ag^+/Li^+[WCA]$^-$		223
$[(FP)\{B(N^iPr_2)(OPPh_3)\}]^+$	$[B(Ar^{CF3})_4]^-$	Com	$[(FP)B(N^iPr_2)]^+$[WCA]$^-$ + Ph_3PO		224
$[(FP)B\{N(^iPr)(CMe_2)\}(Do)]^+$ (Do = $Ph_2C{=}O$, $Me_2C{=}N^iPr$)	$[B(Ar^{CF3})_4]^-$	Com, Other	$[(FP){=}B{=}N^iPr_2]^+$[WCA]$^-$ + Do	 including a Meerwein-Ponndorf β-hydride transfer	225
$[(FP)B(NCy_2)(Do)]^+$ (Do = $C_5H_4PPh_3$, 4-Pic)	$[B(Ar^{CF3})_4]^-$	Com	$[(FP){=}B{=}NCy_2]^+$[WCA]$^-$ + Do		12

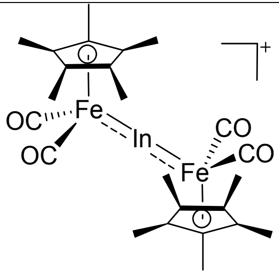
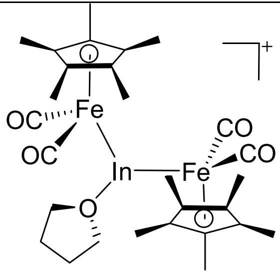
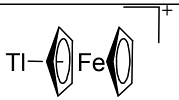
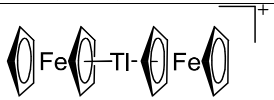
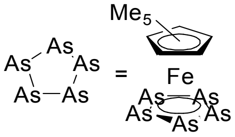
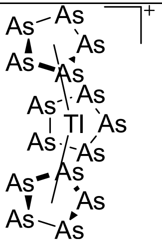
$[CpRu(CO)_2\{B(NCy_2)\text{-}(4\text{-}Pic)\}]^+$	$[B(Ar^{CF3})_4]^-$	Salt, Com	$CpRu(CO)_2\{B(NCy_2)Cl\} + Na^+[WCA]^- +$ 4-Pic		124
$[(FP^*)B(Cl)(LB)]^+$ (Do = 3,5-lutidine, PMe_3, IMe)	$[B(Ar^{Cl})_4]^-$	Salt	$(FP^*)B(Cl_2)(Do) + Na^+[WCA]^-$		226
$[(FP^*)B(nacnac)]^+$	$[B(Ar^{CF3})_4]^-$	Salt, other	 $Na^+[WCA]^-$		227
$[(FP)C(NCy)_2BNR_2]^+$ (R = ^{i}Pr, Cy)	$[B(Ar^{CF3})_4]^-$	Ins	$[(FP)(BNR)_2]^+[WCA]^- +$ RN=C=NR (substoichiometric)		228

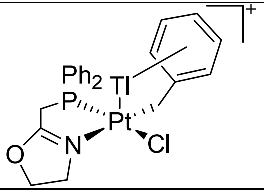
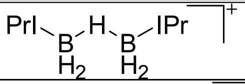
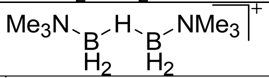
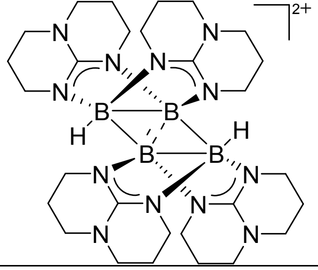
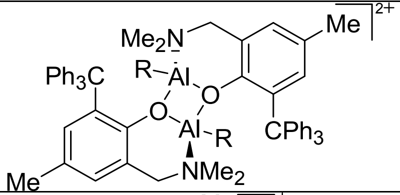
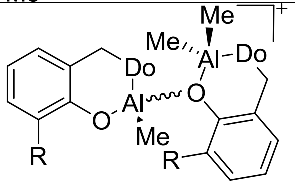
$[(H)(PNP)Pd(BCat)]^+$	$[B(Ar^{CF3})_4]^-$	Other	$[(BCat)(PNP)Pd(BCat)]^+[WCA]^- + H_2O$		117
$[(R_3P)_2Pt\{B(Fc)Br\}]^+$ (R = ^{i}Pr, Cy)	$[B(Ar^{CF3})_4]^-$	Salt	$(R_3P)_2Pt(Br)\{B(Fc)Br\} + Na^+[WCA]^-$		229,230
$[(Cy_3P)_2Pt\{B(X)X'\}]^+$ (X=Br; X′=*ortho*-tolyl, ^{t}Bu, NMe$_2$, Pip, Br; XX′=(NMe$_2$)$_2$, CatB)	$[B(Ar^{CF3})_4]^-$ / $[B(C_6F_5)_4]^-$	Salt	$(Cy_3P)_2Pt(Br)\{B(X)X'\} + Na^+/K^+[WCA]^-$		231
$[(Cy_3P)_2Pt(Br)\{B(NC_5H_4\text{-}4\text{-}R)X\}]^+$ (R = Me, X = NMe$_2$, Pip, Br; R = ^{t}Bu, X = Pip)	$[B(Ar^{CF3})_4]^-$	Salt	$(Cy_3P)_2Pt(Br)\{B(Br)\text{-}(NC_5H_4\text{-}4\text{-}R)X\} + Na^+[WCA]^-$		125
$[(Cy_3P)_2Pt\{B(Br)(NMe_2)\}\text{-}(NCMe)]^+$	$[B(Ar^{CF3})_4]^-$ / $[B_{12}Cl_{12}]^{2-}$	Com / Salt, Com	$(Cy_3P)_2Pt\{B(Br)(NMe_2)\}$ + NCMe / $(Cy_3P)_2Pt\{B(Br)(NMe_2)\}Br + \{Na^+\}_2[WCA]^{2-}$ + MeCN		230
$[(Cy_3P)_2Pt(BCl_2)]^+$	$[B(Ar^{CF3})_4]^-$	Salt	$(Cy_3P)_2Pt(BCl_2)Cl + Na^+[WCA]^-$		230

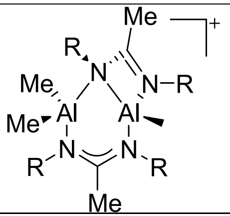
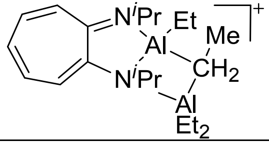
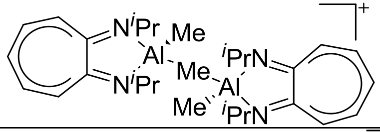
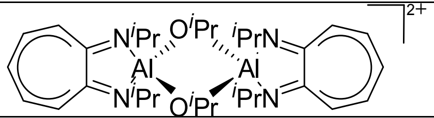
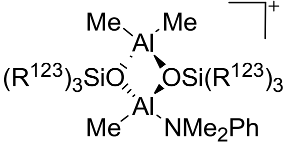
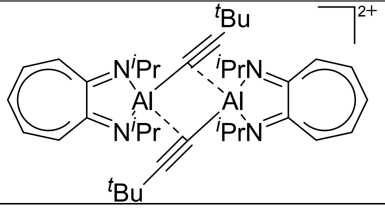
$[Cp^*Ru(P^iPr_3)(BH_2Mes)]^+$	$[B(C_6F_5)_4]^-$	Salt	$Cp^*Ru(P^iPr_3)$-$(BH_2MesCl) + Li^+[WCA]^-\cdot 2.5\ OEt_2$		232
$[(PMAF)_2BH_2]^+$	$[B(C_6F_5)_4]^-$	Hyd, Com	$PMAF–BH_3 + [CPh_3]^+[WCA]^- + PMAF$		212
$[Rh(PPh_3)_2(\kappa^1,\eta$-$PPh_2BH_2\cdot PPh_3)]^+$	$[B(Ar^{CF3})_4]^-$	Salt, Com	$ClRh(PPh_3)_3 + Na^+[WCA]^- + H_3B\cdot PPh_2H$		120
$[FcBMe(bipy)]^+$	$[PF_6]^-$	Salt, Com	$FcBBrMe + bipy + [NH_4]^+[WCA]^-$		126
$[FcB(Pic)_3]^{2+}$	$[B(Ar^{CF3})_4]^-$	Salt, Com	$Br_2BFc + 2\ Na^+[WCA]^- + 3\ Pic$	 rare example of a structurally characterized boron dication	122

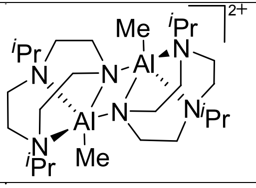
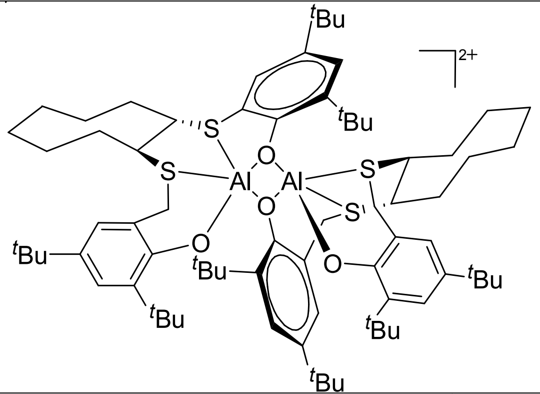
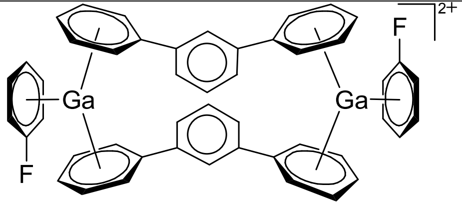
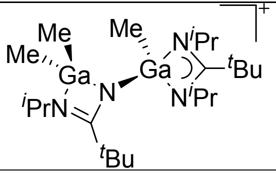
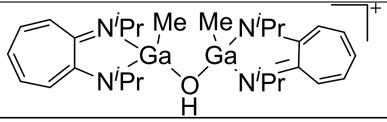
$[(FP)\{C(NCy)_2B\text{-}(NCy)_2CNR_2\}]^+$ (R = ^{i}Pr, Cy)	$[B(Ar^{CF3})_4]^-$	Ins	$[(FP)\{B(NR_2)\}]^+$ + CyN=C=NCy		124,228
$[(dppe)Cp^*FeGaI]^+$	$[B(Ar^{CF3})_4]^-$	Salt	$(dppe)Cp^*FeGaI_2$ + $Na^+[WCA]^-$		233
$[(FP^*)_2Ga]^+$	$[B(Ar^{CF3})_4]^-$	Salt	$(FP^*)_2GaCl$ + $Na^+[WCA]^-$		169
$[(FP^*)_2Ga(4\text{-}Pic)]^+$	$[B(Ar^{CF3})_4]^-$	Salt, Com	$(FP^*)_2GaCl$ + $Na^+[WCA]^-$ + 4-Pic		170

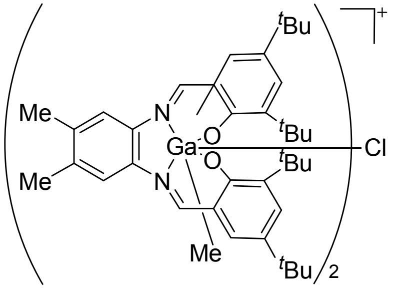
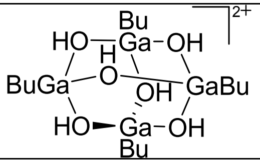
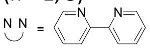
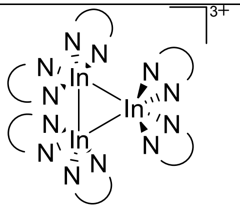
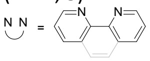
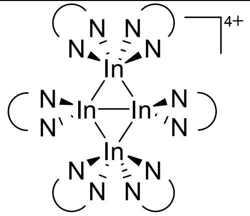
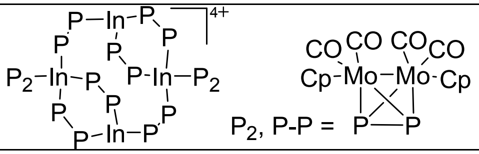
[(FP*)Ga(Mes)(dtbpy)]$^+$	[B(Ar^{CF3})$_4$]$^-$	Salt, Com	(FP*)Ga(Mes)I + Na$^+$[WCA]$^-$ + dtbpy		234
[(FP*)Ga(phen)(Y)]$^+$ (Y = Cl, S^{p}Tol)	[BPh$_4$]$^-$	Salt, Com / Lewis	2 (FP*)GaCl$_2$ + Na$^+$[WCA]$^-$ + phen / [(FP*)Ga(phen)(Cl)]$^+$ + Me$_3$SiS^{p}Tol		171
[(FP)Ga(OEt$_2$){(NCy)$_2$-C^{t}Bu}]$^+$	[B(Ar^{CF3})$_4$]$^-$	Salt, Com	(FP)Ga(Cl){(NCy)$_2$C^{t}Bu} + Na$^+$[WCA]$^-$ in Et$_2$O		235
[(FP)$_2$Ga(bipy)]$^+$	[Cl$_2$Ga(FP)$_2$]$^-$	Lewis, Com	2 ClGa(FP)$_2$ + bipy		236
[InPt(PPh$_3$)$_3$]$^+$	[B(Ar^{CF3})$_4$]$^-$	Com	In$^+$[WCA]$^-$ + Pt(PPh$_3$)$_4$		179,180
[(phen)$_2$In-Ag(η^3-C$_6$H$_5$F)]$^{2+}$	[Al(OR^{PF})$_4$]$^-$	Com	[In(C$_6$H$_5$F)$_n$]$^+$[WCA]$^-$ + phen (n = 2, 3) 	 first cationic indium-silver compound	17

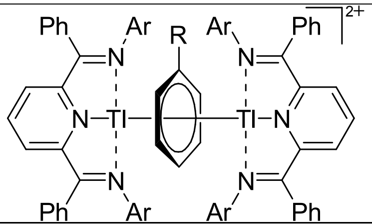
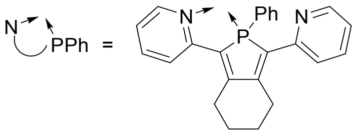
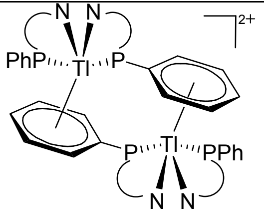
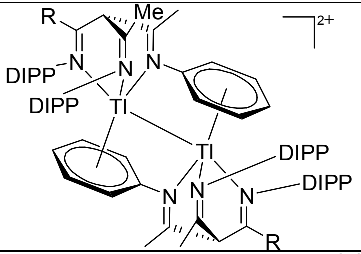
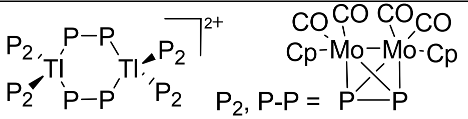
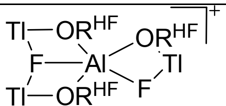
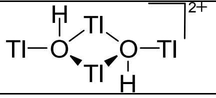
$[(FP^*)_2In]^+$	$[B(Ar^{CF3})_4]^-$	Salt	$(FP^*)_2InCl + Na^+[WCA]^-$		195
$[(FP^*)_2In(THF)]^+$	$[B(Ar^{CF3})_4]^-$	Com	$[(FP^*)_2In]^+[WCA]^- + THF$		195
$[Tl(\eta^5\text{-}FeCp_2)]^+$	$[H_2N\{B(C_6F_5)_3\}_2]^-$	Others	$[Tl(\eta^6\text{-}C_6H_5Me)_3]^+[WCA]^- + 2.2\ FeCp_2$		204
$[Tl_2(\eta^5\text{-}FeCp_2)_3]^{2+}$	$[H_2N\{B(C_6F_5)_3\}_2]^-$	Com	$[Tl(\eta^6\text{-}C_6H_5Me)_2]^+[WCA]^- + FeCp_2$	 1:1 mixture of $[Tl(\eta^5\text{-}FeCp_2)]^+$ and $[Tl(\eta^5\text{-}FeCp_2)_2]^+$	203
$[Tl\{(\eta^5\text{-}As_5)FeCp^*\}_3]^+$	$[FAl\{OC_6F_{10}(C_6F_5)\}_3]^-$	Salt, Com	$Cp^*Fe(\eta^5\text{-}As_5) + Tl^+[PF_6]^- + Li^+[WCA]^-$ 	 trigonal planar complex with no short distances to the next units	176

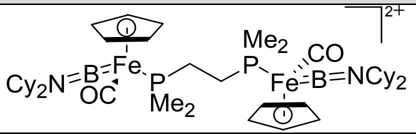
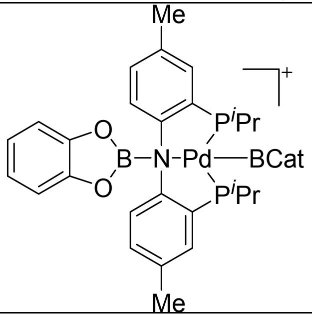
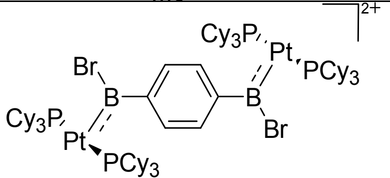
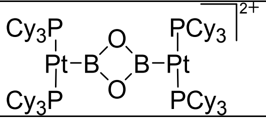
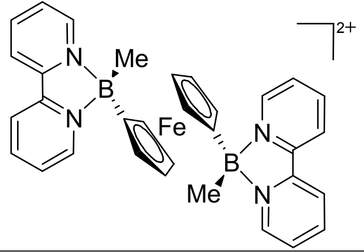
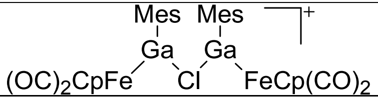
[{P(Ph$_2$)CH$_2$ox}(Cl)(Tl)Pt-CH$_2$Ph}]$^+$	[PF$_6$]$^−$	Other	Tl$^+$[WCA]$^−$ + {P(Ph$_2$)CH$_2$ox}Pt(Cl)-CH$_2$Ph}		208
Multinuclear					
[{IPr(H$_2$B)}$_2$(μ-H)]$^+$	[HB(C$_6$F$_5$)$_3$]$^−$	Hyd	IPr+ B(C$_6$F$_5$)$_3$		118,119
[{Me$_3$N(H$_2$B)}$_2$(μ-H)]$^+$	[B(C$_6$F$_5$)$_4$]$^−$	Hyd	Me$_3$N–BH$_3$ + [CPh$_3$]$^+$[WCA]$^−$		237
[B$_4$H$_2$(μ-hpp)$_4$]$^{2+}$	[HB(C$_6$F$_5$)$_3$]$^−$	Hyd, Com	[HB(μ-hpp)]$_2$ + B(C$_6$F$_5$)$_3$		123
[[{6-(CH$_2$NMe$_2$)-2-CPh$_3$-4-Me-C$_6$H$_2$O}Al(R)]$_2$]$^{2+}$ (R = C$_6$H$_{13}$)	[B(C$_6$F$_5$)$_4$]$^−$	Com	[{6-(CH$_2$NMe$_2$)-2-CPh$_3$-4-Me-C$_6$H$_2$O}Al(^{i}Bu)(BrPh)]$^+$[WCA]$^−$ + 1-hexene		152
[{2-(CH$_2$Do)-6-R-C$_6$H$_3$O}AlMe({2-(CH$_2$Do)-6-R-C$_6$H$_3$O}AlMe$_2$)]$^+$ (R = Ph, ^{t}Bu; Do = NMe$_2$, NC$_4$H$_8$, NC$_5$H$_{10}$)	[MeB(C$_6$F$_5$)$_3$]$^−$	Alk	{2-(CH$_2$Do)-6-R-C$_6$H$_3$O}AlMe$_2$ + B(C$_6$F$_5$)$_3$		238,214

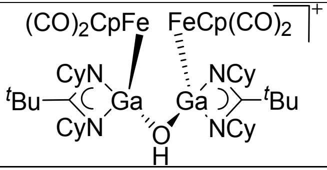
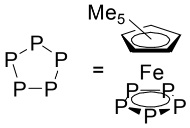
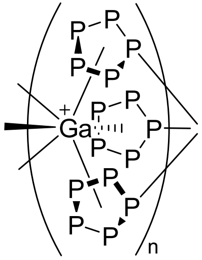
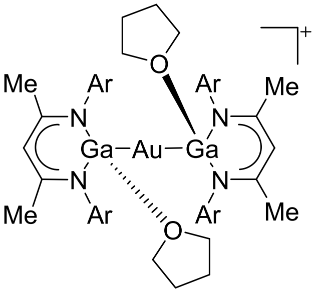
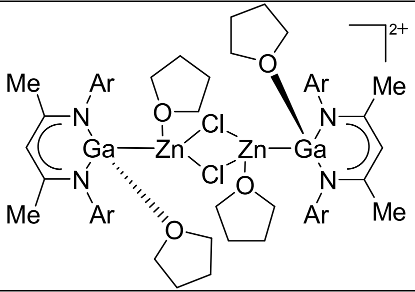
$[\{MeC(NR)_2\}_2Al_2Me_3]^+$ (R = ^{i}Pr, Cy)	$[B(C_6F_5)_4]^-$ / $[MeB(C_6F_5)_3]^-$	Alk, Com	$\{MeC(NR)_2\}AlMe_2$ + $[CPh_3]^+[WCA]^-$ / $B(C_6F_5)_3$		156
$[AlEt(\mu\text{-}\eta^2,\eta^1\text{-}{}^iPr_2\text{-ATI})\text{-}(\mu\text{-Et})AlEt_2]^+$	$[B(C_6F_5]^-$	Com	$[({}^iPr_2\text{-ATI})Al(Et)]^+[WCA]^-$ + $AlEt_3$		141
$[\{({}^iPr_2\text{-ATI})AlMe\}_2(\mu\text{-Me})]^+$	$[B(C_6F_5)_4]^-$	Alk, Com	$({}^iPr_2\text{-ATI})AlMe_2$ + $[CPh_3]^+[WCA]^-$		141,239
$[\{({}^iPr_2\text{-ATI})Al(\mu\text{-O}^iPr)\}_2]^{2+}$	$[B(C_6F_5)_4]^-$	Com	$[({}^iPr_2\text{-ATI})Al(Et)]^+[WCA]^-$ + Aceton		141,153
$[Me_2Al(\mu\text{-OSi}(R^{123})_3)_2Al\text{-Me}(NMe_2Ph)]^+$ (R^1, R^2 = Me; R^3 = Me, ^{t}Bu)	$[B(C_6F_5)_4]^-$	Prot	$Me_2Al(\mu\text{-OSiR}_3)_2AlMe_2$ + $[HNMe_2Ph]^+[WCA]^-$	 (R^1, R^2 = Me; R^3 = Me, ^{t}Bu)	154
$[\{({}^iPr_2\text{-ATI})Al\text{-}(\mu\text{-C}\equiv C^tBu)\}_2]^{2+}$	$[B(C_6F_5)_4]^-$	Com	$[({}^iPr_2\text{-ATI})Al(Et)]^+[WCA]^-$ + *tert*-butyl acetylene		141,153

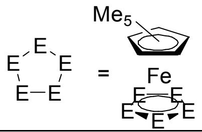
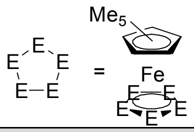
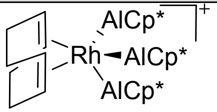
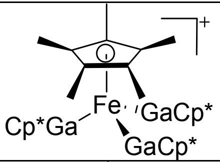
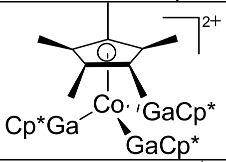
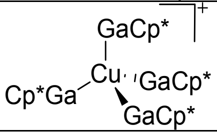
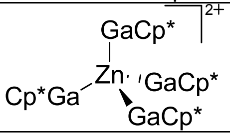
$[\{(\text{tacn})\text{AlMe}\}_2]^{2+}$	$[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$	Alk	$[(\text{tacn})\text{AlMe}_2]_2 + \text{B}(\text{C}_6\text{F}_5)_3$		240
$[\{(\text{OSSO})\text{Al}\}_2]^{2+}$	$[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$	Alk	$(\text{OSSO})\text{AlMe} + \text{B}(\text{C}_6\text{F}_5)_3$		155
$[(\eta^6\text{-C}_6\text{H}_5\text{F})\text{Ga-}(\mu\text{-}\eta^6\text{-}m\text{-TP})_2\text{-Ga}(\eta^6\text{-C}_6\text{H}_5\text{F})]^{2+}$	$[\text{Al}(\text{OR}^{\text{PF}})_4]^-$	Com	$[\text{Ga}(\eta^6\text{-C}_6\text{H}_5\text{F})_n]^+[\text{WCA}]^- + m\text{-TP}$ (n = 2, 3)	 first structurally characterized dicationic *ansa*-arene complex	8,99
$[\{^t\text{BuC}(\text{N}^i\text{Pr})_2\}\text{GaMe-}\{^t\text{BuC}(\text{N}^i\text{Pr})_2\}\text{GaMe}_2]^+$	$[\text{B}(\text{C}_6\text{F}_5)_4]^-$	Alk, Com	$\{^t\text{BuC}(\text{N}^i\text{Pr})_2\}\text{GaMe}_2 + [\text{Ph}_3\text{C}]^+[\text{WCA}]^-$		156
$[\{(^i\text{Pr}_2\text{-ATI})\text{GaMe}\}_2(\mu\text{-OH})]^+$	$[\text{B}(\text{C}_6\text{F}_5)_4]^-$	Other	$[(^i\text{Pr}_2\text{-ATI})\text{Ga}(\text{Me})(\text{NMe}_2\text{Ph})]^+[\text{WCA}]^- +$ H_2O		172

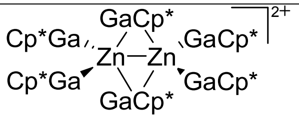
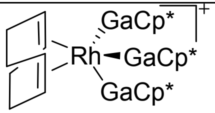
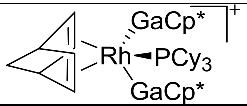
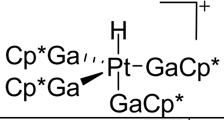
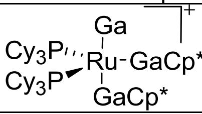
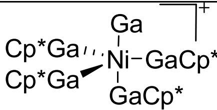
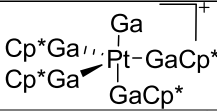
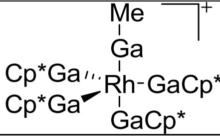
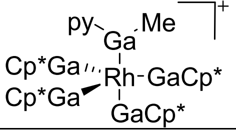
$[\{(\text{Salomphen})\text{Ga}\}(\mu\text{-Cl})]^+$	$[BPh_4]^-$	Salt	(Salomphen)GaCl + $Na^+[BPh_4]^-$		241
$[(\text{BuGa})_4(\mu\text{-OH})_6]^{2+}$	$[HCB_{11}Br_6Me_5]^-$	Other	$[(2,6\text{-}Mes_2C_6H_3)GaBu]^+$ $[WCA]^-$ + H_2O		173
$[\{(PPh_3)_3In\}_2(\mu\text{-}PPh_3)]^{2+}$	$[Al(OR^{PF})_4]^-$	Com	$[In(C_6H_5F)_n]^+[WCA]^-$ + PPh_3 (n = 2, 3)	one PPh_3 moiety functions as a bridge between both In^I cations	162
$[In_3(\text{bipy})_{5\text{-}6}]^{3+}$	$[Al(OR^{PF})_4]^-$	Com	$[In(C_6H_5F)_n]^+[WCA]^-$ + bipy (n = 2, 3) 	 first cationic indium clusters	17
$[In_4(\text{Do})_6]^{4+}$ (Do = bipy, phen)	$[Al(OR^{PF})_4]^-$	Com	$[In(C_6H_5F)_n]^+[WCA]^-$ + phen (n = 2, 3) 	 first cationic indium cluster	17
$[In_4\{(CpMo(CO)_2)_2P_2\}_8]^{4+}$	$[Al(OR^{PF})_4]^-$	Com	$[In(o\text{-}C_6H_4F_2)_2]^+[WCA]^-$ + $\{CpMo(CO)_2\}_2(P_2)$		186

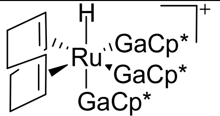
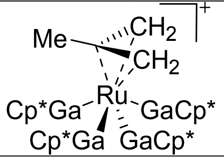
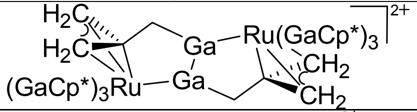
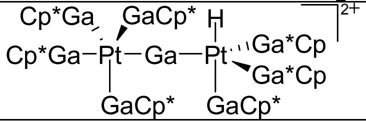
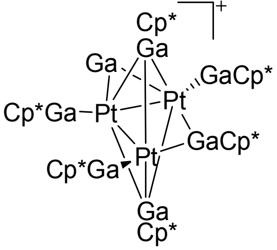
$[\{\{ArN{=}CPh\}_2(NC_5H_3)Tl\}_2(\mu\text{-}\eta^6\text{-}C_6H_5R)]^{2+}$ (Ar = 2,6-$Et_2C_6H_3$, 2,5-$^tBu_2C_6H_3$; R = H, Me)	$[OTf]^-$	Com	2 $[(ArN{=}CPh)_2(C_5H_3N)Tl]^+[WCA]^-$ + C_6H_5R		206
$[Tl_2(NPPh)_4]^{2+}$ NPPh = 2,5-Bis(2-pyridyl)-1-phenylphosphole	$[Al(OR^{PF})_4]^-$	Com	$Tl^+[WCA]^-$ + NPPh in CH_2Cl_2 / *n*-pentane 	 If $[PF_6]^-$ is employed as WCA, a one-dimensional coordination polymer forms	218
$[Tl(\beta\text{-triketimine})_2]^{2+}$ (R = Me, ^tBu)	$[B(Ar^{CF3})_4]^-$	Com	$Tl^+[WCA]^-$ + β-triketimine		14
$[Tl_2(\{CpMo(CO)_2\}_2)_6]^{2+}$	$[Al(OR^{PF})_4]^-$	Com	$\{CpMo(CO)_2\}_2(P_2)$ + $Tl^+[WCA]^-$		207
$[Tl_3F_2Al(OR^{HF})_3]^+$	$[Al(OR^{HF})_4]^-$	Salt, Other	TlF + 2 $Li^+[WCA]^-$		200
$[Tl_4(\mu\text{-}OH)_2]^{2+}$	$[H_2N\{B(C_6F_5)_3\}_2]^-$	Other	$[Tl(OEt_2)_2]^+[WCA]^-$ + H_2O		203
$[\{Tl(OR)_4(\mu\text{-}Cl)_2\}^+]_n$	$[PF_6]^-$	Other	$RuCl_2(DMeOPrPE)_2$ + $Tl^+[WCA]^-$	"arrested" chloride abstraction yielding a one-dimensional coordination polymer	209

Multinuclear Transition-Metal Substituted					
$[(\mathrm{CpFe(CO)\{B(NCy_2)\}})_2\text{-}(\mu\text{-dmpe})]^{2+}$	$[\mathrm{B(Ar^{CF3})_4}]^-$	Com, Salt	$(\mathrm{FP})\{\mathrm{B(NCy_2)}\}\mathrm{Cl}$ + dmpe + $\mathrm{Na^+[WCA]^-}$		124
$[(\mathrm{BCat})(\mathrm{PNP})\mathrm{Pd}(\mathrm{BCat})]^+$	$[\mathrm{B(Ar^{CF3})_4}]^-$ / $[\mathrm{CB_{11}H_{12}}]^-$	Other	$[(\mathrm{PNP})\mathrm{Pd(THF)}]^+$ $[\mathrm{WCA}]^-$ / $(\mathrm{PNP})\mathrm{Pd(CB_{11}H_{12})}$ + CatB–BCat		117
$[(\mathrm{Cy_3P})_2\{\mathrm{Pt(BBr)}\}_2\text{-}(\mu\text{-C_6H_4})]^{2+}$	$[\mathrm{B(C_6F_5)_4}]^-$	Salt	$\{(\mathrm{Cy_3P})_2\mathrm{Pt(Br)(BBr_2)}\}_2\text{-}(\mu\text{-C_6H_4})$ + $\mathrm{K^+[WCA]^-}$		125
$[\{(\mathrm{Cy_3P})_2\mathrm{PtB}\}_2(\mu\text{-O})_2]^{2+}$	$[\mathrm{Al(OR^{PF})_4}]^-$	Salt	$(\mathrm{Cy_3P})_2\mathrm{BrPt(B{\equiv}O)}$ + $\mathrm{Ag^+[WCA]^-}$		242
$[\{(\mathrm{bipy})(\mathrm{Me})\mathrm{B}\}_2(\mu\text{-Fc})]^{2+}$	$[\mathrm{PF_6}]^-$	Salt, Com	$\mathrm{Fc(BBrMe)_2}$ + 2 bipy + $[\mathrm{NH_4}]^+[\mathrm{WCA}]^-$		126,127
$[\{(\mathrm{FP})\mathrm{Ga(Mes)}\}_2(\mu\text{-Cl})]^+$	$[\mathrm{B(Ar^{CF3})_4}]^-$	Salt, Com	$(\mathrm{FP})\mathrm{Ga(Mes)(Cl)}$ + $\mathrm{Na^+[WCA]^-}$		195

$[\{\{FeCp(CO)_2\}Ga\{(NCy)_2\text{-}C^tBu\}\}_2(\mu\text{-}OH)]^+$	$[B(Ar^{CF3})_4]^-$	Other	$[FpGa(OEt_2)\text{-}\{(NCy)_2C^tBu\}]^+[WCA]^- + H_2O$		235
$[\{Ga(P_5FeCp^*)_3\}^+]_n$	$[Al(OR^{PF})_4]^-$	Com	$P_5FeCp^* + [Ga(o\text{-}C_6H_4F_2)_2]^+[WCA]^-$ 	 one-dimensional coordination polymer	176
$[\{(DDP)(THF)Ga\}_2Au]^+$	$[B(Ar^{CF3})_4]^-$	Salt, Com	$\{(DDP)Ga\}_2AuCl + Na^+[WCA]^-$ in THF		174
$[\{(THF)(DDP)GaZn(THF)\}_2\text{-}(\mu\text{-}Cl)_2]^{2+}$	$[B(Ar^{CF3})_4]^-$	Salt, Com	$(DDP)(Cl)GaZn(Cl)(THF)_2 + Na^+[WCA]^-$ in THF		175

$[\{In\{\eta^5\text{-}E_5)FeCp^*\}_3\}^+]_n$ (E = P, As)	$[Al(OR^{PF})_4]^-$	Com	$E_5FeCp^* + In^+[WCA]^-$  	one-dimensional coordination polymer / similar structure to $[\{Ga(P_5FeCp^*)_3\}^+]_n$	176
$[\{Tl\{(\eta^5\text{-}E_5)FeCp^*\}_3\}^+]_n$ (E = P, As)	$[Al(OR^{PF})_4]^-$	Com	$E_5FeCp^* + Tl^+[WCA]^-$  	one-dimensional coordination polymer / similar structure to $[\{Ga(P_5FeCp^*)_3\}^+]_n$	207,176
ECp* Substituted (E = Al, Ga)					
$[Rh(COD)(AlCp^*)_3]^+$	$[B(Ar^{CF3})_4]^-$	Com	$[Rh(COD)_2]^+[WCA]^- + 3\ AlCp^*$	 	157
$[Cp^*Fe(GaCp^*)_3]^+$	$[B(Ar^{CF3})_4]^-$	Com	$[Fe(MeCN)_6]^{2+}\{[WCA]^-\}_2 + 4\ GaCp^*$	 	243
$[Cp^*Co(GaCp^*)_3]^{2+}$	$[B(Ar^{CF3})_4]^-$	Ox, Com	$[Co(MeCN)_6]^{2+}\{[WCA]^-\}_2 + 4\ GaCp^*$	 	243
$[Cu(GaCp^*)_4]^+$	$[B(Ar^{CF3})_4]^-$	Com	$[Cu(MeCN)_4]^+[WCA]^- + 4\ GaCp^*$	 	243
$[Zn(GaCp^*)_4]^{2+}$	$[B(Ar^{CF3})_4]^-$	Prot, Com	$ZnMe_2 + [H(OEt_2)_2]^+[WCA]^- + 4\ GaCp^*$	 	175

[Zn$_2$(GaCp*)$_6$]$^{2+}$	[B(Ar^{CF3})$_4$]$^-$	Other	Zn$_2$Cp*$_2$ + [Ga$_2$Cp*]$^+$[WCA]$^-$ mechanism unclear	 stabilized by dispersion forces	244
[Rh(COD)(GaCp*)$_3$]$^+$	[B(Ar^{CF3})$_4$]$^-$	Com	[Rh(COD)$_2$]$^+$[WCA]$^-$ + 3 GaCp*		157
[{Rh(NBD)(PCy$_3$)-(GaCp*)$_2$}]$^+$	[B(Ar^{CF3})$_4$]$^-$	Com	[Rh(NBD)(PCy$_3$)$_2$]$^+$[WCA]$^-$ + 2 GaCp*		157
[Pt(H)(GaCp*)$_4$]$^+$	[B(Ar^{CF3})$_4$]$^-$	Prot	Pt(GaCp*)$_4$ + [H(OEt$_2$)$_2$*]$^+$[WCA]$^-$		180
[(Ga)Ru(PCy$_3$)$_2$(GaCp*)$_2$]$^+$	[B(Ar^{CF3})$_4$]$^-$	Other	Ru(PCy$_3$)$_2$(GaCp*)$_2$(H)$_2$ + [Ga$_2$Cp*]$^+$[WCA]$^-$		177
[(Ga)Ni(GaCp*)$_4$]$^+$	[B(Ar^{CF3})$_4$]$^-$	Other	Ni(GaCp*)$_4$ + [FeCp$_2$]$^+$[WCA]$^-$		178
[(Ga)Pt(GaCp*)$_4$]$^+$	[B(Ar^{CF3})$_4$]$^-$	Com	Pt(GaCp*)$_4$ + [Ga$_2$Cp*]$^+$[WCA]$^-$		179,180
[(Cp*Ga)$_4$Rh{Ga(Me)}]$^+$	[B(Ar^{CF3})$_4$]$^-$	Prot	(Cp*Ga)$_4$Rh-(η^1-Cp*GaMe) + [H(OEt$_2$)$_2$]$^+$[WCA]$^-$		181
[(Cp*Ga)$_4$Rh{Ga(Me)-(py)}]$^+$	[B(Ar^{CF3})$_4$]$^-$	Com	[(Cp*Ga)$_4$Rh(GaMe)]$^+$[WCA]$^-$ + py		181

$[Ru(COD)(H)(GaCp^*)_3]^+$	$[B(Ar^{CF3})_4]^-$	Com	$[Ru(COD)(H)(DMH)_3]^+[WCA]^- + 3\ GaCp^*$		245
$[Ru(GaCp^*)_4\text{-}\{\eta^3\text{-}(CH_2)_2C(Me)\}]^{2+}$	$[B(Ar^{CF3})_4]^-$	Prot	$Ru(GaCp^*)_3(TMM) + [H(OEt_2)_2]^+[WCA]^-$ $TMM=\eta^4\text{-}C(CH_2)_3$		177
$[\{Ru(GaCp^*)_3\text{-}[(CH_2)_2C\{CH_2(\mu\text{-}Ga)\}]\}_2]^+$	$[B(Ar^{CF3})_4]^-$	Com	$Ru(GaCp^*)_3(TMM) + [Ga_2Cp^*]^+[WCA]^-$		177
$[\{(GaCp^*)_4Pt\}\{Pt(H)\text{-}(GaCp^*)_3\}(\mu\text{-}Ga)]^{2+}$	$B(Ar^{CF3})_4]^-$	Prot, Com	$Pt(GaCp^*)_4 + [H(OEt_2)_2^*]^+[WCA]^-$		180
$[Pt_3(GaCp^*)_6(\mu\text{-}Ga)]^+$	$[B(Ar^{CF3})_4]^-$	Other	$Pt(GaCp^*)_4 + [FeCp_2]^+[WCA]^-$ (substoichiometric)	 metal-rich molecules as discrete models for intermetallic phases	178

* Classification according to the introduction (**Table 2**).

Group 14 Cations

Already in 1887, Henderson described the synthesis of trityl malonate starting from triphenylmethyl bromide and ethylic sodiomalonate[246] and 15 years later, Bayer and Villiger realized that the yellow color of a solution of triphenylmethane in concentrated sulfuric acid is the result of the formation of a carbocation.[247] Despite these early discoveries, it took another 63 years until the structure of this cation could be determined.[248] While the first structure determination succeeded with $[ClO_4]^-$, the structure of the trityl cation is nowadays known with several different anions (e.g. [249]) and it has become a common reagent for the generation of various other cations. Only one earlier structure determination of a carbocation was published: the structure of triphenylcyclopropenium perchlorate in 1963.[250] Since then, many rPBCs of group 14 were synthesized and characterized. Carbocations have drawn a lot of interest, due to their role as intermediates in organic chemistry. Silylium ions are more electrophilic and more reactive than their carbon analogues, so that the structural characterization of a truly free silylium ion was only achieved in 2002[24] and is still in the focus of interest. But also the heavier elements of group 14 were subject to extensive research and today a multitude of interesting rPBCs are known, part of which have been reviewed in the articles included with Table 5.

Table 5: Review articles including cationic group 14 compounds

Year	Title	Ref
1995	Modern Approaches to Silylium Cations in Condensed Phase	251
2005	Cations of Group 14 Organometallics	252
2005	Carbon, silicon, germanium, tin and lead	253
2010	Silylium ions in catalysis	254
2010	H^+, CH_3^+, and R_3Si^+ Carborane Reagents: When Triflates Fail	255
2011	N-Heterocyclic Carbene Analogues with Low-Valent Group 13 and Group 14 Elements: Syntheses, Structures, and Reactivities of a New Generation of Multitalented Ligands	256
2013	Catenated Compounds – Group 14 (Ge, Sn, Pb)	257
2015	Cations and dications of heavier group 14 elements in low oxidation states	258

Carbon

Homopolyatomic and Cluster Cations: In group 14, carbon is the only element for which homopolyatomic cations are known in condensed phase. While $[C_{76}]^+$,[44] and $[C_{60}]^+$,[259] are already known for more than ten years, there is only one more recently published compound of that class. In $[C_{60}]^{2+}([AsF_6]^-)_2$,[260] the cations build a 1D polymeric structure, in which the $[C_{60}]^{2+}$ cations are connected alternatingly by single C-C bonds and four-membered carbon rings. Along with the before mentioned $[C_{60}]^+$, the protonated Buckminsterfullerene $[HC_{60}]^+$ was published[259] and by oxidation of the $[C_{59}N]_2$ dimer, $[C_{59}N]^+$ was synthesized and structurally characterized.[261]

Carbonium Ions: As mentioned before, the classification according to onium-, enium and inium-cations is not always consistent and in literature, the term carbonium ion is often used to describe what is mostly a carbenium ion. A prototype for a carbonium ion is the 2-norbornyl cation, whose structure has been controversially discussed. In 2013, 49 years after its first preparation under stable ion conditions,[262] its structure could be determined by scXRD.[86] This finally provided a crystallographic proof that the 2-norbornyl cation adopts the non-classical structure **(Figure 31**).

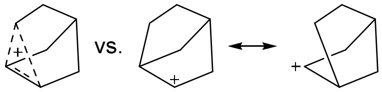


Figure 31. Non-classical vs. classical structure of the 2-norbornyl cation.

It remains the only structurally characterized non-classical carbonium ion. Substituted relatives exhibit distinctly distorted structures that are better classified as carbenium ions.[263]

Carbenium Ions: The first simple structurally characterized alkyl cation, was the *tert*-butyl cation with $[Sb_2F_{11}]^-$ as the counterion,[264] and later also with $[HCB_{11}Me_5Cl_6]^-$. [265] In the same publication, two more carbocations with slight variations in the alkyl chains were presented (**Figure 32**).[265] Recent additions include the super-acidic room temperature Ionic Liquid $[(CH_3)_3C]^+[Al_2Br_7]^-$[266] and an additional structure of the *tert*-butyl cation with the $[HCB_{11}Cl_{11}]^-$ anion.[267] In 2000, *ion-like* $(CH_3)_2CF(AsF_6)$ was the first structural characterized example of a fluorinated carbocation and was published together with a higher substituted variant.[268] In both compounds, each cation is stabilized by two stronger contacts to the anion. The higher substituted $[(m\text{-}CF_3C_6H_4)(C_6H_5)CF]^+$ derivative, contains the less coordinating $[As_2F_{11}]^-$ anion in the structure with only weak interaction between the ions.[268] With $[HCB_{11}I_{11}]^-$, two more fluoro-substituted carbocations and one with fluorine substituted aryl residues could be isolated (see **Figure 32**).[56] Apart from $[CF_3]^+$, all $[CX_3]^+$ cations are now synthesized and structurally characterized (see **Figure 32**). First, $[CI_3]^+[Al(OR^{PF})_4]^-$ was published in 2003[269] and shortly after $[CCl_3]^+$ and $[CBr_3]^+$ with $[Sb(OTeF_5)_6]^-$ as the counterion.[270] In addition, the latter was used to stabilize related $[C(OTeF_5)_3]^+$.[270] Later, also $[CCl_3]^+$ and $[CBr_3]^+$ were synthesized with the $[Al(OR^{PF})_4]^-$ and the $[(R^{PF}O)_3Al\text{–}F\text{–}Al(OR^{PF})_3]^-$ counterions.[271] In all of those compounds containing $[CX_3]^+$ cations, still some weak interactions between cation (mainly halogen atoms) and anion exist. These interactions are weaker between $[Br\text{-}C(SBr)_2]^+$ and the mentioned alkoxyaluminate, due to delocalization of the charge.[117] Although comparable, far stronger interaction between cation and anion was found in $[(MeO)(MeS)CSH]^+[SbF_6]^-$.[272] However, there is no close contact between the carbon atom and the fluorine atoms of the anion. Instead, the anion forms hydrogen bonds to the thiol group of the cation.

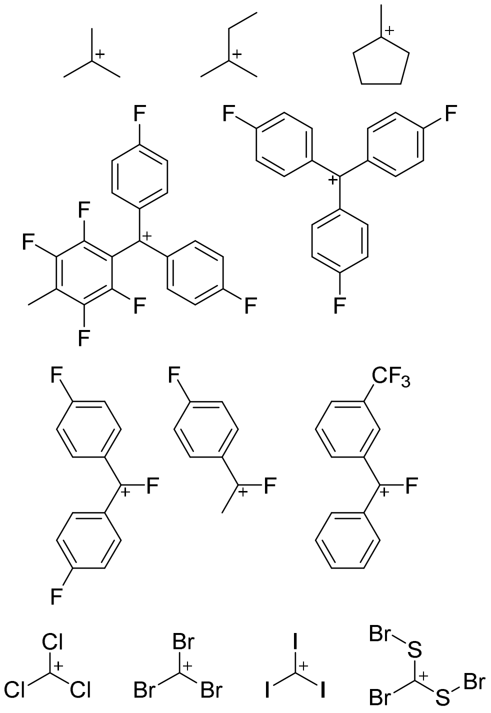


Figure 32. Structurally characterized carbenium ion salts.

In 2004, the structure of the benzonorbornenyl cation was published, with an intramolecular stabilization of the cationic center by the aromatic ring.[273] Intermolecular stabilized carbenium cations are known of the $[CI_3]^+$ with the weak bases PX_3 (X = Cl, Br, I) and AsI_3 (**Figure 33**).[274] Only two related vinyl cations are known (see **Figure 33**).[275,276] Both are β-substituted by two silyl groups, which help to stabilize the positive charge.

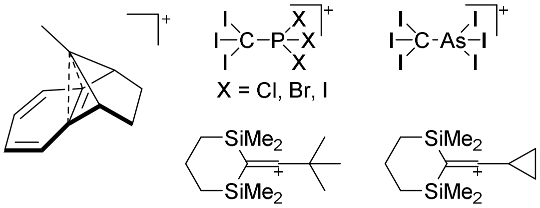


Figure 33. Structurally characterized ligand-stabilized carbenium ions and vinyl cation salts.

Delocalized (Cyclic) Carbocations: Only shortly after the first structural characterization of an alkyl cation, the first structure determination of an arenium ion – $[C_6Me_7]^+[AlCl_4]^-$ – was published.[277] To date, more structurally characterized arenium ions with several WCAs are known (**Figure 34**).

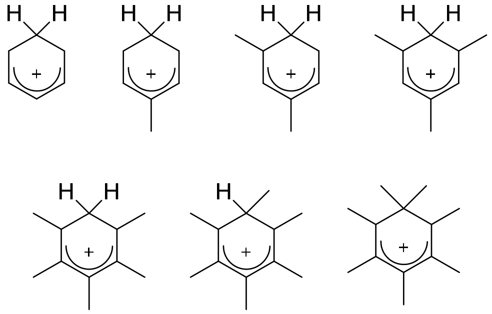


Figure 34. Protonated and methylated structurally characterized arenium ion salts.

An exception is the radical cation $[C_6F_6]^{\cdot +}$ in the solid state structures with $[Sb_2F_{11}]^-$ and $[Os_2F_{11}]^-$: it yields two different forms.[278] One cation can be described as a quinoidal cation and the other as a bisallyl cation (see **Figure 35**) and both are separated by a barrier of ar38ound 13 kJ mol^{-1} according to calculations.

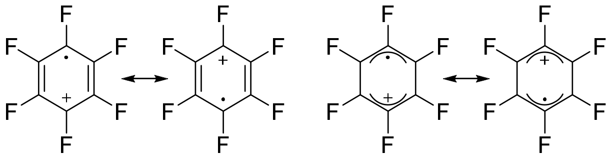


Figure 35. Lewis structures of the canonical forms of the quinoid and the bisallyl cationic form of $[C_6F_6]^{\cdot +}$.

Shortly after the publication of the radical cation of the hexafluorobenzene, some more related structures were presented. Among them, the other perhalogenated benzene radical cations[279,280] and some partially and mixed substituted analogs, including the $[C_6F_5\text{-}C_6F_5]^{\cdot -}$[280,281] (**Figure 36**). The only other example displaying both a quinoidal and a bisallyl cationic form is $[2,4,6\text{-}{}^tBu_3C_6H_2NH_2]^{\cdot +}$.[282] At 123 K, this cation adopts the bisallylic structure but upon heating, a transition to the quinoidal form occurs.

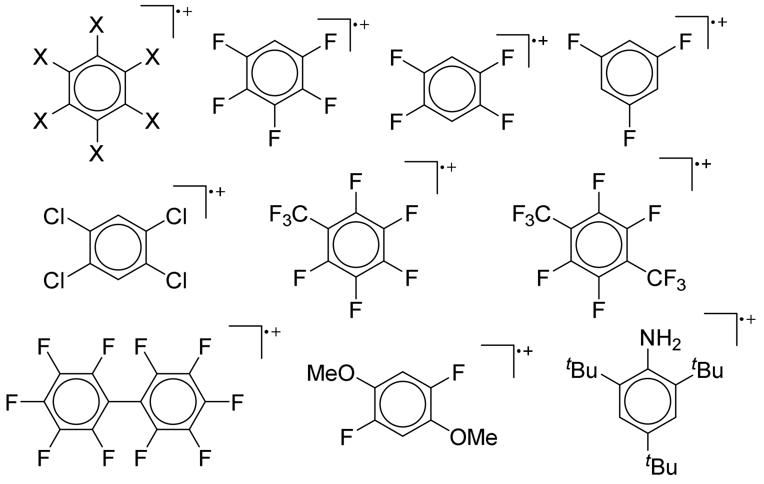


Figure 36. Structurally characterized substituted benzene radical cation salts.

A different type of delocalized cations are the allyl cations amongst which the cyclopropenyl cations take a special position. Already since 1986, two examples, $[(Cy)_3C_3]^+$ and $[(Cy)_2(Ph)C_3]^+$, are known[283] and in the same year, an allyl cation stabilized by an hydroxyl group has been published (**Figure 37**).[284] In 2002, the structure of $[C_5Me_5H_2]^+$ was determined although it was by mistake addressed as an $[C_5Me_5]^+$ cation, probably due to its unexpected formation during the reaction of C_5Me_5H with $[Ph_3C]^+$.[285] Finally a silyl stabilized allyl cation was characterized, which formed via an interesting mechanism that starts with the formation of a silylium cation (**Figure 37**).[286]

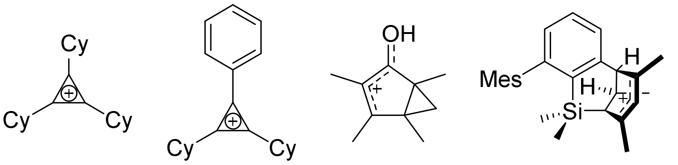


Figure 37. Structurally characterized delocalized cation salts.

Ion-like Carbon Compounds: As mentioned before, in the analog structure of $[(m\text{-}CF_3\text{-}C_6H_4)(Ph)CF]^+$ with $[AsF_6]^-$ instead of $[AsF_{11}]^-$, stronger interactions to the anions are present.[268] The same applies to the related $Me_2CF(AsF_6)$.[268] Also known is the *ion-like* $(Me_2CH)(HCB_{11}Me_5Br_6)$, which displays a covalent C-Br distance of about 210 pm.[287] Along with the latter, the preparation of $H_3C(HCB_{11}Me_5Br_6)$ and $H_3C(HCB_{11}Me_5Cl_6)$ was reported, but no structural data from XRD was presented. In 2010, the strongly methylating *ion-like* $Me_2B_{12}Cl_{12}$ was structurally characterized with a C-Cl bond length of 182 pm.[288]

Silicon

Silylium Ions (CN = 3): Silylium ions are certainly amongst the most electrophilic cations known and thus exhibit an enormous Lewis acidity. Most of them are either stabilized by bulky ligands, or display a strong interaction with the corresponding WCA and have therefore to be categorized as *ion-like* compounds. In addition, the first claimed "stable silyl cation" $[Et_3Si]^+$ in 1993 contained a coordinating toluene ligand – a feature typical for many silylium ions.[289] In order to obtain a truly tricoordinate silylium ion without stabilization through the anion or an additional ligand, bulkier substituents were needed. Hence, the first structurally characterized compound featuring a free silylium ion was $[Mes_3Si]^+[HCB_{11}Me_5Br_6]^-$ [24] and in 2013, $([Pemp_3Si]^+)_2[B_{12}Cl_{12}]^{2-}$ was published (**Figure 38**).[290] The latter was afterwards also synthesized and characterized with $[Al(OR^{PF})_4]^-$.[291] In all three structures, the cation has no closer contacts to the anion.

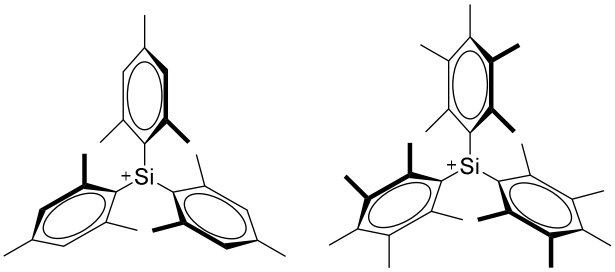


Figure 38. Structurally characterized tricoordinate silylium ions.

Delocalized Cyclic Cations: Despite the early characterization of cyclopropenyl cations, the first example for a comparable silicon ion was published only in 2000 (**Figure 39**, left).[292] In this compound, however, it is not the three-membered silicon-ring with a delocalized π-system but rather a silicon butterfly with one Si-Si-σ-bond stabilizing the positive charge. A direct equivalent of a cyclopropenyl cation was finally published in 2005 (**Figure 39**, middle).[293] One more example is known with the positive charge being partially delocalized over four silicon atoms.[294] An example for a Si(II) cation with 6π-aromaticity provides the silyliumylidene-like species introduced by Driess et al (**Figure 39**, right).[295] This compound is stabilized by delocalization so that, although produced through protonation with $[H(OEt_2)_2]^+[B(C_6F_5)_4]^-$, no ether molecule remains coordinated to the cation.

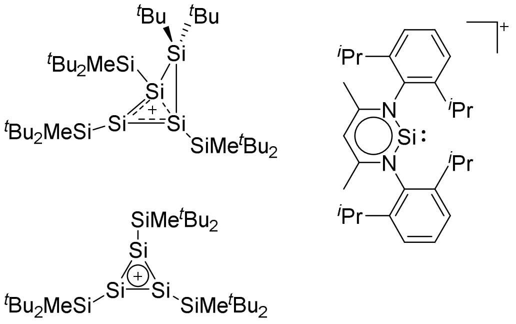


Figure 39. Delocalized cyclic silicon centered cations.

Ligand-stabilized Silicon Cations: Already in 1983, pyridine stabilized $[Me_3Si]^+$ was reported.[296] Yet, this compound is stable to such an extent that Br^- and I^- are sufficient as anions and that it can be prepared just by reacting Me_3SiX with pyridine. Many of these $[R_3Si\text{-}L]^+$ ions stabilized by different σ-donors are known: with nitriles,[297–299] pyridine,[296,300] water,[301] o-dichlorobenzene[81], sulfur dioxide[81] and bipyridine.[302] Even though 2,6-bis(2,6-difluorophenyl)phenyldimethylsilylium ion has no additional ligand acting as a σ-donor, the cationic center is stabilized by one fluorine of each 2,6-difluorophenyl-substituent (**Figure 40**).[303] With the stronger stabilizing DMAP, the dication $[Me_2Si(dmap)_2]^{2+}$ has been synthesized.[302]

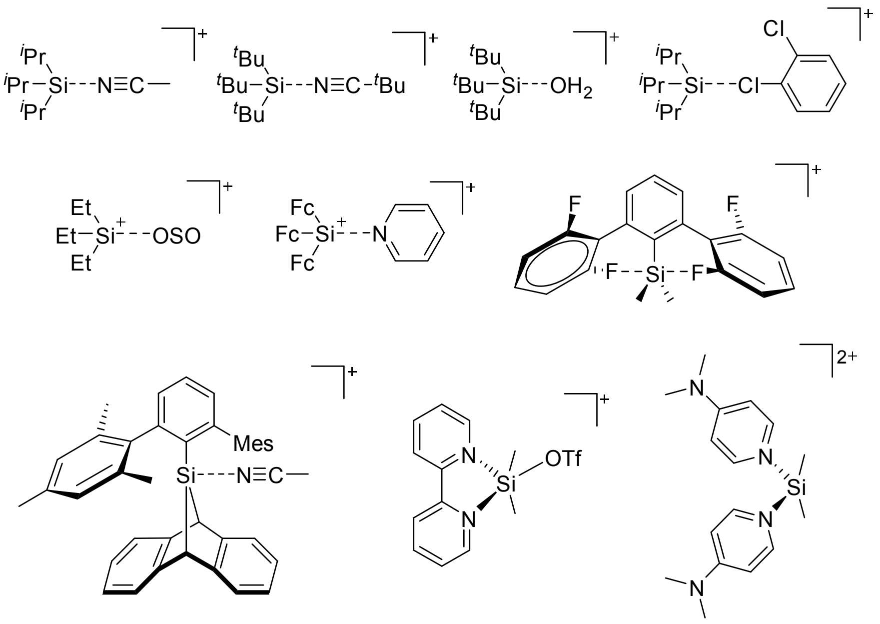


Figure 40. Structurally characterized silylium ions stabilized by σ-donors.

$[R_3Si\text{-}L]^+$ ions with π-donor ligands L = arenes like the before mentioned $[Et_3Si(C_7H_8)]$ are less stabilized than those with σ-donors (**Figure 42**).[289] Several different arene adducts of $[Me_3Si]^+$ were reported by Schulz and Villinger et al (**Figure 42**).[304] As can be seen in **Figure 41**, some of these compounds are coordinated by a second arene molecule binding in an η6-fashion to the proton *ipso* to the silylium center. This also shows that these arena adducts are also very strong cationic Bronsted acids.

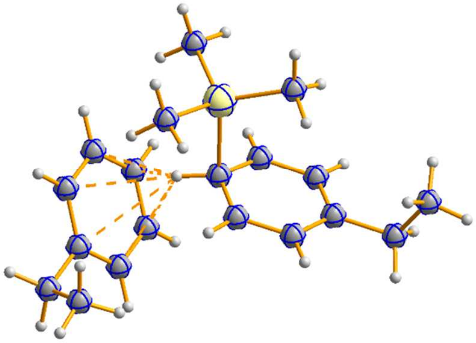


Figure 41. Molecular structure of $[Me_3Si(C_8H_{10})\cdot(C_8H_{10})]^+$. The weak interaction between the stabilized cation and the adjacent ethylbenzene is indicated by the dashed bonds. M. F. Ibad, P. Langer, A. Schulz, A. Villinger *J. Am. Chem. Soc.* 2011, *133*, 21016–21027. Data from this Reference were used to draw this figure.

Comparable to the before mentioned 2,6-bis(2,6-difluorophenyl)phenyldimethylsilylium ion without any additional ligand, a 2,6-diarylphenyldimethylsilyl cation is existing, which is stabilized by intramolecular π-donation.[76]

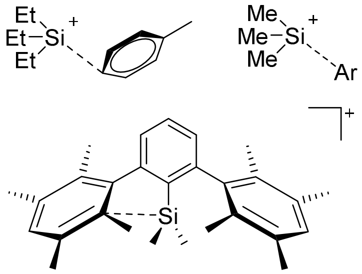
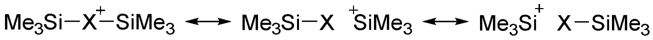


Figure 42. Structurally characterized silylium ions stabilized by internal or external π-donors. Ar = benzene, toluene, ethylbenzene, *n*-propylbenzene, and *iso*-propylbenzene, o-xylene, m-xylene, p-xylene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, mesitylene.

Compounds of the type $[R_3Si\text{-}X\text{-}SiR_3]^+$ have to be treated as a special case of ligand stabilization. The first example of this type is the initially as $[Et_3Si]^+$ misinterpreted $[Et_3Si\text{-}H\text{-}SiEt_3]^+$,[305] whose structure determination has been published about two years ago.[306] $[Me_3Si\text{-}H\text{-}SiMe_3]^+$ [81] is also known as well as the analogous $[Me_3Si\text{-}X\text{-}SiMe_3]^+$ compounds with X = F, Cl, Br, I[307] and trifluoromethanesulfonate.[308] The X-bridged species are typically addressed as halonium ions, but it appears more reasonable to address them as ligand-stabilized silylium ions (see Figure 43).



$$Me_3Si{-}\overset{+}{X}{-}SiMe_3 \longleftrightarrow Me_3Si{-}X\ \ {}^{+}SiMe_3 \longleftrightarrow Me_3Si^{+}\ \ X{-}SiMe_3$$

Figure 43. Canonical structures of the halogen-bridged bis-silylium ions.

Calculations state that the positive charge is still located at the silicon atoms and F, Cl and Br are negatively charged.[307] Only in the case of iodine, a small positive charge is located at the bridging atom.[307] Additionally, bissilylated pseudohalonium cations $[Me_3Si\text{-}X\text{-}SiMe_3]^+$ with X = CN, OCN, SCN, and NNN are known.[309] Of these, only in $[(Me_3Si)_2NNN]^+$ both silyl groups are attached to the same atom,[309] so that the structure of the cation is analog to the protonated hydrogen azide[310] (see **Figure 44** and **Table 7** for $[H_2N_3]^+[SbF_6]^-$). Some more examples with bridged SiR_3-groups, in which both groups are connected with each other, are known (**Figure 44**).[311–315]

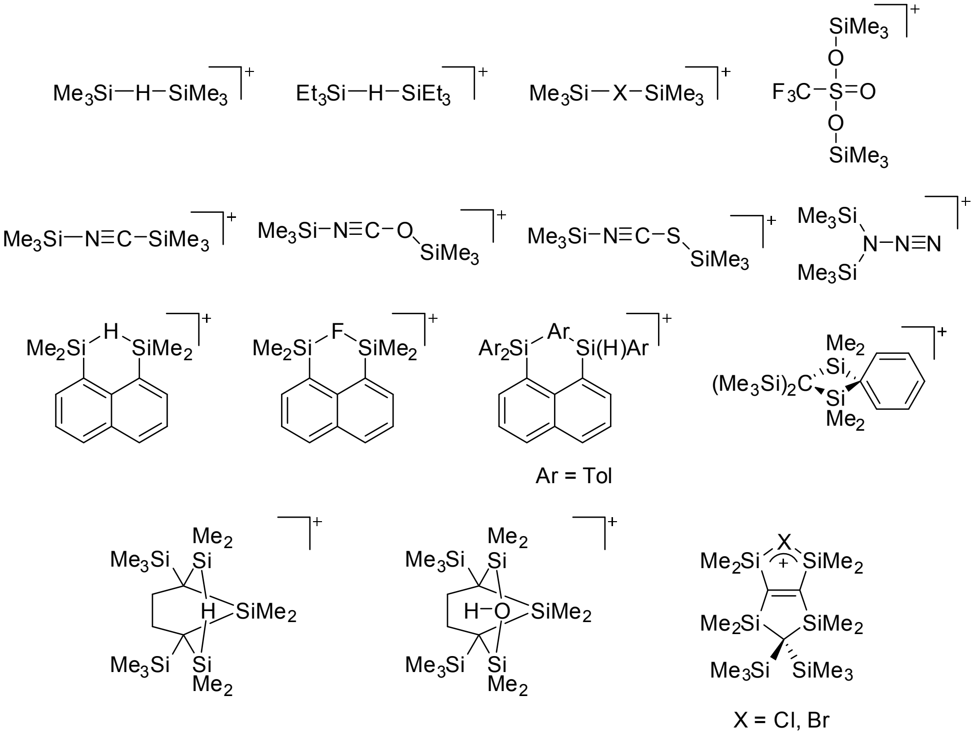


Figure 44. Structurally characterized bridged bissilylium ion salts.

A special case of intramolecular ligand stabilization can be observed in [FcSiMe^{t}Bu]$^+$.[316] Here the silicon is dipped towards the iron atom due to two 3c2e bonds between C$_{ipso}$, Si and Fe and C'$_{ipso}$, Si and Fe, respectively (**Figure 45**).[316]

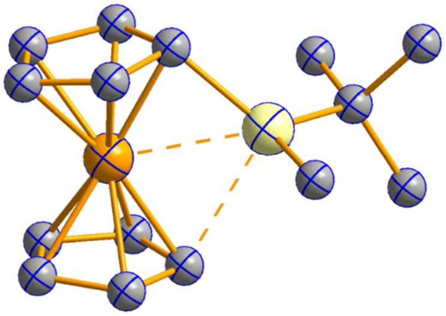


Figure 45. Molecular structure of [FcSiMe^{t}Bu]$^+$. K. Müther, R. Fröhlich, C. Mück-Lichtenfeld, S. Grimme, M. Oestreich, *J. Am. Chem. Soc.* 2011, *133*, 12442–12444. Data from this Reference were used to draw this figure.

More intramolecular σ-donor stabilized silylium ions are known: [RSi(R')$_2$]$^+$ or [RSi(R')(R'')]$^+$ with R being a pincer ligand can be seen as an extra class of ligand-stabilized silicon cations. In 2009, several silylium ions with OCO and SCS pincer ligands were published by Jutzi et al (**Figure 46**).[317]

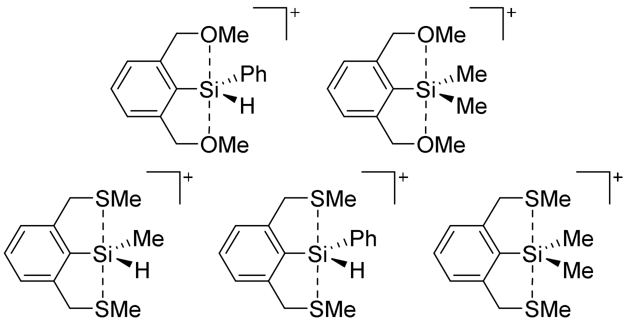


Figure 46. Structurally characterized silylium ion salts with intramolecular stabilization by pincer ligands.

All before mentioned ligand-stabilized silicon cations contain an inter- or intramolecularly by additional donor atoms stabilized $[R_3Si]^+$ cation. Two more different types of ligand-stabilized silicon cations were published with silicon in oxidation state +IV. Both were synthesized by oxidation of silicon(II) cations through elemental sulfur (**Figure 47**).[318,319] These cations containing subvalent silicon are very rare and most of the known examples are bearing a cyclopentadienyl substituent (see Cyclopentadienyl Substituted Cations). However, with well stabilizing ligands, two $[LSiCl]^+$ cations were synthesized (**Figure 47**).[318,320] Both are prepared just by adding the chelating ligand to NHC·$SiCl_2$. The NHC ligand is being replaced by L and yields the $[LSiCl]^+$ cation with chloride as the anion. This shows that the silicon cationic center is largely stabilized by coordination. By using well stabilizing NHCs, it was possible to generate an $[(L)(L')SiI]^+[I]^-$ and even the dication $[L_3Si]^{2+}([I]^-)_2$.[321] In addition, two related silicon(II) monocations $[RSi(L)_n]^+$ were structurally characterized in which the residue R is not a halogen atom (**Figure 48**).[319]

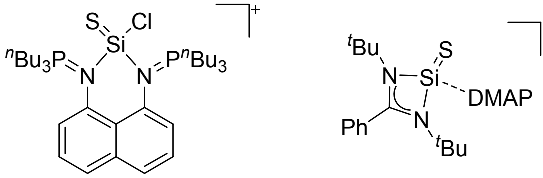


Figure 47. Structurally characterized ligand-stabilized silathionium cations.

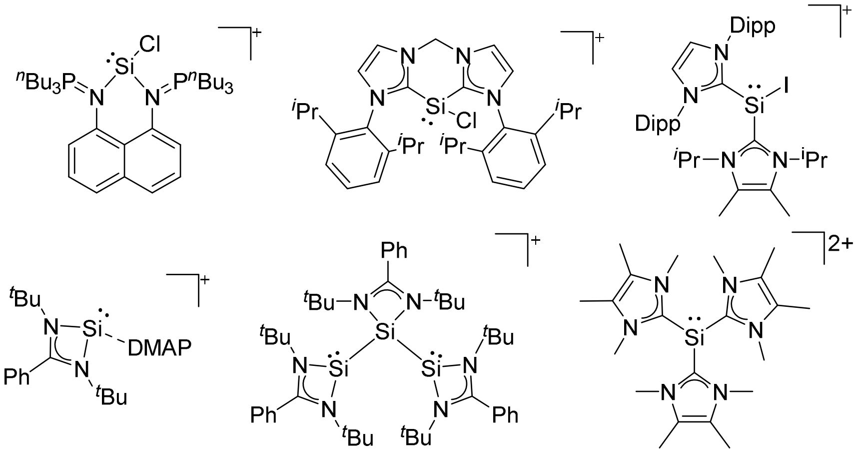


Figure 48. Structurally characterized ligand-stabilized cations of subvalent silicon.

Cyclopentadienyl Substituted Cations: So far, two cyclopentadienyl substituted silicon cations without any further stabilization through additional ligands were structurally characterized. First $[(C_5Me_5)Si]^+$ with $[B(C_6F_5)_4]^-$ was published in 2004[322] and two years later, the synthesis and characterization of $[(C_5{}^iPr_5)Si]^+[Al(OR^{PF})_4]^-$ was presented[323]. However, the latter structure determination was of poor quality and did not allow obtain any exact structural parameters. Additionally, two ether stabilized $[(C_5Me_5)Si]^+$ cations are known (**Figure 49**).[324]

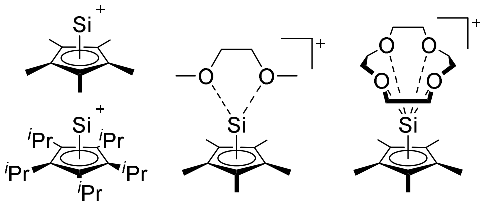


Figure 49. Structurally characterized cyclopentadienyl substituted silicon cation salts with and without additional ligands.

***Ion-like* Silylium Compounds:** In alkylsilylium ion salts without an additional stabilizing ligand, interactions between the cation and the corresponding WCA can be observed. The first structurally characterized $R_3Si(WCA)$ was the *iso*-propyl substituted compound in 1993.[325] Today, at least one example with the most common alkyl substituents ^tBu, ^iPr, Et and Me is known.[326–328,81,329,297,330] Additionally, with $^tBu_2MeSi(CB_{11}H_6Br_6)$ one mixed substituted *ion-like* silylium compound was published.[328] Another example might be $Fc_3Si(OTf)$. However, its Si-O interaction is with 175 pm in the range of a normal Si-O bond.[331]

Germanium, Tin and Lead

Cluster Cations: As for silicon, no homopolyatomic cations comparable to the fullerenium ions are known for germanium, tin and lead. Nevertheless, one example of a germanium cluster exists (**Figure**

50).[332] The cluster is composed of ten germanium atoms, of which seven bear substituents. The remaining three unsubstituted germanium atoms carry the positive charge, which is evenly distributed.

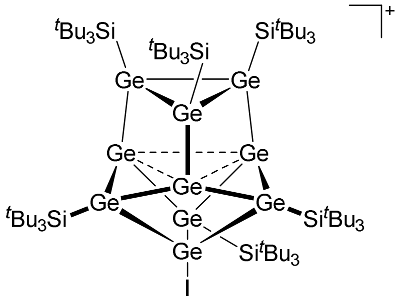


Figure 50. Lewis structure of the 5-iodo-2,4,6,8,9,10-hexakis(tri-*tert*-butylsilyl)heptacyclo[4.4.0.0^{1,3}.0^{2,5}.0^{3,9}.0^{4,7}.0^{8,10}]decagerman-7-ylium ion.

Enium Ions: Just as for silicon, enium ions of Ge, Sn and Pb need substituents with a high steric demand to shield the cationic center. The first example of the heavier elements of group 14 – $[^n\mathrm{Bu}_3\mathrm{Sn}]^+[\mathrm{CB}_{11}\mathrm{Me}_{12}]^-$ – does have, as expected, interactions between cation and the $[\mathrm{CB}_{11}\mathrm{Me}_{12}]^-$ WCA.[333] At about the same time, Lambert et al. and Sekiguchi et al. published the first examples of free enium ions of germanium and tin. While Lambert relied on bulky aryl substituents to synthesize $[(\mathrm{Tipp})_3\mathrm{Sn}]^+$,[34] Sekiguchi deployed silyl groups and managed to produce $[(^t\mathrm{Bu}_2\mathrm{MeSi})_3\mathrm{Ge}]^+$[334] and $[(^t\mathrm{Bu}_2\mathrm{MeSi})_3\mathrm{Sn}]^+$,[335] all with $[\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_4]^-$ as their counterpart (**Figure 51**). Although enium ions with aryl substituents have always been under the first examples for carbon, silicon and tin, it kept lacking an example for germanium until in 2009 $[\mathrm{Ge}(\{2,6\text{-O}^t\mathrm{Bu}\}_2\mathrm{C}_6\mathrm{H}_3)_3]^+[\mathrm{Al}(\mathrm{OR}^{\mathrm{PF}})_4]^-$ was synthesized and characterized.[336] However, the cationic center is stabilized by contacts to the oxygen atoms of the *tert*-butoxy residues at 286 and 288 pm.[336] More recently, a mixed substituted enium ion of tin has been published (**Figure 51**).[337] Examples for lead are still missing and the only formally $[\mathrm{R}_3\mathrm{Pb}]^+$ containing *ion-like* substance $\mathrm{Et}_3\mathrm{Pb}(\mathrm{HCB}_{11}\mathrm{H}_5\mathrm{Br}_6)$ has like its Si, Ge and Sn analogs stronger interactions between the ions.[338]

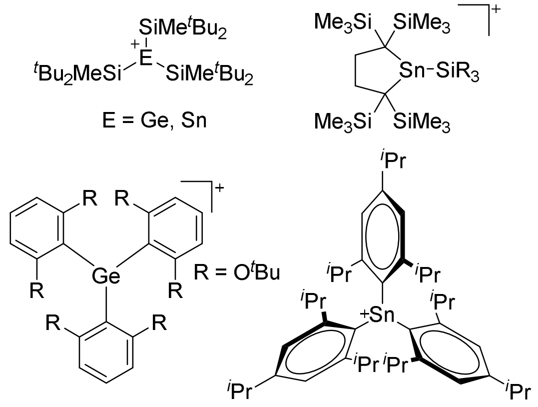


Figure 51. Structurally characterized enium ions of germanium and tin.

Delocalized Cyclic Cations: The germanium compound $[Ge_3(Si^tBu_3)_3]^+$, has been published long before the first silicon analog of a cyclopropenyl cation.[339] Although it is known with a few different anions,[340,341] it is still the only example of delocalized cyclic cations of the heavier elements of group 14 (similar to **Figure 39**, middle).

Ligand-stabilized: Far less ligand-stabilized cations of Ge, Sn and Pb in oxidation state +IV are known than of Si. $[Me_3Sn(OPPh_3)_2]^+[(MeSO_2)_2N]^-$ and $[Ph_3Sn(OPPh_3)_2]^+[(MeSO_2)_2N]^-$ were synthesized already in 1994[342] and six years later, the $[^tBu_3E(NC\text{-}^tBu)]^+$ cations were synthesized with E = Ge and Sn, but only for the germanium compound the crystal structure is known.[298] In addition, together with the analogous silicon complex, $[Me_2Ge(bipy)(OTf)]^+[OTf]^-$ has been published.[302] Interesting is however, that the corresponding substances with DMAP coordinating to germanium and the ones with DMAP or bipyridine coordinating to tin have to be described as ion-like, since in all of them both $[OTf]^-$ anions do have close contacts to the cationic center.[302] As already stated for silicon, symmetrical compounds of the type $[R_3E\text{-}X\text{-}ER_3]^+$ are somewhat special since the positive charge is evenly distributed and it is not possible to speak of an cation and a ligand anymore. Contrary to silicon, only one cation belonging to this type is known for the heavier homologues (**Figure 52**).[343] Additionally, for germanium and tin ligand-stabilized dimeric cations are known, both synthesized by oxidation of their E(II) precursors through elemental sulfur (**Figure 52**).[344,345]

Norbornyl cations with the heavier group 14 elements were classified in here as ligand-stabilized cations, although one may address them as onium ions. Although the heavier norbornyl cation analogues were all published – also with silicon – no crystal structure could be determined.[346] However, by addition of acetonitrile to the norbornyl cations, the stronger σ-donor replaces the weaker π-donating C=C double bond. An exception is the plumbanorbornyl cation, which gets coordinated by acetonitrile additionally and remains coordinated by the alkene (scXRD).[346] A comparable π-stabilization as in the norbornyl cations can be found in the 1,4,5-trigermabicyclo[2.1.0]pent-2-en-5-ylium ion, in which the cationic center is coordinated intramolecularly by a C=C double bond.[347] Another unique π-stabilization can be observed in bis(cyclopentenemethyl)plumbylium.[348] This cation is intramolecularly stabilized by the C-C double bonds of the two cyclopentene substituents (**Figure 52**).

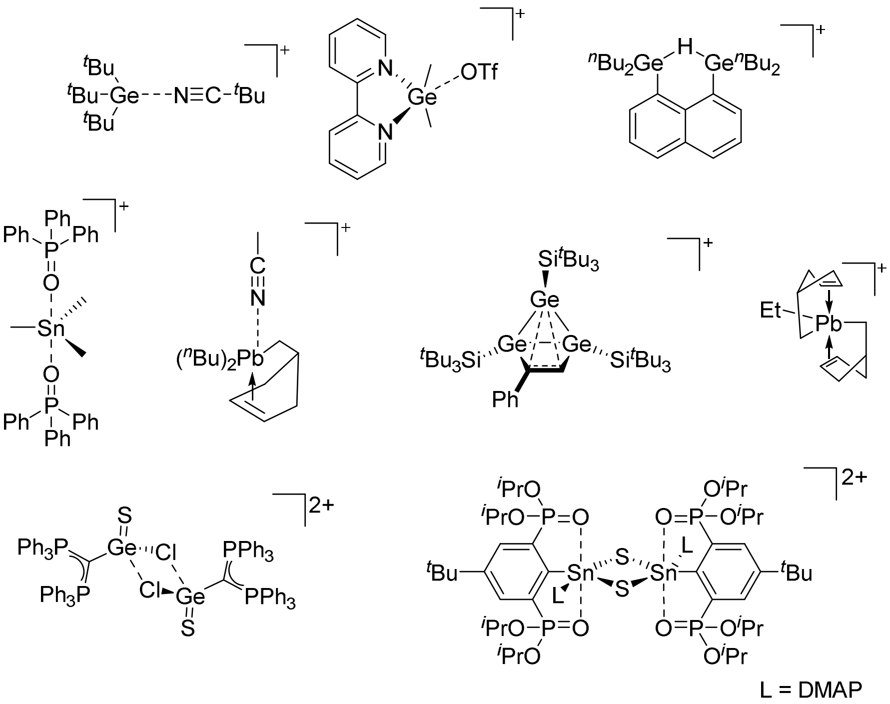


Figure 52. Ligand-stabilized cations of germanium, tin and lead in oxidation state IV.

Hard to classify are two germanium cations stabilized by a monoanionic bidentate bis(NHC)borate ligand (**Figure 53**).[349] Both originate from the attempt to synthesize a germanium dication stabilized by the before mentioned ligand through the reaction of LGeH with $[Ph_3C]^+[B(C_6F_5)_4]^-$. Instead of delivering the desired germanium dication, two different products were obtained. In one, instead of abstraction the hydride, the trityl cation attacks the lone pair of the Ge(II) cation, forming the adduct. In the other, the hydride is indeed abstracted by the trityl cation, but the resulting germanium dication is coordinated by unreacted starting material.

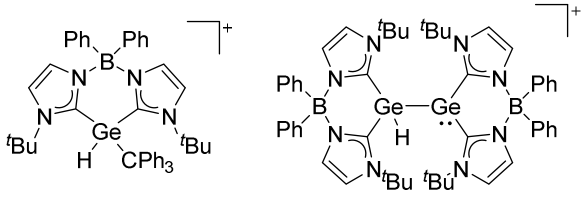


Figure 53. Germanium cations stabilized by a monoanionic bidentate bis(NHC)borate ligand.

Apart from those examples, the ligand-stabilized cations of the heavier group 14 elements are in oxidation state +II. Already as early as 1989, $[Sn([15]crown\text{-}5)_2]^{2+}$ has been published along with its crystal structure.[350] This cation is accessible directly through the reaction of $SnCl_2$ with two equivalents of the crown ether, which is why $[SnCl_3]^-$ serves as the counterion. In this or a similar fashion it has been possible to synthesize a portfolio of different crown ether complexes of tin(II) and lead(II).[351–353]

To isolate the first related Ge(II) compound, better stabilizing ligands were needed. By employing NHC ligands, a germanium dication was isolated (**Figure 54**).[354] The germanium center is highly stabilized by its ligands, and – although iodides are the counterions – only weak interactions between the ions are present. Another germanium containing dication was synthesized with the encapsulating cryptand [2.2.2],[355] and a few years later the analogous tin complex[356]. Today, quite a few different crown ether complexes of germanium are known as well (**Table 6**).[357] By using other well stabilizing chelating N-donor ligands, it was also possible to isolate [(L)Ge]$^{2+}$ cations.[358]

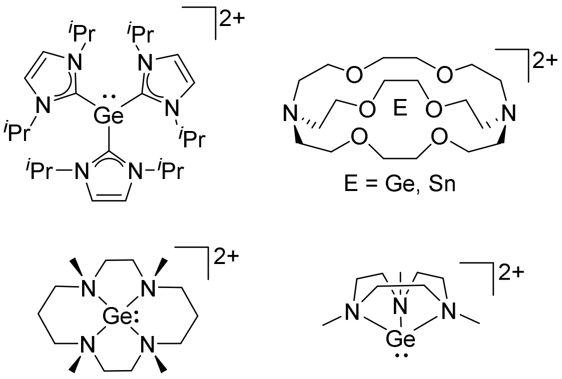
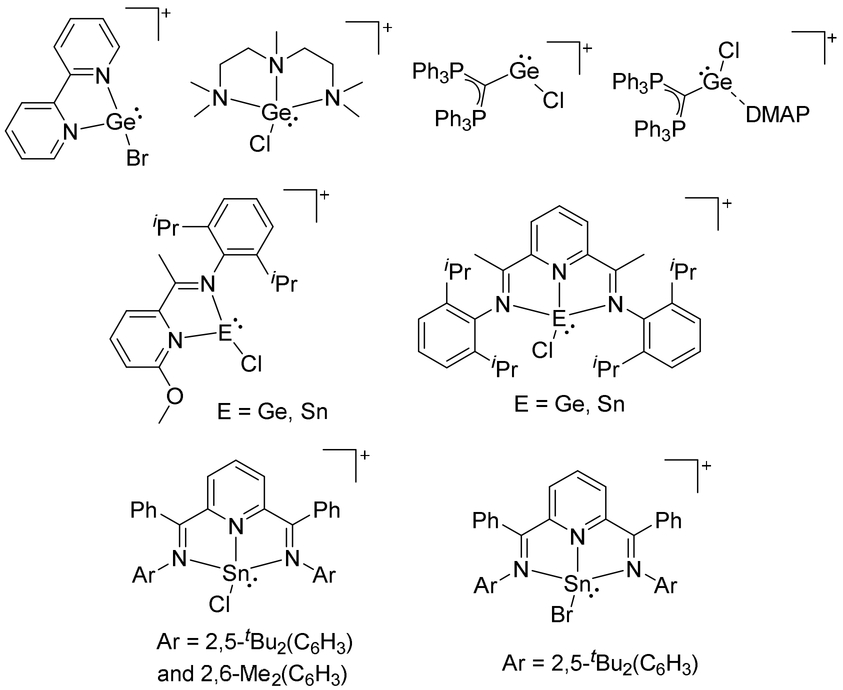


Figure 54. Structurally characterized dicationic compounds of germanium and tin.

The autoionization reaction used for the preparation of many of the crown ether complexes has also been applied to synthesize most of the structurally characterized [(L)EX]$^{+}$[WCA]$^{-}$ compounds of germanium and tin (**Figure 55**).[359–362,344] With even stronger donating ligands, comparable salts [(L)GeCl]$^{+}$Cl^{-} were prepared.[363,364] These compounds are strongly stabilized so that even halides are sufficient as anions (**Figure 56**). Related [RE(L)]$^{+}$ cations with the residue R not being an halogen atom are also known. In these cations, the residue is capable to stabilize the cationic center by an additional σ- or π-donation (**Figure 57**).[365–367,80,368,345] In case of bulky residues it was possible to work without an additional ligand and to obtain the free [RE]$^{+}$ cations (**Figure 57**).[369,365,366] For lead, one additional [RE(L)]$^{+}$ cation is known with R being a bulky aryl ligand and with a toluene molecule coordinating to the lead atom.[370]



E = Ge, Sn

E = Ge, Sn

Ar = 2,5-^{t}Bu$_2$(C$_6$H$_3$) and 2,6-Me$_2$(C$_6$H$_3$)

Ar = 2,5-^{t}Bu$_2$(C$_6$H$_3$)

Figure 55. Ligand-stabilized cations $[(L)EX]^+$ of germanium and tin.

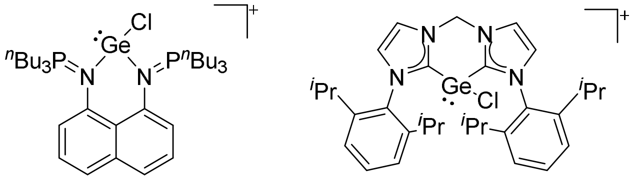


Figure 56. Ligand-stabilized cations $[(L)GeCl]^+$ with chloride as their counterion.

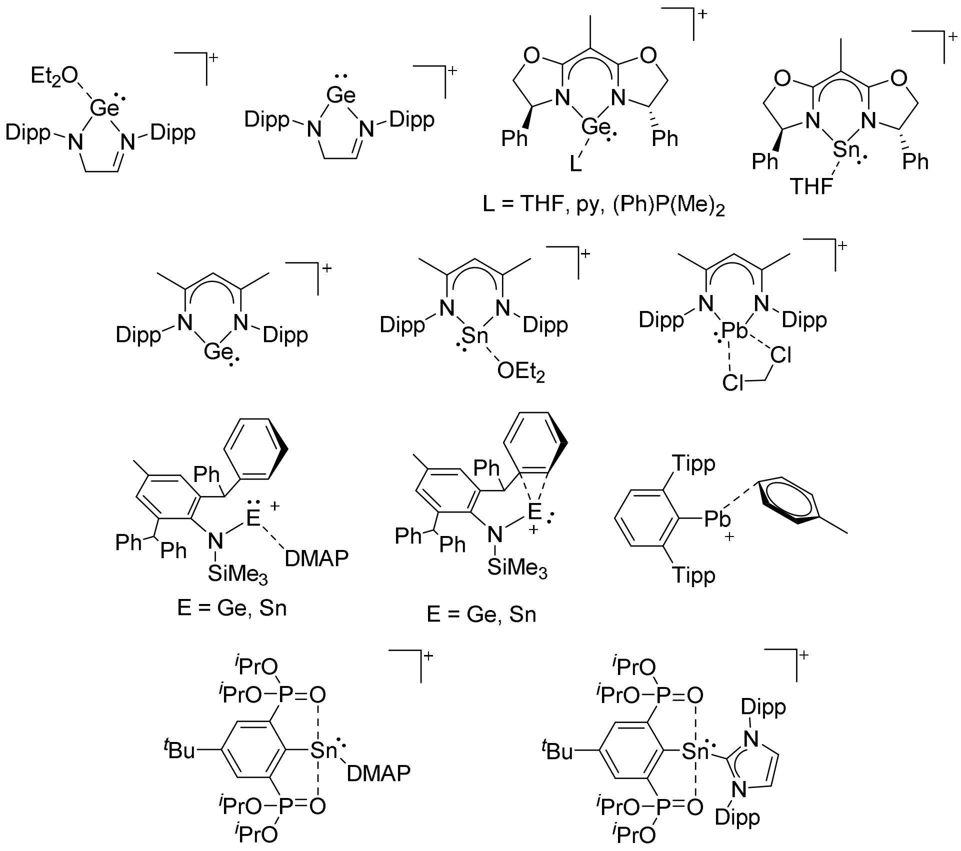


Figure 57. Structurally characterized $[RE(L)]^+$ and $[RE]^+$ cations of germanium, tin and lead.

A rather special case is $[Sn(C_7H_8)_3]^+$, in which a tin(II) cation is coordinated by three toluene molecules.[371] Although lots of arene complexes of tin(II) are known, almost all of them do still have strong interactions to the anions, mostly halides and/or $[AlCl_4]^-$ (see for some examples [19]). An exception is the Sn(II) complex with [2.2.2]paracyclophane.[372] Only one of the two $[AlCl_4]^-$ ions is coordinated to the tin atom, the other one does not have interactions with the cation. However, $[Sn(C_7H_8)_3]^{2+}([B(C_6F_5)_4]^-)_2$ is the first example of a tin(II) complex with independent arenes and without additional stabilization by the anion (**Figure 58**).

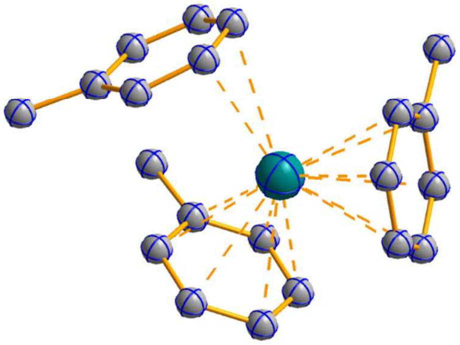


Figure 58. Molecular structure of $[Sn(C_7H_8)_3]^{2+}$. A. Schäfer, F. Winter, W. Saak, D. Haase, R. Pöttgen, T. Müller, *Chem. Eur. J.* **2011**, *17*, 10979–10984. Data from this Reference were used to draw this figure.

Cyclopentadienyl Substituted Cations: The tin analog of the $[(C_5Me_5)Si]^+$ cation was already published in 1979,[373] about 25 years before the silicon compound was characterized by XRD. This is due to the fact, that $[(C_5Me_5)Sn]^+$ could be synthesized as its $[BF_4]^-$ salt, which is not possible in case of $[(C_5Me_5)Si]^+$ because of its instantaneous decomposition.[374] In $[(C_5Me_5)Sn][BF_4]$ are still some stronger interactions present between the fluorine atoms and tin. In 2005, the structure of the $[(C_5Me_5)Sn][B(C_6F_5)_4]$ was determined in which these interactions are a lot weaker[375] and with the same anion, $[(C_5Me_5)Pb]^+$ was synthesized and structurally characterized.[375] The sole exception is germanium, whose $[(C_5Me_5)Ge]^+$ was only characterized by XRD with $[BF_4]^-$ [376] and $[SnCl_3]^-$ [377] as its counterion and not with any larger WCA. In addition, interesting triple-decker cations are known for tin and lead: $[(\{Me_5C_5\}Sn)_2(\mu\text{-}Me_5C_5)]^+$ was first synthesized and structurally characterized with the $[Ga(C_6F_5)_4]^-$ anion,[378] its structure was subsequently published with $[B(C_6F_5)_4]^-$ together with the analogous lead compound.[375]

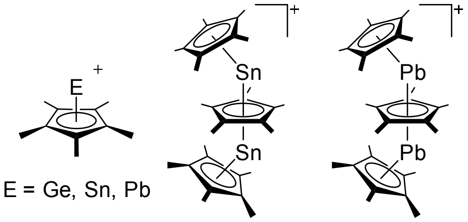


Figure 59. Structurally characterized cyclopentadienyl substituted cations of germanium, tin and lead.

Ion-like Compounds of germanium, tin and lead: As for silicon, alkyl substituted enium ions of the heavier group 14 elements without any additional ligand need stabilizing interactions with the WCA. However, far less examples are known for E = Ge, Sn and Pb, although already in 2000, the first example was published with $^{n}Bu_3Sn(CB_{11}Me_{12})$.[333] The other known examples are the $Et_3E(HCB_{11}H_5Br_6)$ compounds were already mentioned before.[338]

Transition-Metal substituted Cations of germanium, tin and lead: Other than for silicon, more transition metal coordinated cations are known for the heavier elements of group 14, especially for tin. Via a salt elimination reaction, the complex cation $[(dppe)_2W{\equiv}Sn\text{-}C_6H_3\text{-}2,6\text{-}Mes_2]^+$ was synthesized with $[PF_6]^-$ as its counterion in which the W-Sn-C angle is close to 180 °.[379] A similar germanium compound was published one year after, in 2004. In $[(MeCN)(dppe)_2W{\equiv}Ge\text{-}(\eta^1\text{-}Cp^*)]^+$, the germanium is substituted by a Cp* and the tungsten atom is coordinated additionally by an acetonitrile molecule.[380] As WCA serves $[B(C_6F_5)_4]^-$ in this case. A new complex cation featuring a Sn-Pt bond was published in 2010. In *trans*-$[Pt(Me)(SnCl_2)(2\text{-}PyPPh_2)_2][BF_4]$, the tin atom is pentacoordinated and adopts a trigonal-bipyramidal geometry.[381] Along with that, comparable compounds were synthesized with the remaining group 10 metals, but no crystal structure determination was performed. By using an OCO-pincer ligand, a chromiumpentacorbonyl coordinated tin(II) cation was synthesized. Two variants were published, $\{2,6\text{-}(MeOCH_2)_2C_6H_3\}(H_2O)SnCr(CO)_5(OTf)$, in which the tin is coordinated additionally by a water molecule and $[\{2,6\text{-}(MeOCH_2)_2C_6H_3\}(THF_2)SnCr(CO)_5]^+[CB_{11}H_{12}]^-$, in which the tin is hexacoordinated with two THF molecules complementing the coordination sphere.[382] The former has indeed no contact between the triflate and the tin atom, but a strong hydrogen bond between the coordinated water molecule and the anion is existing, with an O-O distance of about 261 pm. Two more chromiumpentacorbonyl coordinated tin(II) cations were published in 2013, both also with a pincer-type ligand (**Figure 60**).[383] The same ligand was used to prepare the $[RSn\{W(CO)_3Cp\}_2]^+$, with R = R = 4-^{t}Bu-2,6-$\{P(O)(O^iPr)_2\}_2C_6H_2$) and $[W(CO)_3Cp]^-$ as its counterion.[384] Recently, new platinum-coordinated cations of tin and lead were published. Starting from $(Cy_3P)_2Pt(SnBr_2)$, $[\{(Cy_3P)_2Pt\text{-}SnBr\}_2]^+$ was synthesized with two different anions.[385] The analogous dimeric lead cation $[\{(Cy_3P)_2Pt\text{-}PbCl\}_2]^+$ was accessible by using $(Cy_3P)_2Pt(PbCl_2)$ as a starting material.[385] Through further reaction with AlX_3, $\{(Cy_3P)_2Pt\}_2Sn(AlBr_4)_2$ respectively $\{(Cy_3P)_2Pt\}_2Pb(AlCl_4)_2$ were synthesized.[385] However, in both dications some interactions between the ions are present. Additionally, the dimeric lead cation was also synthesized with iodine instead of chlorine.[385]

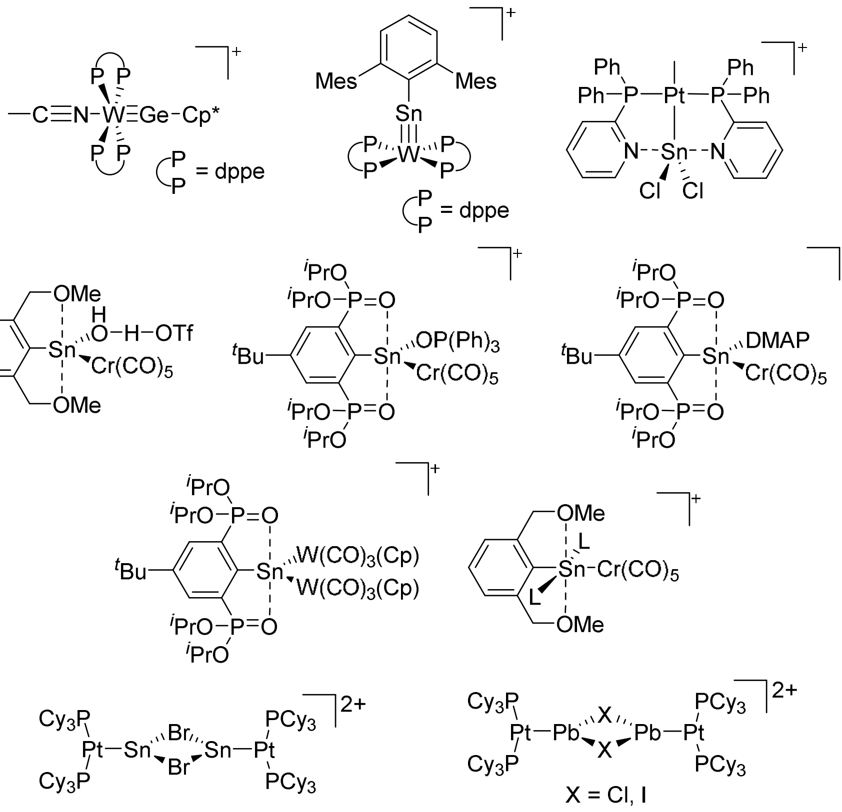
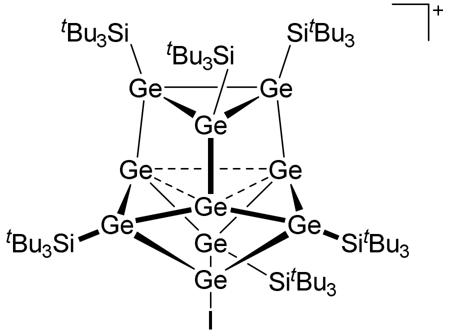
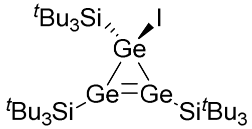
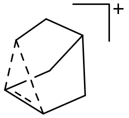
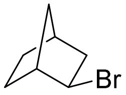
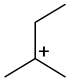
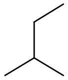
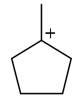
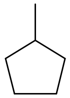
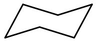
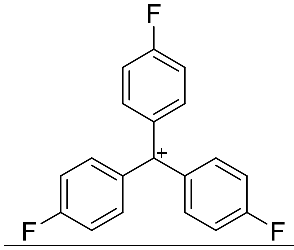
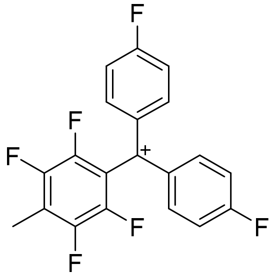
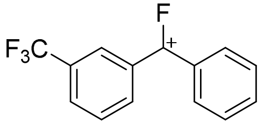
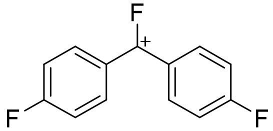
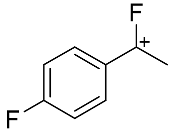
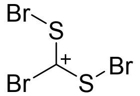
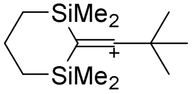
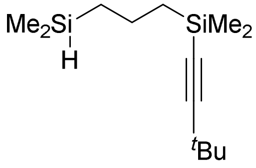
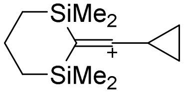
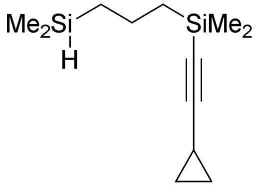
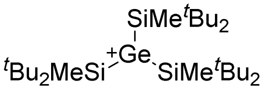
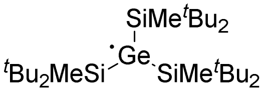


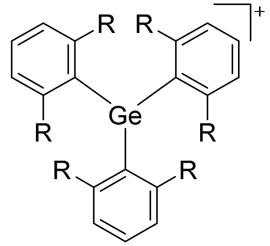
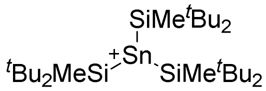
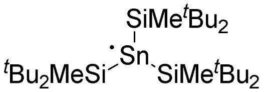
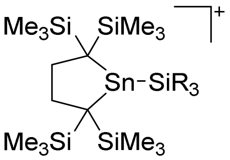
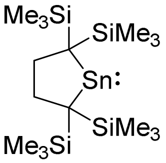
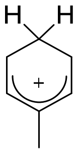
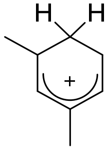
Figure 60. Structurally characterized transition metal substituted cations of germanium, tin and lead.

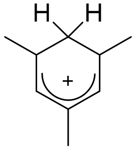
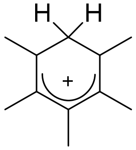
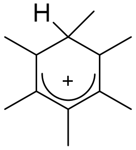
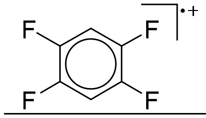
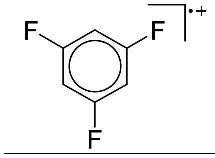
Table 6. Overview on structurally characterized cations of group 14.

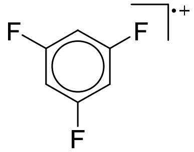
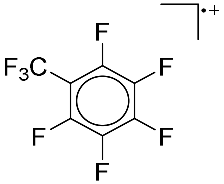
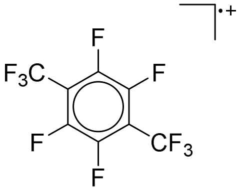
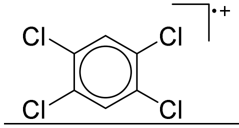
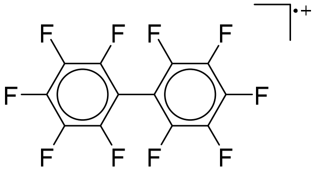
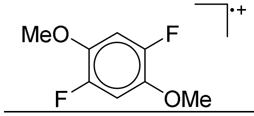
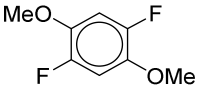
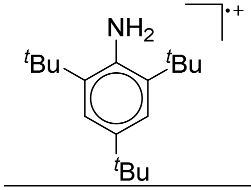
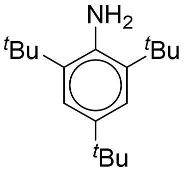
Cation	Anion	Class.*	Synthesis	Comment	Ref.
Homopolyatomic and Cage Cations					
$[C_{76}]^{+}$	$[HCB_{11}H_5Br_6]^{-}$	Ox	C_{76} + $[Ar_3N]^{+}[WCA]^{-}$		44
$[C_{60}]^{+}$	$[HCB_{11}H_5Cl_6]^{-}$	Ox	C_{60} + $[Ar_3N]^{+}[WCA]^{-}$		259
$[C_{60}]^{2+}$	$[AsF_6]^{-}$	Ox	C_{60} + 3 AsF_5	Polymeric	260
$[HC_{60}]^{+}$	$[HCB_{11}H_5Cl_6]^{-}$	Prot	C_{60} + H(WCA)		259
$[C_{59}N]^{+}$	$[Ag(HCB_{11}H_5Cl_6)_2]^{-}$	Ox	$(C_{59}N)_2$ + 2 $[HBPC]^{\cdot+}[WCA]^{-}$		261
	$[B(C_6F_4H)_4]^{-}$	Other	 + KI + $K^{+}[WCA]^{-}$		332
Onium Ions					
	$[Al_2Br_7]^{-}$	Lewis	 + 2 $AlBr_3$		86
Enium Ions					
$[(CH_3)_3C]^{+}$	$[HCB_{11}Me_5Cl_6]^{-}$	Hyd	^{n}BuH + $Me^{+}[WCA]^{-}$ or ^{t}BuH + Me(WCA)		265
$[(CH_3)_3C]^{+}$	$[Al_2Br_7]^{-}$	Lewis	^{t}BuBr + 2 $AlBr_3$		266
$[(CH_3)_3C]^{+}$	$[HCB_{11}Cl_{11}]^{-}$	Other	thermal decomposition of $[Et_2Cl][CHB_{11}Cl_{11}]$		267
	$[HCB_{11}Me_5Br_6]^{-}$	Hyd	*n*-pentane + Me(WCA) or  + Me(WCA)		265

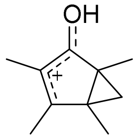
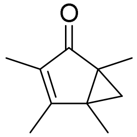
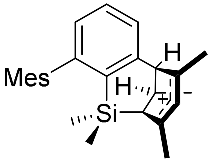
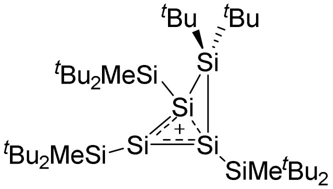
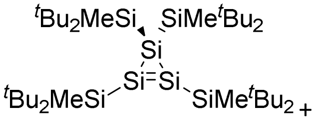
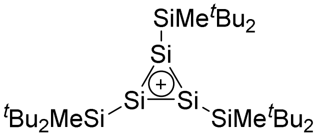
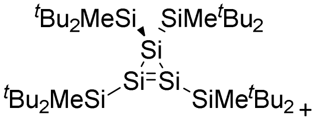
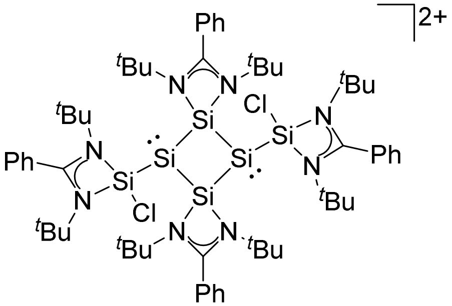
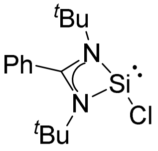
	$[HCB_{11}Me_5Br_6]^-$	Hyd	 + Me(WCA) or  + Me(WCA)		265
	$[HCB_{11}I_{11}]^-$	Lewis	*p*-CH_3-C_6F_4-CF_3 + Et_3Si(WCA) + PhF		56
	$[HCB_{11}Cl_{11}]^-$	Lewis	*p*-CH_3-C_6F_4-CF_3 + Et_3Si(WCA) + PhF		56
	$[As_2F_{11}]^-$	Lewis	$C_6H_5CF_3$ + AsF_5	excess AsF_5	268
	$[HCB_{11}I_{11}]^-$	Lewis	*p*-F-$C_6H_4CF_3$ + Et_3Si(WCA) + PhF		56
	$[HCB_{11}I_{11}]^-$	Lewis	CH_3CF_3 + Et_3Si(WCA) + PhF		56
$[CI_3]^+$	$[Al(OR^{PF})_4]^-$	Salt	CI_4 + $Ag^+[WCA]^-$		269

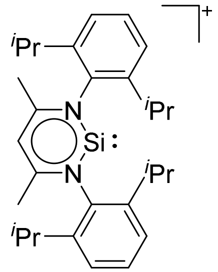
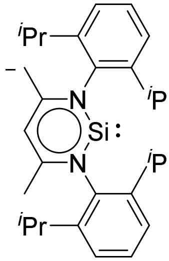
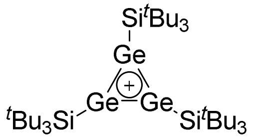
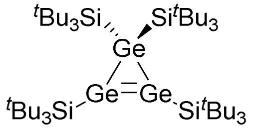
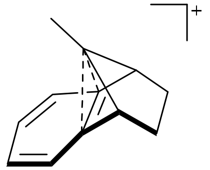
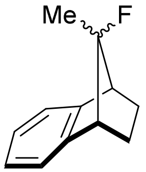
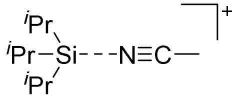
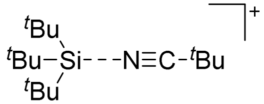
$[CCl_3]^+$	$[Sb(OTeF_5)_6]^-$	Ox	$CCl_4 + [XeOTeF_5]^+[WCA]^-$	270
$[CCl_3]^+$	$[Al(OR^{PF})_4]^-$, $[(R^{PF}O)_3Al\text{-}F\text{-}Al(OR^{PF})_3]^-$	Salt	$CCl_4 + Ag^+[WCA]^-$	271
$[CBr_3]^+$	$[Sb(OTeF_5)_6]^-$	Ox	$CBr_4 + [XeOTeF_5]^+[WCA]^-$	270
$[CBr_3]^+$	$[Al(OR^{PF})_4]^-$, $[(R^{PF}O)_3Al\text{-}F\text{-}Al(OR^{PF})_3]^-$		$CBr_4 + Ag^+[WCA]^-$	271
$[C(OTeF_5)_3]^+$	$[Sb(OTeF_5)_6]^-$	Ox	$CBr_4 + [XeOTeF_5]^+[WCA]^-$	270
	$[Al(OR^{PF})_4]^-$	Ox	$CS_2 + [AsBr_4]^+[WCA]^-$ and $CS_2 + Br_2 + Ag^+[WCA]^-$	117
	$[B(C_6F_5)_4]^-$	Hyd	 + $[Ph_3C]^+[WCA]^-$	275
	$[B(C_6F_5)_4]^-$	Hyd	 + $[Ph_3C]^+[WCA]^-$	276
$[Mes_3Si]^+$	$[HCB_{11}Me_5Br_6]^-$	Other	$Mes_3Si(CH_2CH{=}CH_2) + Et_3Si(WCA)$	24
$[Pemp_3Si]^+$	$[B_{12}Cl_{12}]^{2-}$	Hyd	$2\ Pemp_2MeSiH + [Ph_3C]_2^+[WCA]^-$	290
$[Pemp_3Si]^+$	$[Al(OR^{PF})_4]^-$	Hyd	$1.5\ Pemp_2MeSiH + [Ph_3C]^+[WCA]^-$	291
	$[B(C_6F_5)_4]^-$	Ox	 $+ [Ph_3C]^+[WCA]^-$	334

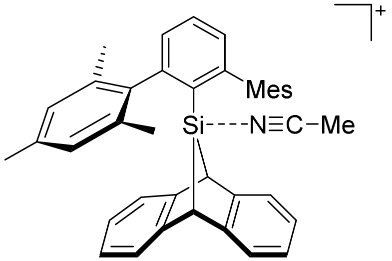
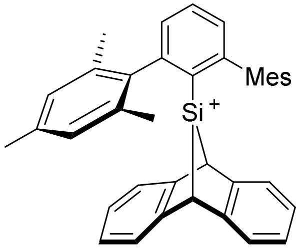
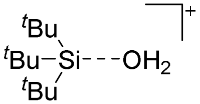
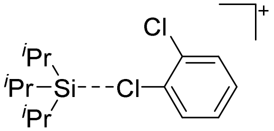
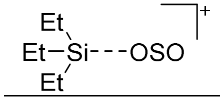
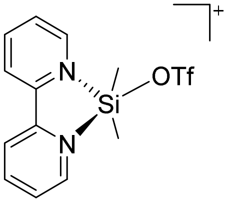
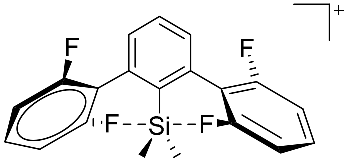
	$[Al(OR^{PF})_4]^-$	Salt	$(Ar)_3GeBr + Ag^+[WCA]^-$	R = O^{t}Bu	336
	$[B(C_6F_5)_4]^-$	Ox	 + $[Ph_3C]^+[WCA]^-$		335
$[(Tipp)_3Sn]^+$	$[B(C_6F_5)_4]^-$	Other	$(allyl)(Tipp)_3Sn + [E]^+[WCA]^-$	$[E]^+$ not exactly defined, likely $[Et_3Si(C_6H_6)]^+$ or comparable	34
	$[B(C_6F_5)_4]^-$	Com, Lig	 + $[R_3Si(C_7H_8)]^+[WCA]^-$	R = Et, ^{i}Pr	337
Delocalyzed (Cyclic) Cations					
$[C_6H_7]^+$	$[HCB_{11}Me_5Br_6]^-$	Prot	$C_6H_6 + H(WCA)$		386
	$[HCB_{11}H_5Br_6]^-$	Prot	$C_6H_6 + H(WCA)$		387
	$[HCB_{11}H_5Br_6]^-$	Prot	$C_6Me_2H_4 + H(WCA)$		387

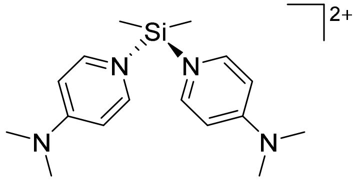
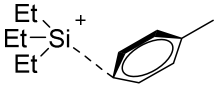
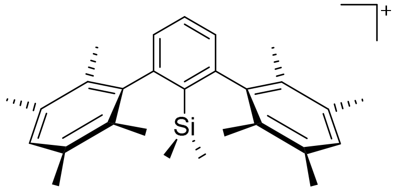
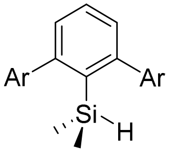
	$[HCB_{11}H_5Br_6]^-$	Prot	$C_6Me_3H_3$ + H(WCA)		387
	$[B(C_6F_5)_4]^-$	Prot	Et_3Si(WCA) + HCl + $C_6(Me)_5H$	C-H···F-C interactions	388
	$[HCB_{11}H_5Br_6]$	Prot	C_6Me_6 + H(WCA)		387
$[C_6Me_7]^+$	$[AlCl_4]^-$	Other	$C_6Me_6 + CH_3Cl + AlCl_3$		277
$[C_6F_6]^{\cdot+}$	$[Sb_2F_{11}]^-$	Ox	$C_6F_6 + [O_2]^+[WCA]^-$	crystallized out of HF	278
$[C_6F_6]^{\cdot+}$	$[Os_2F_{11}]^-$	Ox	$C_6F_6 + OsF_6 + SbF_5$	in HF	278
$[C_6Cl_6]^{\cdot+}$	$[Sb_2F_{11}]^-$	Ox	$C_6F_6 + SbF_5$		279
$[C_6Br_6]^{\cdot+}$	$[As_2F_{11}]^-$	Ox	$C_6Br_6 + [O_2]^+[AsF_6]^- + HSO_3F$		280
$[C_6I_6]^{\cdot+}$	$[AsF_6]^-$	Ox	$C_6I_6 + AsF_5$	in HF	279
$[C_6I_6]^{\cdot+}$	$[SbF_6]^-$	Ox	$C_6I_6 + SbF_5$	in HF	279
$[C_6I_6]^{\cdot+}$	$[OTf]^-$	Other	$[C_6I_6][AsF_6]$ + HOTf		279
$[C_6HF_5]^{\cdot+}$	$[AsF_6]^-$	Ox	$C_6HF_5 + [O_2]^+[WCA]^-$		279
	$[SbF_6]^-$	Ox	$C_6H_2F_4 + [O_2]^+[WCA]^-$		279
	$[AsF_6]^-$	Ox	$C_6H_3F_3 + [O_2]^+[WCA]^- + AsF_5$		279

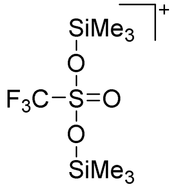
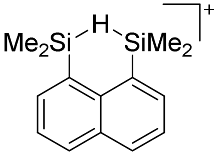
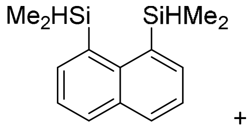
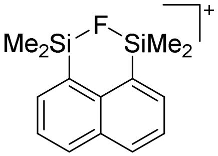
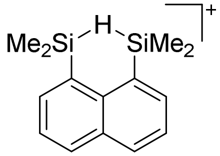
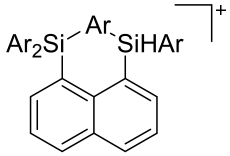
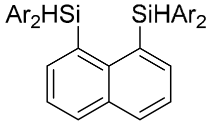
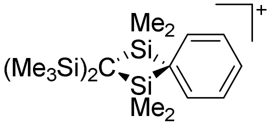
	$[SbF_6]^-$	Ox	$C_6H_3F_3 + [O_2]^+[Sb_2F_{11}]^-$	in HF	279
	$[Sb_2F_{11}]^-$	Ox	$C_6F_5(CF_3) + [O_2]^+[WCA]^-$	in HF	280
	$[Sb_2F_{11}]^-$	Ox	$C_6F_4(CF_3)_2 + SbF_5$	in HF	280
	$[Sb_2F_{11}]^-$	Ox	$C_6H_2Cl_4 + [O_2]^+[WCA]^-$		280
	$[Sb_3F_{16}]^-$	Ox	$[C_6F_5\text{-}C_6F_5] + [O_2]^+[WCA]^- + SbF_5$		280
	$[Nb_2F_{11}]^-$	Ox	 $+ NbF_5$		281
	$[SbF_6]^-$	Ox	 $+ Ag^+[WCA]^-$		282

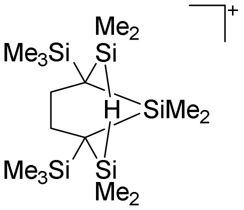
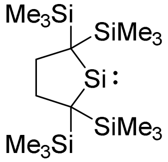
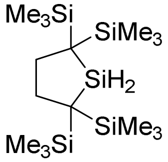
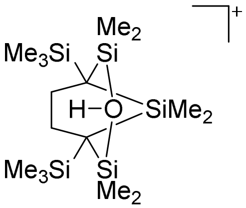
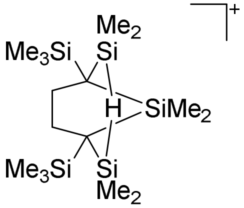
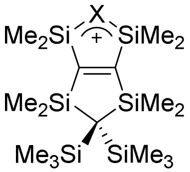
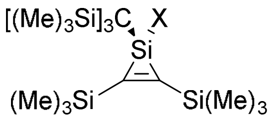
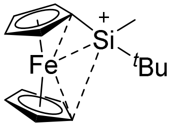
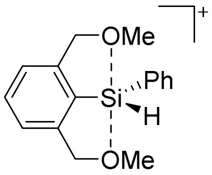
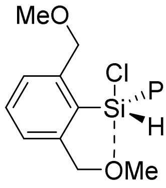
$[Cy_3C_3]^+$	$[SbF_6]^-$	Salt	$[Cy_3C_3]Cl + Ag^+[WCA]^-$		283
$[Cy_2PhC_3]^+$	$[BF_4]^-$	Lewis	$[Cy_2(Ph)C_3]F + BF_3$		283
	$[SbCl_6]^-$	Prot	 + HCl + $SbCl_5$		284
	$[HCB_{11}Me_5Br_6]^-$	Hyd	$ArMe_2SiH + [Ph_3C]^+[WCA]^-$		286
	$[B(C_6F_5)_4]^-$	Other	 $[Et_3Si(C_6H_6)]^+[WCA]^-$		292
	$[B(C_6F_4R)_4]^-$	Other	 $[Ph_3C]^+[WCA]^-$	R = 4-SiMe$_2{}^t$Bu	293
	$[Zr_2Cl_7Cp^*{}_2]^-$	Lewis	 + Cl_3ZrCp^*		294

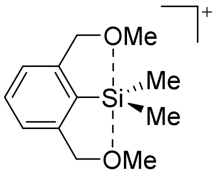
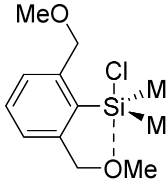
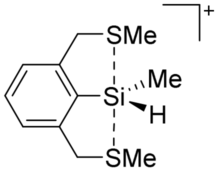
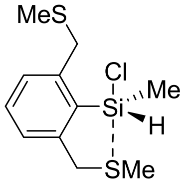
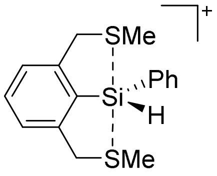
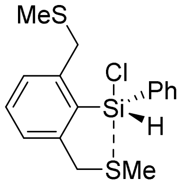
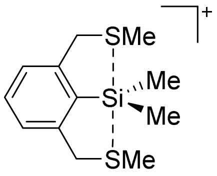
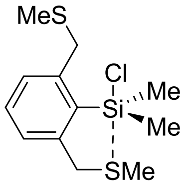
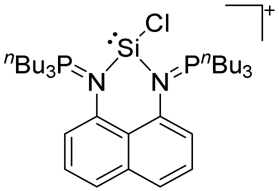
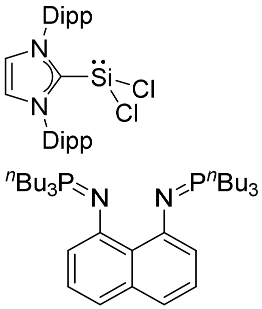
	$[B(C_6F_5)_4]^-$	Prot	 + $[H(OEt_2)_2]^+[WCA]^-$		295
	$[B(C_6H_5)]^-$, $[B(Ar^{CF3})_4]^-$, $[B(C_6F_4R)_4]^-$	Other	 + $[Ph_3C]^+[WCA]^-$	R = 4-Si(Me)$_2$(^{t}Bu)	339340, 341
Ligand-stabilized Cations					
	$[Sb_2F_{11}]^-$	Lewis	 + 2 SbF_5		273
$[I_3C\text{-}PX_3]^+$	$[Al(OR^{PF})_4]^-$	Comp	$[CI_3]^+[WCA]^-$ + PX_3	X = Cl, Br, I	274
$[I_3C\text{-}PI_3]^+$	$[(R^{PF}O)_3Al\text{-}F\text{-}Al(OR^{PF})_3]$	Comp	$[CI_3]^+[WCA]^-$ + PI_3		274
$[I_3C\text{-}AsI_3]^+$	$[Al(OR^{PF})_4]^-$	Comp	$[CI_3]^+[WCA]^-$ + AsI_3		274
 $[{}^{i}Pr_3Si{-}{-}{-}N{\equiv}C{-}]^+$	$[HCB_9H_4Br_5]^-$	Hyd	$^{i}Pr_3SiH$ + $[Ph_3C]^+[WCA]^-$ + MeCN		297
 $[{}^{t}Bu_3Si{-}{-}{-}N{\equiv}C{-}{}^{t}Bu]^+$	$[B(C_6F_5)_4]^-$	Other	$^{t}Bu_3Si\text{-}Si^{t}Bu_3$ + 2 $[Ph_3C]^+[WCA]^-$ + $^{t}BuCN$		298

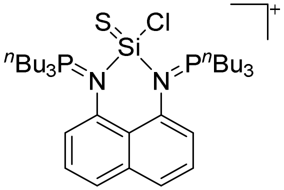
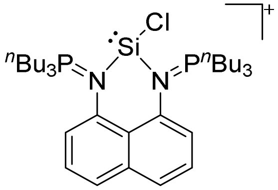
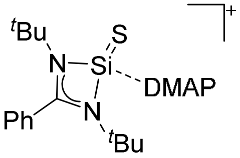
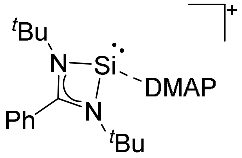
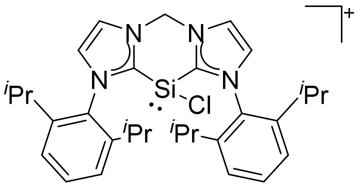
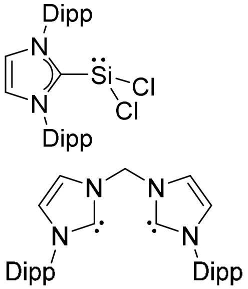
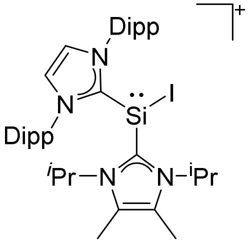
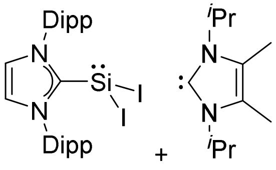
	$[B(C_6F_5)_4]^-$	Com		+ MeCN	299
$[Fc_3Sipy]^+$	$[B(Ar^{CF3})_4]^-$	Lig	$[Fc_3Si(THF)]^+$ + py		300
	$[HCB_{11}H_5Br_6]^-$	Ion	${}^tBu_3Si(WCA) + H_2O$		301
	$[HCB_{11}Cl_{11}]^-$	Ion	${}^iPr_3Si(WCA) + C_6H_4Cl_2$		81
	$[HCB_{11}Me_5Br_6]^-$	Ion	$Et_3Si(WCA) + SO_2$		81
	$[OTf]^-$	Ion	$Me_2Si(OTf)_2$ + bipy		302
	$[B(C_6F_5)_4]^-$	Hyd	$Me_2ArSiH + [Ph_3C]^+[WCA]^-$		303

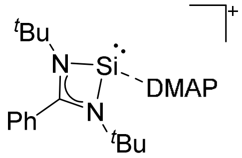
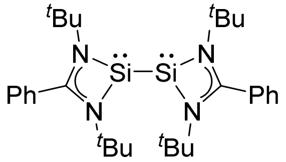
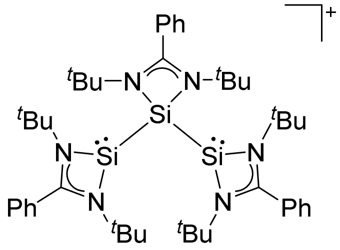
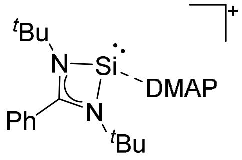
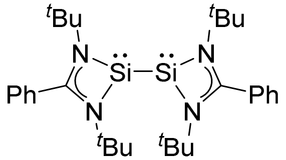
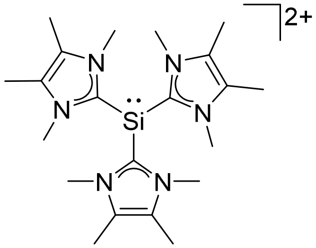
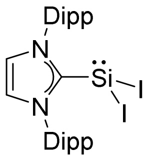
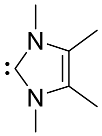
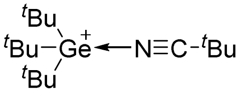
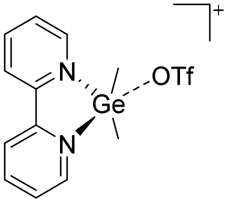
	$[OTf]^-$	Ion	$Me_2Si(OTf)_2$ + 2 DMAP		302
	$[B(C_6F_5)_4]^-$	Hyd	$Et_3SiH + [Ph_3C]^+[WCA]^-$		289
$[Me_3Si(Ar)]^+$	$[B(C_6F_5)_4]^-$	Lig	$[Me_3SiHSiMe_3]^+[WCA]^-$ + arene	Ar = benzene, toluene, ethylbenzene, *n*-propylbenzene, and *iso*-propylbenzene, *o*-xylene, m-xylene, *p*-xylene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, mesitylene,	304
	$[B(C_6F_5)_4]^-$	Hyd	 + $[Ph_3C]^+[WCA]^-$		76
$[Me_3SiHSiMe_3]^+$	$[HCB_{11}HCl_{11}]^-$	Hyd	$2\ Me_3SiH + [Ph_3C]^+[WCA]^-$		81
$[Et_3SiHSiEt_3]^+$	$[B(C_6F_5)_4]^-$	Hyd	$2\ Et_3SiH + [Ph_3C]^+[WCA]^-$		306
$[Me_3SiXSiMe_3]^+$	$[B(C_6F_5)_4]^-$	Ion	$Me_3SiX + Me_3Si(WCA)$	X = F, Cl, Br, I	307
$[Me_3Si\text{-}CN\text{-}SiMe_3]^+$	$[B(C_6F_5)_4]^-$	Ion	$Me_3SiCN + Me_3Si(WCA)$		309
$[Me_3Si\text{-}OCN\text{-}SiMe_3]^+$	$[B(C_6F_5)_4]^-$	Ion	$Me_3SiOCN + Me_3Si(WCA)$		309
$[Me_3Si\text{-}SCN\text{-}SiMe_3]^+$	$[B(C_6F_5)_4]^-$	Ion	$Me_3SiSCN + Me_3Si(WCA)$		309

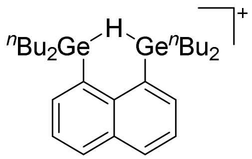
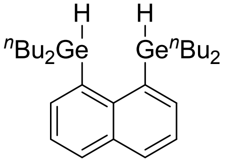
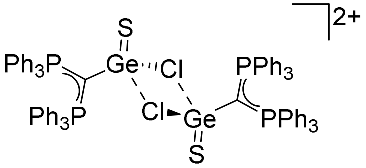
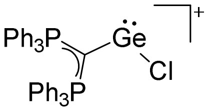
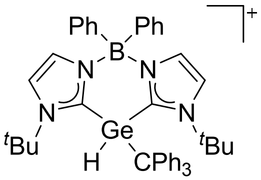
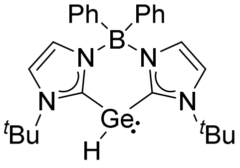
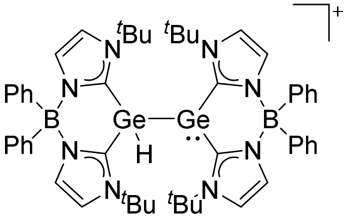
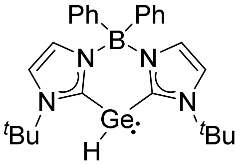
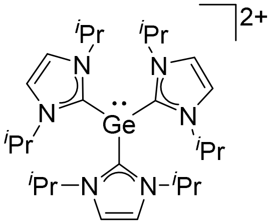
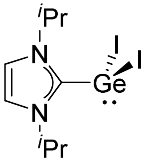
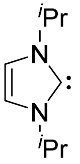
$[(Me_3Si)_2NNN]^+$	$[B(C_6F_5)_4]^-$	Ion	$Me_3SiNNN + Me_3Si(WCA)$	309
	$[B(C_6F_5)_4]^-$	Ion	$Me_3Si(OTf) + Me_3Si(WCA)$	308
	$[B(C_6F_5)_4]^-$	Hyd	 + $[Ph_3C]^+[WCA]^-$	311
	$[B(C_6F_5)_4]^-$	Other	 + $C_6H_5CF_3$ or $C_{10}H_{21}F$ or $[Ph_3C]^+[WCA]^-$	311
	$[B(C_6F_5)_4]^-$	Hyd	 + $[Ph_3C]^+[WCA]^-$ Ar = Tol	312
	$[B(C_6F_5)_4]^-$	Other	$(Me_3Si)_3CSiMePhH + [Ph_3C]^+[WCA]^-$	313

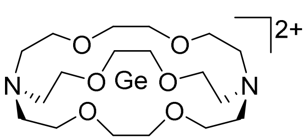
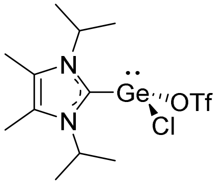
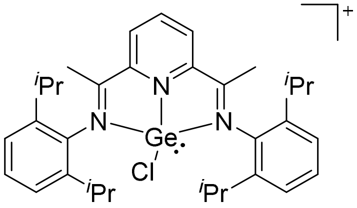
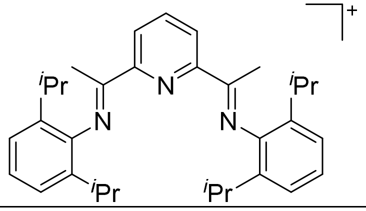
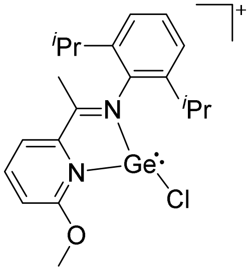
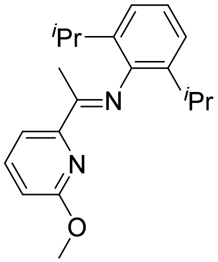
	$[B(C_6F_5)_4]^-$	Other	 + $[(Me_5C_6)_3Si]^+[WCA]^-$ or $[Et_3Si(C_6H_6)]^+[WCA]^-$ or  + $[Ph_3C]^+[WCA]^-$		314
	$[B(C_6F_5)_4]^-$	Other	 + H_2O		314
	$[B(C_6F_5)_4]^-$	Other	 + $[Et_3Si(C_6H_6)]^+[WCA]^-$	X = Cl, Br	315
	$[B_{12}Cl_{12}]^{2-}$	Hyd	2 FcMe^{t}BuSiH + $[Ph_3C]_2^+[WCA]^-$		316
	$[OTf]^-$	Lewis	 + Me_3SiOTf		317

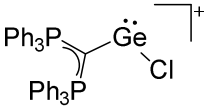
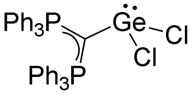
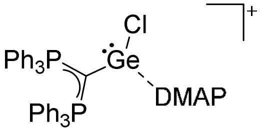
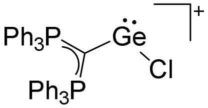
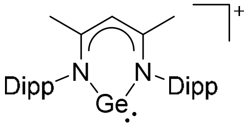
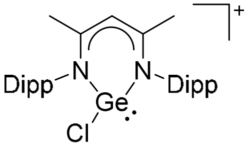
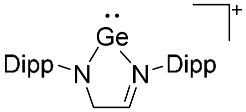
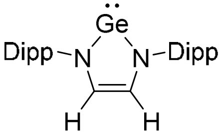
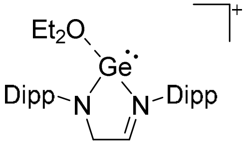
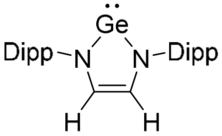
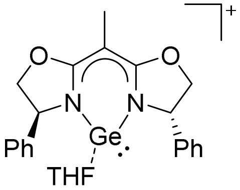
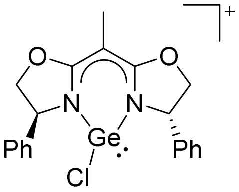
	$[OTf]^-$	Lewis	 + Me_3SiOTf	317
	$[OTf]^-$	Lewis	 + Me_3SiOTf	317
	$[OTf]^-$	Lewis	 + Me_3SiOTf	317
	$[OTf]^-$	Lewis	 + Me_3SiOTf	317
	Cl^-	Ion	 +	318

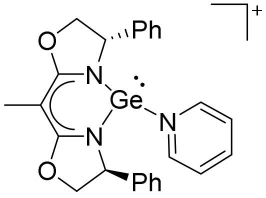
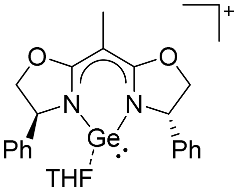
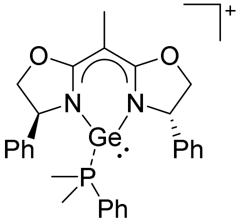
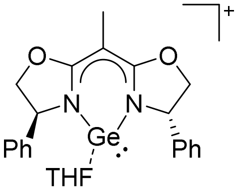
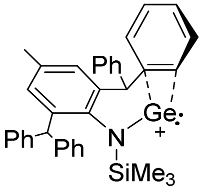
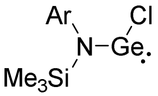
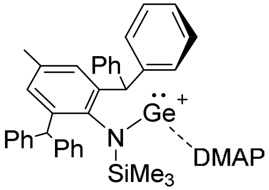
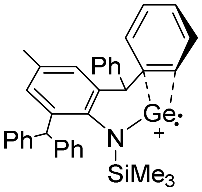
	Cl^-	Ox	 Cl^- + 1/8 S_8	318
	$[OTf]^-$	Ox	 $[WCA]^-$ + 1/8 S_8	319
	Cl^-	Ion	 +	320
	I^-	Ion		321

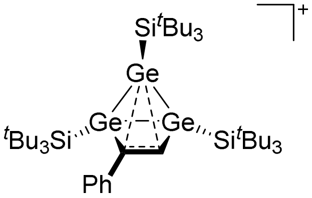
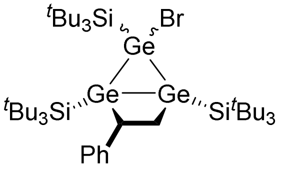
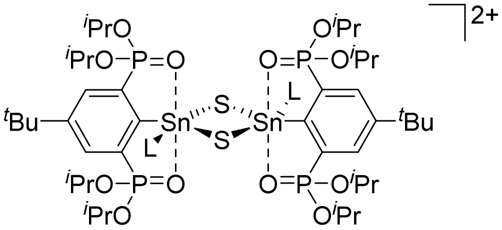
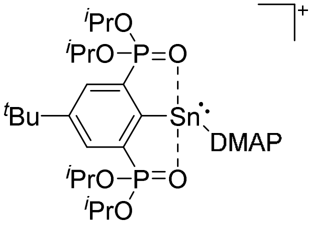
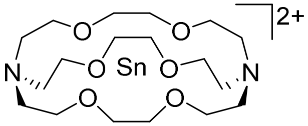
	$[OTf]^-$	Ox	 + $[Me_3Si\text{-}DMAP]^+[WCA]^-$ + 2 DMAP	319
		Other	 $^+[WCA]^-$ + 	319
	I^-	Ion	 + 3 	321
 $^tBu_3Ge^+ \leftarrow N{\equiv}C\text{-}^tBu$	$[B(C_6F_5)_4]^-$	Ox	$^tBu_3Ge\text{-}Ge^tBu_3$ + 2 $[Ph_3C]^+[WCA]^-$ + ^tBuCN	298
	$[OTf]^-$	Ion	$Me_2Ge(OTf)_2$ + bipy	302

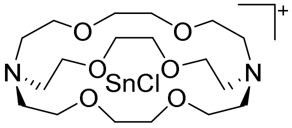
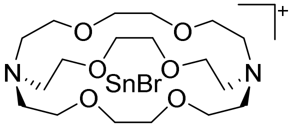
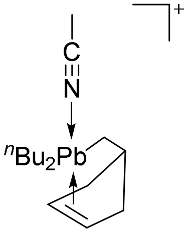
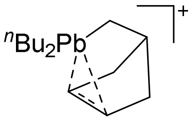
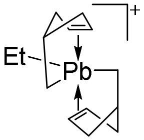
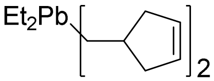
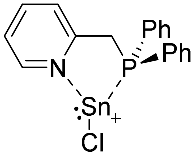
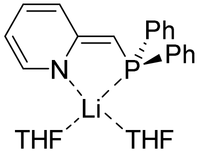
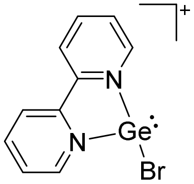
	$[B(C_6F_5)_4]^-$	Hyd	 + $[Ph_3C]^+[WCA]^-$	343
	$[AlCl_4]^-$	Ox	 $[WCA]^-$ + 1/8 S_8	344
	$[B(C_6F_5)_4]^-$	Ox or Com	 + $[Ph_3C]^+[WCA]^-$	349
	$[B(C_6F_5)_4]^-$	Hyd	 + $[Ph_3C]^+[WCA]^-$	349
	I^-	Ion	 + 2 	354

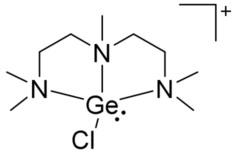
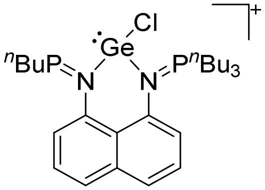
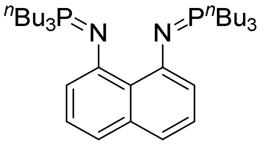
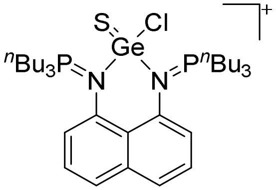
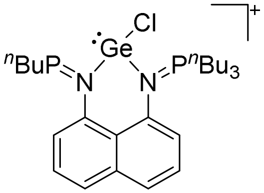
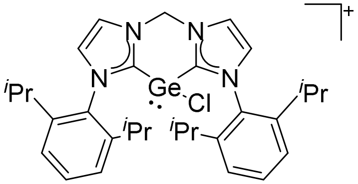
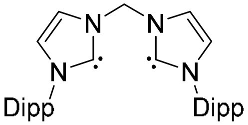
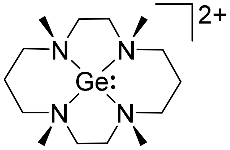
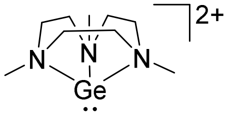
	$[OTf]^-$	Ion, Lig	 + cryptand[2.2.2]	355
$[Ge([12]\text{-crown-}4)_2]^{2+}$	$[GeCl_3]^-$	Ion	$GeCl_2$·dioxane + [12]crown-4	357
$[Ge([12]\text{-crown-}4)_2]^{2+}$	$[OTf]^-$	Ion	$GeCl_2$·dioxane + [12]crown-4 + 2 $Me_3Si(OTf)$	357
$[GeCl([15]\text{-crown-}5)]^+$	$[GeCl_3]^-$	Ion	2 $GeCl_2$·dioxane + [15]crown-5	357
$[Ge(OTf)([15]\text{-crown-}5)]^+$	$[OTf]^-$	Ion	$GeCl_2$·dioxane + [15]crown-5 + 2 $Me_3Si(OTf)$	357
$[GeCl([18]\text{-crown-}6)]^+$	$[GeCl_3]^-$	Ion	2 $GeCl_2$·dioxane + 1.5 [18]crown-6	357
	$[GeCl_3]^-$	Ion	2 $GeCl_2$·dioxane + 	360
	$[GeCl_3]^-$	Ion	 2 $GeCl_2$ +	361

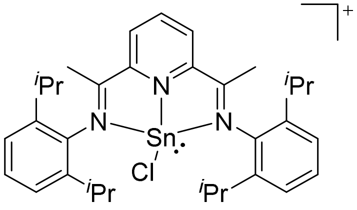
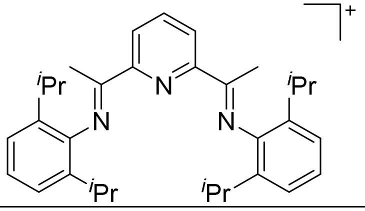
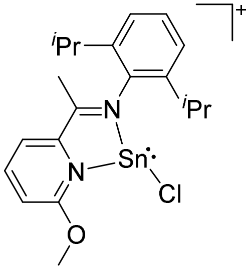
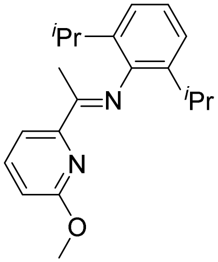
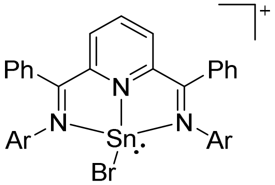
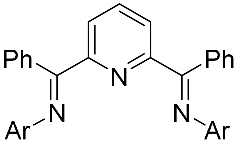
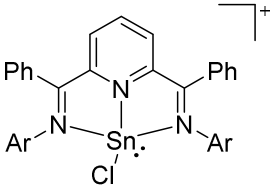
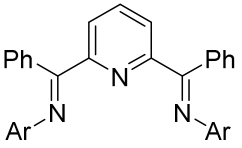
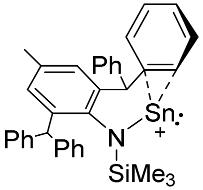
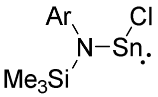
	$[AlCl_4]^-$	Lewis	 $+ AlCl_3$		344
	$[B_{12}Cl_{12}]^{2-}$	Com	 $[AlCl_4]^-$ $+ DMAP + 0.2\ K_2^+[WCA]^-$		344
	$[HO\{B(C_6F_5)_3\}_2]^-$	Lewis	 $+ B(C_6F_5)_3 + H_2O$		369
	$[B(C_6F_5)_4]^-$	Prot	 $+ [Et_3Si(C_6H_6)]^+[WCA]^-$	Protonated by acidified benzene	365
	$[B(C_6F_5)_4]^-$	Prot	 $+ [H(OEt_2)_2]^+[WCA]^-$		365
	$[SbF_6]^-$	Salt	 $+ Ag^+[WCA]^- + THF$		80

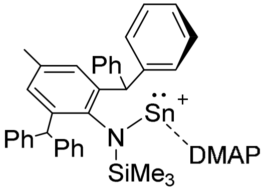
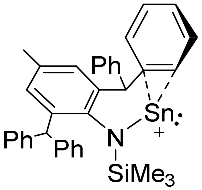
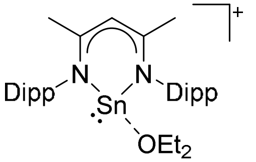
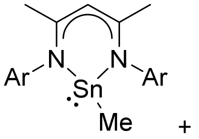
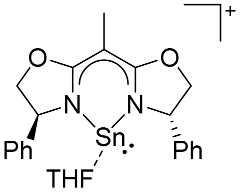
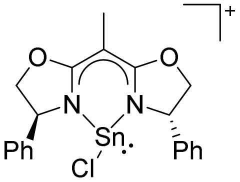
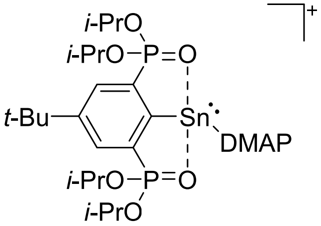
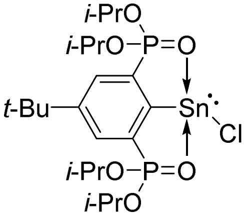
	$[SbF_6]^-$	Lig	 $[WCA]^-$ + py	80
	$[SbF_6]^-$	Lig	 $[WCA]^-$ + PMe_2Ph	80
	$[Al(OR^{PF})_4]^-$	Salt	 + $Ag^+[WCA]^-$ or $Li^+[WCA]^-$	366
	$[Al(OR^{PF})_4]^-$	Lig	 + DMAP	366

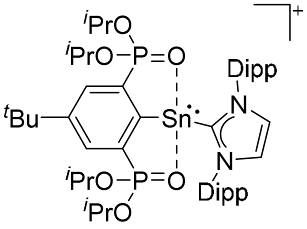
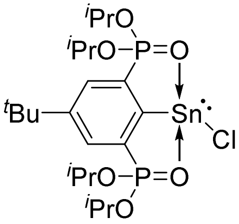
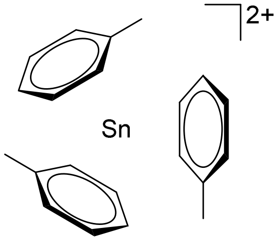
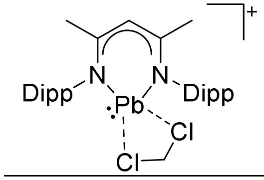
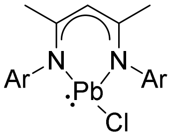
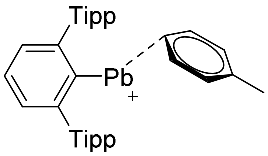
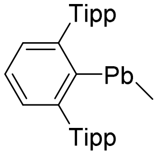
	$[B(C_6F_5)_4]^-$	Lewis	 + $[Et_3Si(C_6H_6)]^+[WCA]^-$	347
$[Me_3Sn(OPPh_3)_2]^+$	$[(MeSO_2)_2N]^-$	Ion	$Me_3SnN(SO_2Me)_2$ + 2 $OPPh_3$	342
	$[B(Ph)_4]^-$	Ox	 $[WCA]^-$ + 1/8 S_8 L = DMAP	345
$[Sn([15]crown\text{-}5)_2]^{2+}$	$[SnCl_3]^-$	Ion	2 $SnCl_2$ + 2 [15]crown-5	350
$[Sn([12]crown\text{-}4)_2]^{2+}$	$[OTf]^-$	Ion	$Sn(OTf)_2$ + 2 [12]crown-4	352
$[Sn([15]crown\text{-}5)_2]^{2+}$	$[OTf]^-$	Ion	$Sn(OTf)_2$ + 2 [15]crown-5	352
$[Sn([18]crown\text{-}6)(OTf)]^+$	$[OTf]^-$	Ion	$Sn(OTf)_2$ + [18]crown-6	352
$[Sn([18]crown\text{-}6)(F)]^+$	$[PF_6]^-$	Other	$[Sn([18]crown\text{-}6)]^{2+}[WCA]_2^-$ + KF	353
	$[OTf]^-$	Ion	$Sn(OTf)_2$ + cryptand[2.2.2] or 2 $SnCl_2$ + cryptand[2.2.2] + 4 $Me_3Si(OTf)$	356

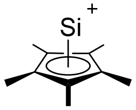
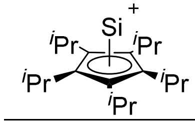
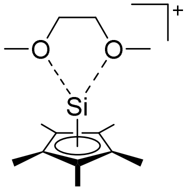
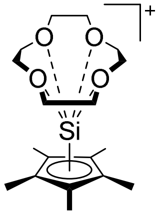
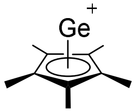
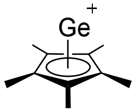
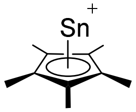
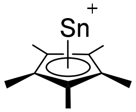
	$[SnCl_3]^-$	Ion	2 $SnCl_2$ + cryptand[2.2.2]		356
	$[SnBr_3]^-$	Ion	2 $SnCl_2$ + cryptand[2.2.2] + 4 Me_3SiBr		356
	$[B(C_6F_5)_4]^-$	Com	 + MeCN		346
	$[B(C_6F_5)_4]^-$	Other	 + $[Ph_3C]^+[WCA]^-$		348
	$[SnCl_3]^-$	Salt	$SnCl_2$ + 		389
	$[GeBr_3]^-$	Ion	$GeBr_2$ + bipy	bulk product is $GeBr_2(bipy)$	359

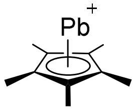
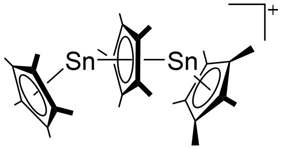
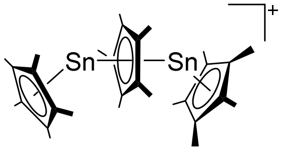
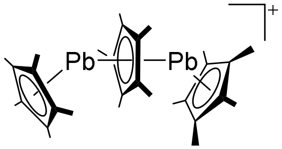
	$[GeCl_3]^-$	Ion	$GeCl_2$·dioxane + pmdta	359
	Cl^-	Ion	$GeCl_2$·dioxane + 	363
	Cl^-	Ox	 + 1/8 S_8	363
	Cl^-	Ion	$GeCl_2$·dioxane + 	364
	$[GeCl_3]^-$	Ion	$GeCl_2$·dioxane + Me_4-cyclam	358
	$[GeBr_3]^-$ + Br^-	Ion	$GeBr_2$ + Me_3-tacn	358

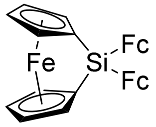
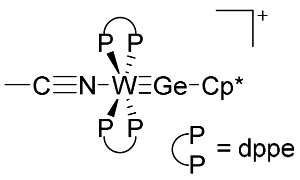
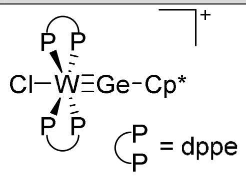
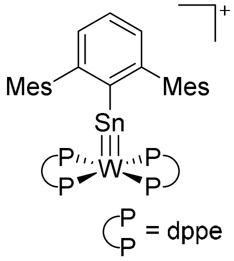
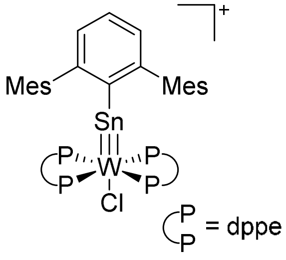
	$[SnCl_3]^-$	Ion	2 $SnCl_2$ + 		360
	$[SnCl_3]^-$	Ion	 2 $SnCl_2$ +		361
	$[SnBr_3]^-$	Ion	$SnBr_2$ + 	Ar = 2,5-^{t}Bu$_2$(C$_6$H$_3$)	390
	$[SnCl_3]^-$	Ion	$SnCl_2$ + 	Ar = 2,5-^{t}Bu$_2$(C$_6$H$_3$) and 2,6-Me$_2$(C$_6$H$_3$)	390
	$[Al(OR^{PF})_4]^-$	Salt	 + Ag$^+$[WCA]$^-$ or Li$^+$[WCA]$^-$		366

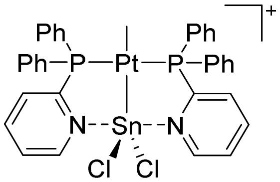
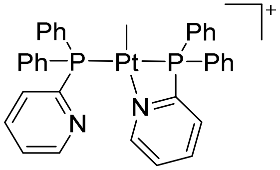
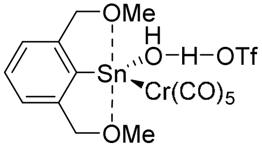
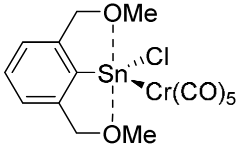
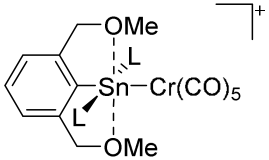
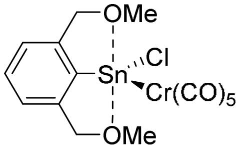
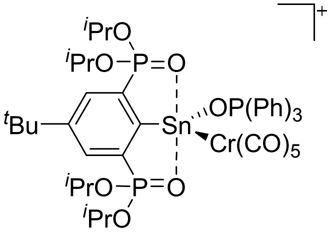
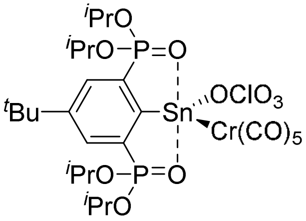
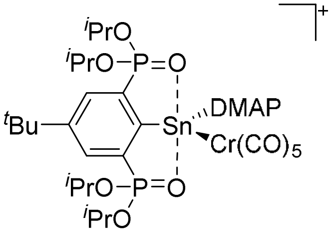
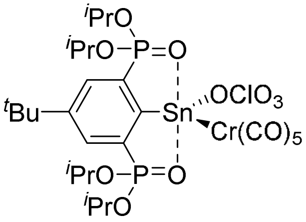
	$[Al(OR^{PF})_4]^-$	Lig	 + DMAP	366
	$[MeB(C_6F_5)_3]^-$	Lewis	 + $B(C_6F_5)_3$	367
	$[SbF_6]^-$	Salt	 + $Ag^+[WCA]^-$	368
	$[B(Ph)_4]^-$	Salt	 + $Na^+[WCA]^-$	345

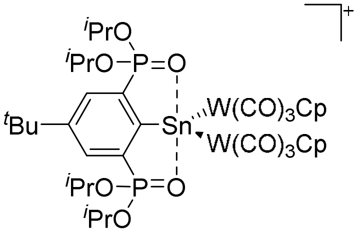
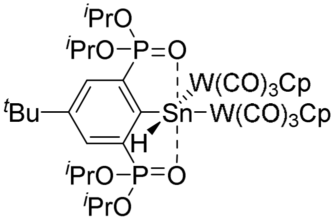
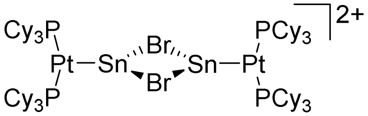
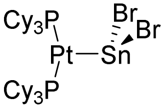
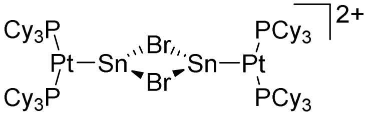
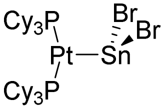
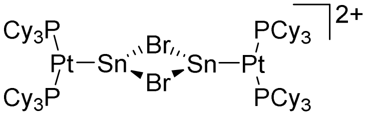
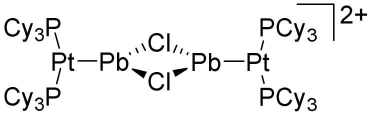
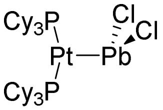
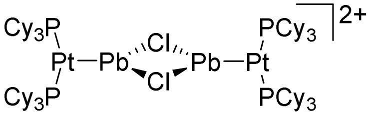
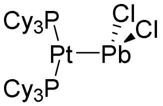
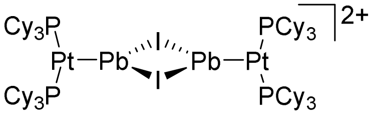
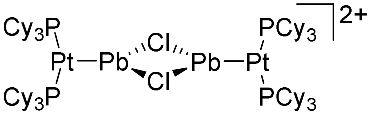
	$[B(Ar^{CF3})_4]^-$	Salt	 + $Na^+[WCA]^-$	345
	$[B(C_6F_5)_4]^-$	Other	$(Tipp)_2Sn + [Et_3Si(C_7H_8)]^+[WCA]^-$	371
$[Pb(NO_3)([12]\text{-crown-}4)_2]^+$	$[Pb(NO_3)_3([12]\text{crown-}4)]^-$	Ion	$Pb(NO_3)_2$ + [12]crown-4	351
$[Pb([15]\text{-crown-}5)_2]^{2+}$	$[Pb(NO_3)_3([15]\text{crown-}5)]^-$	Ion	$Pb(NO_3)_2$ + 2 [15]crown-5	351
$[Pb(\text{benzo-}[15]\text{-crown-}5)_2]^{2+}$	$[Pb(NO_3)_3(\text{benzo-}[15]\text{crown-}5)]^-$	Ion	$Pb(NO_3)_2$ + benzo-[15]crown-5	351
	$[B(C_6F_5)_4]^-$	Salt	 + $Li^+[WCA]^-$	367
	$[B(C_6F_5)_3(CH_3)]^-$	Lewis	 + $B(C_6F_5)_3$	370

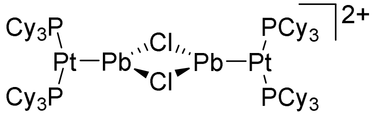
Cyclopentadienyl Substituted Cations				
	$[B(C_6F_5)_4]^-$	Prot	$(Me_5C_5)_2Si + [Me_5C_5H_2]^+[WCA]^-$	322
	$[Al(OR^{PF})_4]^-$	Prot	$(Me_5C_5)(^iPr_5C_5)Si + [H(OEt_2)_2]^+[WCA]^-$	323
	$[B(C_6F_5)_4]^-$	Com	$[(Me_5C_5)Si]^+[WCA]^-$ + dme	324
	$[B(C_6F_5)_4]^-$	Com	$[(Me_5C_5)Si]^+[WCA]^-$ + [12]crown-4	324
	$[BF_4]^-$	Prot	$(C_5Me_5)_2Ge$+ H(WCA)	376
	$[SnCl_3]^-$	Lewis	$(C_5Me_5)GeCl + SnCl_2$	377
	$[BF_4]^-$	Prot	$(C_5Me_5)_2Ge$ + H(WCA)	373
	$[B(C_6F_5)_4]^-$	Salt	$(C_5Me_5)SnCl + Li^+[WCA]^-$	375

	$[B(C_6F_5)_4]^-$	Salt	$(C_5Me_5)PbCl + Li^+[WCA]^-$		375
	$[Ga(C_6F_5)_4]^-$	Other	$(C_5Me_5)_2Sn + Ga(C_6F_5)_3$		378
	$[B(C_6F_5)_4]^-$	Com	$[(C_5Me_5)Sn]^+[WCA]^- + (C_5Me_5)_2Sn$		375
	$[B(C_6F_5)_4]^-$	Com	$[(C_5Me_5)Pb]^+[WCA]^- + (C_5Me_5)_2Pb$		375
Ion-like compounds					
$Me_2(B_{12}Cl_{12})$		Salt	$[Li]_2^+[WCA]^- + 2.2\ MeF + 2.6\ AsF_5$	1:1 mixture with $[Li]_2^+[WCA]^-$	288
$(Me_2CH)(HCB_{11}Me_5Br_6)$		Lewis	$(H_3C)_2CHCl + (H_3C)(HCB_{11}H_5Br_6)$		287
$Me_2CF(AsF_6)$		Lewis	$(H_3C)_2CF_2 + AsF_5$		268
(m-CF_3-C_6H_4)(Ph)$CF(AsF_6)$		Lewis	$C_6H_5CF_3 + AsF_5$		268
$Me_3Si(HCB_{11}F_{11})$		Hyd	$Me_3SiH + [Ph_3C]^+[WCA]^-$		326
$Me_3Si(C_2H_5CB_{11}F_{11})$		Hyd	$Me_3SiH + [Ph_3C]^+[WCA]^-$		326
$Me_3Si(FAl(OR^{PF})_3)$		Other	$Ag^+[Al(OR^{PF})_4]^- + Me_3SiCl$ or $AlEt_3 + 3\ HOR^{PF} + Me_3SiF$		327
$Et_3Si(HCB_{11}H_5Br_6)$		Hyd	$Et_3SiH + [Ph_3C]^+[WCA]^-$		328
$Et_3Si(HCB_{11}Cl_{11})$		Hyd	$Et_3SiH + [Ph_3C]^+[WCA]^-$		81
$^iPr_3Si(HCB_{11}H_5Br_6)$		Hyd	$^iPr_3SiH + [Ph_3C]^+[WCA]^-$		325
$^iPr_3Si(HCB_{11}H_5Cl_6)$		Hyd	$^iPr_3SiH + [Ph_3C]^+[WCA]^-$		329
$^iPr_3Si(HCB_{11}H_5I_6)$		Hyd	$^iPr_3SiH + [Ph_3C]^+[WCA]^-$		329
$^iPr_3Si(HCB_9H_4Br_5)$		Hyd	$^iPr_3SiH + [Ph_3C]^+[WCA]^-$		297

$^t\mathrm{Bu_3Si(HCB_{11}H_5Br_6)}$		Hyd	$^t\mathrm{Bu_3SiH + [Ph_3C]^+[WCA]^-}$	328
$^t\mathrm{Bu_3Si(FAl(OR^{PF})_3)}$		Other	$^t\mathrm{Bu_3SiI + 15\ (^tBu)_3SiF + Ag^+[Al(OR^{PF})_4]^-}$	330
$^t\mathrm{Bu_2MeSi(HCB_{11}H_5Br_6)}$		Hyd	$^t\mathrm{Bu_2MeSiH + [Ph_3C]^+[WCA]^-}$	328
$\mathrm{Fc_3Si(OTf)}$		Prot	 + HOTf	331
$\mathrm{Et_3Ge(HCB_{11}H_5Br_6)}$		Hyd	$\mathrm{Et_3GeH + [Ph_3C]^+[WCA]^-}$	338
$\mathrm{Et_3Sn(HCB_{11}H_5Br_6)}$		Lewis	$\mathrm{Et_3SnCl + (Et)_3Si(WCA)}$	338
$^n\mathrm{Bu_3Sn(CB_{11}Me_{12})}$		Ox	$^n\mathrm{Bu_6Sn_2 + 2\ CB_{11}Me_{12}}$	333
$\mathrm{Et_3Pb(HCB_{11}H_5Br_6)}$		Lewis	$\mathrm{Et_3PbCl + (Et)_3Si(WCA)}$	338
Transition-Metal substituted Cations				
	$[\mathrm{B(C_6F_5)_4}]^-$	Salt	 $+\ \mathrm{Li^+[WCA]^- + MeCN}$	380
	$[\mathrm{PF_6}]^-$	Salt	 $+\ \mathrm{Tl^+[WCA]^-}$	379

	$[BF_4]^-$	Com	 $[WCA]^-$ + $SnCl_2$ or [PtMeCl(cod)] + 2 2-$PyPPh_2$ + $SnCl_2$ + $[NBu_4]^+[BF_4]^-$		381
		Salt	 + $Ag^+[WCA]^-$ + H_2O		382
	$[CB_{11}H_{12}]^-$	Salt	 + $Ag^+[WCA]^-$	L = THF	382
	$[ClO_4]^-$	Ion	 + $OP(Ph)_3$		383
	$[ClO_4]^-$	Ion	 + DMAP		383

	$[W(CO)_3Cp]^-$	Prot	 + $HW(CO)_3(Cp)$	384
	$[AlBr_4]^-$	Lewis	 + $AlBr_3$	385
	$[B(Ar^{Cl})_4]^-$	Salt	 + $Na^+[WCA]^-$	385
$\{(Cy_3P)_2Pt\}_2Sn(AlBr_4)_2$		Lewis	 + $AlBr_3$	385
	$[AlCl_4]^-$	Lewis	 + $AlCl_3$	385
	$[B(Ar^{Cl})_4]^-$	Salt	 + $Na^+[WCA]^-$	385
	$[AlCl_4]^-$	Salt	 + 2 NaI	385

$\{(Cy_3P)_2Pt\}_2Pb(AlCl_4)_2$	Lewis	 + $AlCl_3$	385

Group 15 Cations

Of all the pnictogen elements, especially phosphorus has a rich cation chemistry. The analogy between CR_4 and $[PR_4]^+$ displays the possibility of creating a large variety of cationic phosphorus frameworks (**Figure 61**).

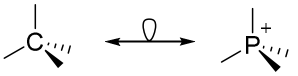


Figure 61. Analogy between cationic phosphorus atom and carbon.

Over the last decades a multitude of catenated phosphorus cations were synthesized. The classical phosphino-phosphonium cation (**Figure 62**, left), which can be synthesized through halide abstraction from PR_2Cl and formal insertion / coordination of the resulting $[PR_2]^+$ (see section "Oxidation state +III" below) into a R_2P-R bond / to PR_3 stands for an entire substance class of compounds typically containing organic residues R.[391] However, we refer the interested reader to the multitude of recent reviews especially on these cations,[392,393] the analogous interpnictogen cations (**Figure 63**)[394] and other types of cationic pnictogen compounds (**Table 7**).

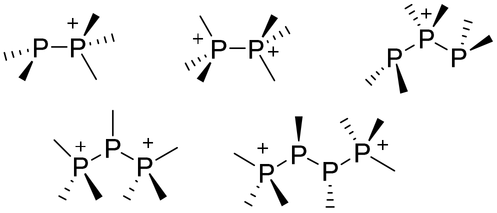


Figure 62. Examples for catenated phosphorus cations in the formal phosphino-phosphonium or diphosphonium form. Also cyclic versions are available.

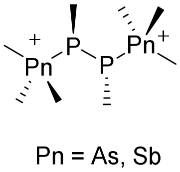


Figure 63. Example for a catenated interpnictogen cation.

Table 7. Review articles including cationic group 15 compounds.

Year	Title	Ref
2004	Homoatomic Cages and Clusters of the Heavier Group 15 Elements. Neutral Species and Cations	395
2008	Catena-Phosphorus Cations	393
2011	Homo- and Heteroatomic Polycations of Groups 15 and 16. Recent Advances in Synthesis and Isolation using Room Temperature Ionic Liquids	66
2012	Multiple-Charged P_1-Centered Cations: Perspectives in Synthesis	396
2013	Catenated Phosphorus Compounds	392
2013	Recent Advances in the Syntheses of Homopolyatomic Cations of the Non-Metallic Elements C, N, P, S, Cl, Br, I and Xe	11
2013	Catenated Compounds – Group 15 (As, Sb, Bi)	397
2014	Interpnictogen Cations: Exploring New Vistas in Coordination Chemistry	394
2014	The Chemistry of Cationic Polyphosphorus Cages - Syntheses, Structure and Reactivity	398

2015	Coordination Chemistry of Homoatomic Ligands of Bismuth, Selenium and Tellurium	399,400

Homopolyatomic Cations: Except for the long-known bismuth cations, all homopolyatomic pnictogen cations were synthesized in the last 16 years. In late 1999 the third all-nitrogen molecule $[N_5]^+$ – besides N_2 and N_3^- – was prepared through a reaction of $[N_2F]^+[AsF_6]^-$ and HN_3.[401] The obtained compound $[N_5]^+[AsF_6]^-$ is explosive but an anion exchange led to the more stable $[N_5]^+[SbF_6]^-$ and to the crystal structure of $[N_5]^+[Sb_2F_{11}]^-$.[402] In 2004 the reduction of $SbCl_3$ with $[Ga]^+[GaCl_4]^-$ in a $GaCl_3$-benzene solution led to the square-antiprismatic *arachno*-$[Sb_8]^{2+}$ Wade cluster cation.[403] Recently also the first – formally electron precise and Zintl type – phosphorus cation $[P_9]^+$ was synthesized through the reaction of P_4 and the nitrosyl salt of the $[Al(OR^{PF})_4]^-$ WCA.[29] By contrast, bismuth has a rich cation chemistry. The first structure of a bismuth cation was measured already in 1962. Most of them were synthesized through high temperature solid state reactions. The newer room temperature approaches are based on ionic liquids.[404] Normally the clusters formed are badly soluble, but there is evidence that the use of very weakly coordinating anions like $[Al(OR^{PF})_4]^-$ can lead to $[Bi_n]^+$ clusters, which are soluble in solvents like CH_2Cl_2 or SO_2.[405] Besides the lighter noble gases and fluorine, only arsenic has still no homopolyatomic cation. Yellow arsenic (As_4), which has now a relatively stable storage form (see section "Metal-Pnictogen Complexes") might be a good starting point for a future synthesis.

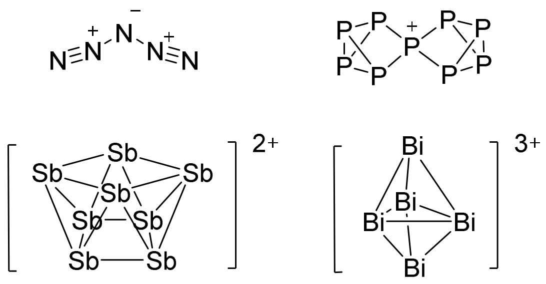


Figure 64. Examples for homopolyatomic pnictogen cations (only for bismuth, several entries are known).

Metal-Pnictogen Complexes: There are still only a few complexes with pnictogen modifications as ligands in the literature. Early examples of tetrahedro-P_4 complexes like $(PPh_3)_2Rh^ICl(\eta^2\text{-}P_4)$ are better viewed as phosphide complex $(PPh_3)_2Rh^{III}(P_4^{2-})$. By contrast, the d^{10}-metal cation Ag^+ is ideal for the stabilization of the non-metallic clusters and the electronic structure of the ligand stays relatively unaffected (see also chapter chalcogen cations). In 2001, the WCA $[Al(OR^{PF})_4]^-$ made it possible to crystallize the $[Ag(P_4)_2]^+$ complex and later through salt metathesis with CuI also the copper complex $[Cu(P_4)_2]^+$ was accessible. In 2012 the gold complex was obtained as $[GaCl_4]^-$ salt and completed the whole series $[M(P_4)_2]^+$ (M = Cu, Ag, Au). Recently light-stable (!) $[Ag(As_4)_2]^+[Al(OR^{PF})_4]^-$ was synthesized, which finally serves as a good storage form of yellow arsenic (As_4). As such, As_4 is both thermally and photochemically unstable. The salt made it possible to transfer the As_4 tetrahedron to gold in $[Ph_3PAu(As_4)]^+$ and opens new possibilities in the synthesis of arsenic complexes.[406]

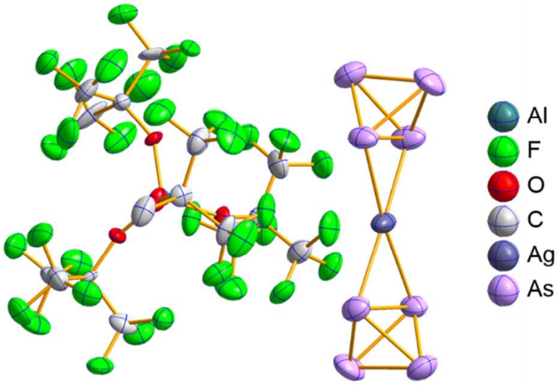
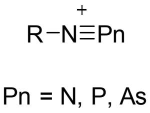


Figure 65. Molecular structure of $[Ag(As_4)_2]^+[Al(OR^{PF})_4]^-$. C. Schwarzmaier, M. Sierka, M. Scheer, *Angew. Chem. Int. Ed.* **2013**, *52*, 858–861. C. Schwarzmaier, M. Sierka, M. Scheer, *Angew. Chem.* **2013**, *125*, 891–894. Data from this Reference were used to draw this figure. The disorder of the anion was omitted for clarity.

Diazonium Cations and Heavier Homologues: There is a multitude of crystal structures of different cluster or cluster-like cations that contain pnictogen atoms.[393,398,394,392] We decided to give an overview and to list parent (model)-compounds like $[N_2Ph]^+$ and $[N_2Mes]^+$ in case of diazonium cations[407] as examples for the entire diazonium substance classes. The heavier homologues of the diazonium cations $[RNPn]^+$ (Pn = P, As) need sterically demanding groups like Mes* (2,4,6-^{t}$Bu_3C_6H_2$) to protect the highly reactive triple bonds.[408,409]



$$R{-}\overset{+}{N}{\equiv}Pn$$

Pn = N, P, As

Figure 66. The diazonium cation and its heavier homologues. R e.g. Mes*.

Cluster and Cage Cations: The reaction of phosphorus halides PX_3 with halide abstractors led to very reactive carbene-analogous $[PX_2]^+$ cations (see chapter “Phosphenium Ions”), which are able to formally insert in the X_2P-X bonds of a second equivalent to form $[P_2X_5]^+$ clusters or in the P-P bond of white phosphorus to produce $[P_5X_2]^+$ for instance. Insertion in P_4S_3 or halide abstraction from $P_4S_3I_2$ followed by rearrangements led to the phosphorus-sulphur cluster cations $[P_5S_2X_2]^+$ [134] and $[P_7S_6I_2]^+$.[234] Reference [134] contains investigations on the nature of this formal insertion reaction, which is not as simple as thought and rather follows a concerted, orbital controlled mechanism.

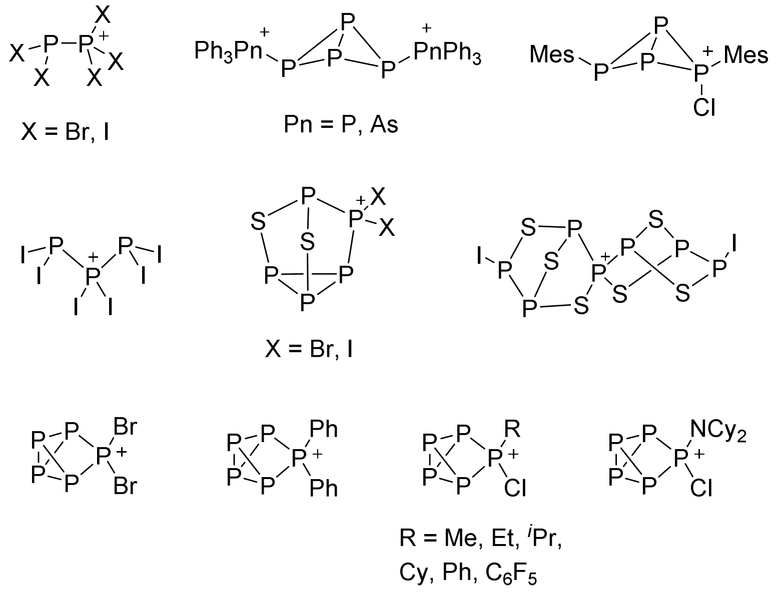


Figure 67. Typical examples for phosphorus cations.

The binary group 15 and 16 cations have also a strong tendency to form clusters. The newer examples like the antimony-chalcogen cations $[Sb_{10}Se_{10}]^{2+}$ and $[Sb_7Te_8]^{5+}$ were synthesized in ionic liquids or $GaCl_3$ melts.[410,411] Very recently $[P_3Se_4]^+$, the first binary P-Se-cation was prepared by six different groups with three different approaches.[412] It is accessible from solution, but also through solid state syntheses.[413] In 2004 the synthesis of the sulphur- and selenium-bismuth cations from a chloroaluminate melt completed the series of the heterocubane cluster cations $[Bi_4Ch_4]^{4+}$ (Ch = S, Se, Te).[414,415]

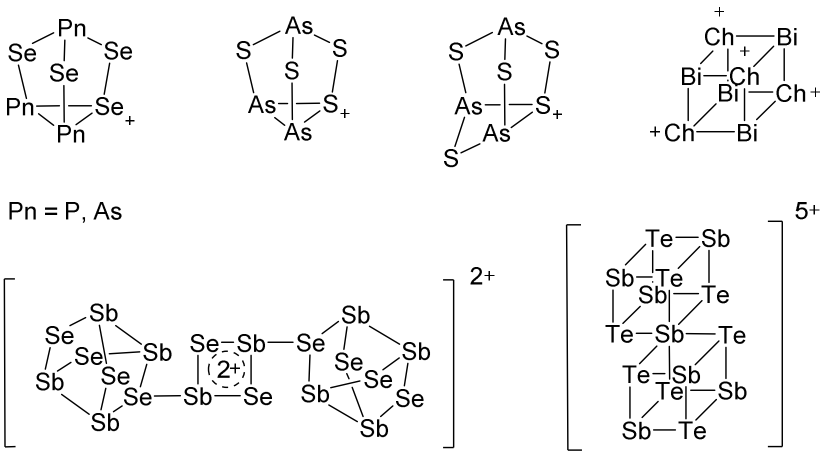


Figure 68. Examples for binary pnictogen containing cations.

(4n+2)π-Cations: The pnictogen cations with planar delocalized π-systems can be described as (pseudo-)aromatic systems. The four-membered rings were all synthesized through halide abstraction from the neutral rings with two halogen atoms. The five-membered As-N ring was prepared through cycloaddition of the highly reactive $[AsNMes^*]^+$, which reacts as dienophile with the 1,3 dipole tritylazide N_3CPh_3.

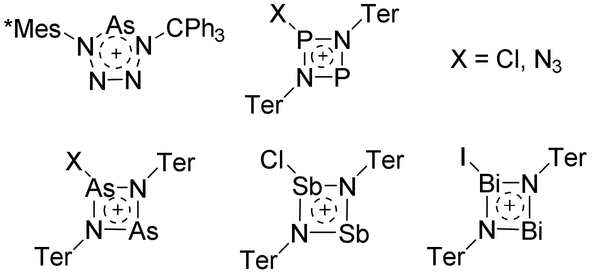


Figure 69. Heteroatomic, cationic aromatic 6π-systems containing pnictogen atoms.

π*-π*-Complexes: Like the chalcogen compounds, the pnictogen cations containing π*-π*-interactions can be described as dimers of chalcogen radicals, whose half-occupied interacting orbitals have π*-character. The interannular π*-π*-bonds between the "monomers" are relatively weak. They were synthesized through halide abstraction from the chlorides of the monomers.[416]

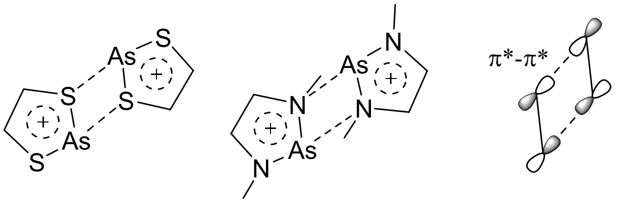


Figure 70. Arsenic cations containing π*-π*-interactions.

Radical Cations: Radical cations of pnictogens can be obtained through direct oxidation of Pn_2 fragments with stabilizing ligands like N-heterocyclic carbenes (NHC) or cyclic alkylaminocarbenes (CAAC). As one-electron-oxidants the trityl salt of $[B(C_6F_5)_4]^-$ was used.[417,208,418]

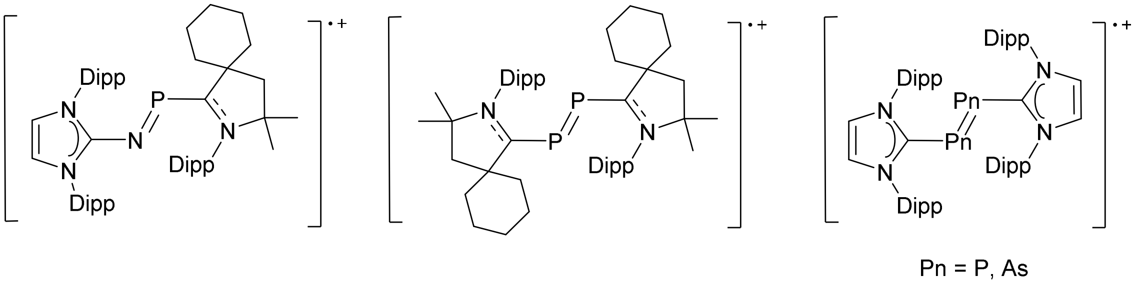


Figure 71. Cationic phosphorus radicals stabilized by NHCs or CAACs.

Bulky arylphosphines and -diphosphines (**Figure 72**) can also be oxidized to their radical cations, if the cation is stabilized by a WCA.[419,420]

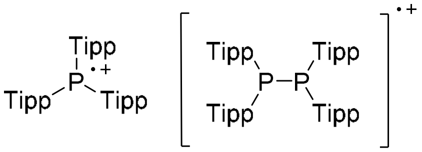


Figure 72. Phosphorus radical cations.

The delocalization of the single electron over a ring system also leads to stabilization. The four-membered radical cation ring systems with different pnictogen atoms (**Figure 73**) were obtained through direct oxidation with silver and nitrosyl salts of WCAs.[421]

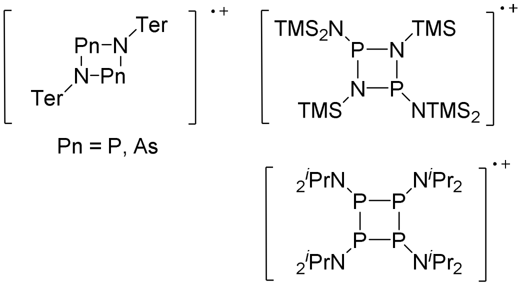


Figure 73. Cyclic pnictogen radical cations.

Formal Oxidation state +I: In some compounds like $[P_3Ph_6]^+$ [422] the oxidation state of the central pnictogen "P^+" can be described as +I, which is for example supported by the unusual high field shift in ^{31}P-NMR of the central phosphorus atom in these cations (–210 to –270 ppm).[423] In case of the ligand-stabilized arsenic cation $[AsDppDIMPY]^+$ this is also supported by the synthesis: (DppDIMPY = [α,α'-{2,6-^{i}Pr$_2$PhNC(Me)}$_2$(C$_5$H$_3$N)]). The reduction of $AsCl_3$ with $SnCl_2$ led to a cation with a planar carbenoid-like structure.[424] Under the same conditions with a different ligand an arsa-carbenoid of type $[As(NR)_2C_2H_2]^+$ was obtained (**Figure 78**). This displays the difficulty of a clear assignment of oxidation states in such systems.

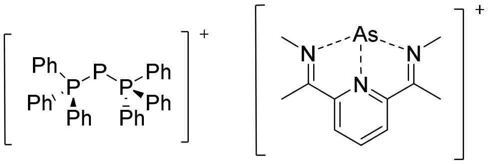


Figure 74. Phosphorus and arsenic cations in formal oxidation state +I.

Phosphenium Ions (Oxidation state +III): The chemistry of the highly reactive phosphenium ions $[P(R/Y)_2]^+$ (**Figure 75**) was part of many studies in the past. The stability increases with the π-donor-ability of the substituent and the Lewis acidity with a stronger negative inductive effect (FIA: $[P(NH_2)_2]^+ < [PCl(NH_2)]^+ < [PCl_2]^+$).[425]

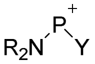
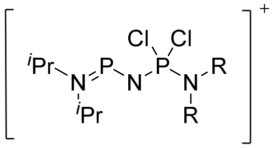


Figure 75. Structurally characterized simple phosphenium ions.

For most of the reactive phosphorus cations, the decomposition is normally accompanied by the formation of strong P-X bonds (X = F, Cl…). This makes it necessary to use weakly coordinating anions stable against electrophilic cations. For the homoleptic halogen substituted cations, extremely weak anions are needed. The first examples of the less, but still highly reactive mixed amino-halogen substituted phosphenium cations were published already in 1976. Through the use of a halide-abstractor (MCl_3, M= Al, Ga, Fe) is was possible to prepare $[P(NR_2)Cl]^+$ (R = Me, Et, ^{i}Pr) (X = $[AlCl_4]^-$) but no crystallographic data was obtained. It was not until 2012 that the first crystal structure of a halogen and a pseudohalogen mono-substituted phosphenium cation was determined. The structures of $[P(NR_2)X]^+$ (R = TMS; X = Cl, N_3, NCO, NCS) and (R = ^{i}Pr ; X = Cl, N_3) were determined by scXRD. All cations were stabilized with the $[GaCl_4]^-$ anion. Especially the azidophosphenium compound turned out to be a versatile starting material for further chemistry, and made it possible to derive more complex phosphor-centered cations like iminophosphorane-substituted-phosphonium salts $[^iPr_2NPNP(Cl)_2NR_2]^+[GaCl_4]^-$ [R = ^{i}Pr, $SiMe_3$] (**Figure 76**) – for instance through the reaction with the corresponding chlorophosphane R_2NPCl_2.



R = ^{i}Pr, $SiMe_3$

Figure 76. Iminophosphorane-substituted phosphorus cation.

Miscellaneous Cations in Oxidation State +III: There are also some examples of the heavier homologues in oxidation state +III (**Figure 77**). They were typically synthesized through halide abstraction with Lewis acids.

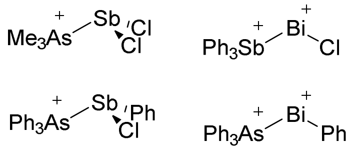


Figure 77. Pnictogen cations with pnictogen atoms in formal oxidation state +III.

Another example of ligand-stabilized pnictogen cations are the N-heterocyclic carbenoid rings $[Pn(NR)_2C_2H_2]^{2+}$ (Pn = P, As, Sb), which are formally 1,4-diaza-1,3-butadiene complexes of a pnictogen cation in oxidation state +III, but the delocalization of the positive charge supports also a description as a neutral pnictogen atom. In case of the 1,3,2-Diazaphospholidinium rings $[Pn(NR)_2C_2H_4]^+$ (Pn = P, As) the double bond between C4 and C5 is missing.

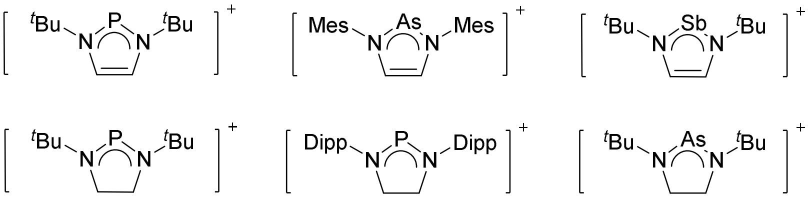
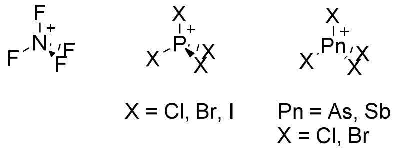


Figure 78. Examples for pnictogen carbenoids.

Reactive Pnictonium Cations (Oxidation state +V): The halo-pnictonium cations $[PnX_4]^+$ with pnictogen atoms in oxidation state +V (**Figure 79**), have a very different presence in the literature. For phosphorus, all four cations (X = F, Cl, Br, I) have been synthesized but for $[PF_4]^+$ no crystal structure was determined. A multitude of structures of $[PX_4]^+$ with different anions was characterized, but only a few of $[AsX_4]^+$ and $[SbX_4]^+$ are known. The cations are normally prepared from PnX_3, X_2 and a Lewis acid.

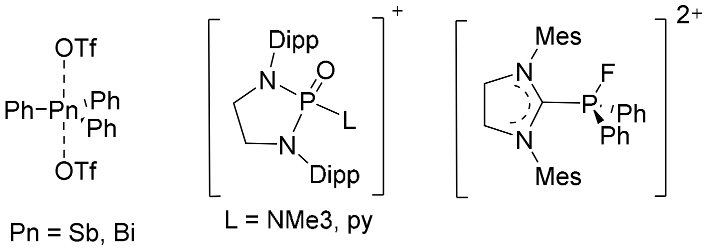


X = Cl, Br, I

Pn = As, Sb
X = Cl, Br

Figure 79. Classical halo-pnictonium cations in oxidation state +V.

But there are also some newer, highly oxidized cations in the literature: The formal $[PnPh_3]^{2+}$ cations (**Figure 80**), which have a strong contact to the anion, serve as useful starting materials for further coordination chemistry of Pn^V compounds.[426] The ligand stabilized formal "PO^+" cations were prepared through the oxidation of a phosphorus carbenoid (**Figure 80**, see also the phosphorus carbenoids above) with the amine-N-oxides Me_3NO and pyO.[427] The charge of the carbene-stabilized formal "$[PFPh_2]^{2+}$", which was prepared from the carbene-stabilized "$[PF_2Ph_2]^+$" through fluoride abstraction is likely partially localised on the strongly bound ligand (**Figure 80**).[428]

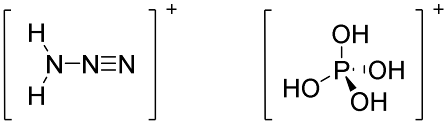


Pn = Sb, Bi

L = NMe3, py

Figure 80. Examples for recent pnictogen cations in oxidation state +V.

Protonated Cations: With the super acidic system HF/MF_5 (M = As, Sb) it is possible to protonate hydrazoic or phosphoric acid for instance and obtain the aminodiazonium $[H_2N_3]^+$ and phosphatacidium (tetrahydroxyphosphonium) cation $[P(OH)_4]^+$. The structure determinations of the $[SbF_6]^-$ salts revealed the structures of the cations (**Figure 81**). [429]



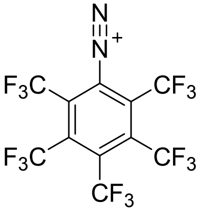
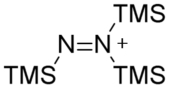
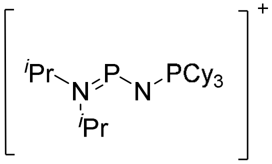
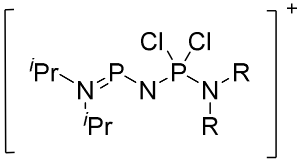
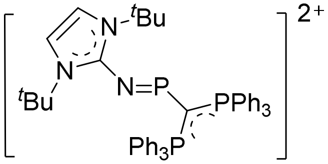
$[H_2N_3]^+$

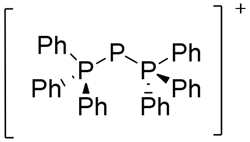
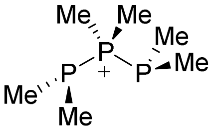
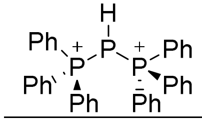
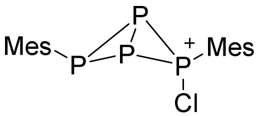
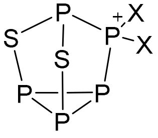
$[P(OH)_4]^+$

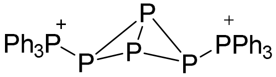
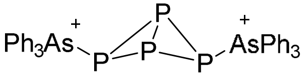
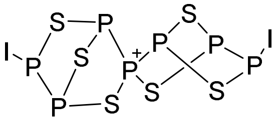
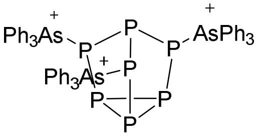
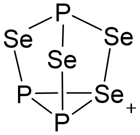
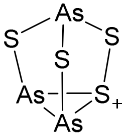
Figure 81. Structures of $[H_2N_3]^+$ and $[P(OH)_4]^+$ in their $[SbF_6]^-$ salts.

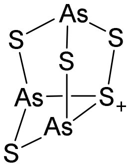
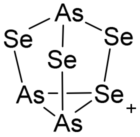
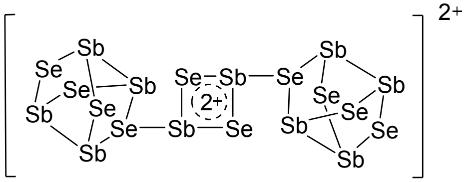
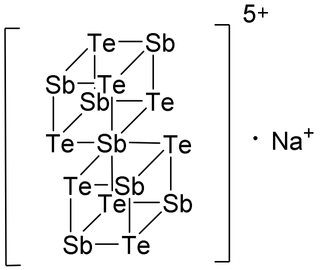
Table 8. Overview on selected and structurally characterized pnictogen cations.

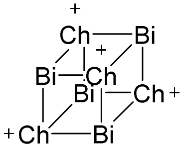
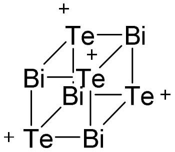
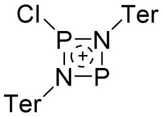
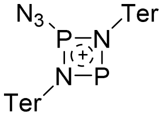
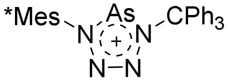
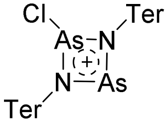
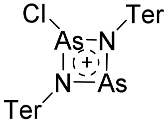
Cation	Anion	Class.*	Synthesis	Comment**	Ref.
Homopolyatomic Cations					
$[N_5]^+$	$[Sb_2F_{11}]^-$	Other	$[N_2F]^+[SbF_6]^-$ + HN_3 in aHF		402
$[P_9]^+$	$[Al(OR^{PF})_4]^-$	Ox	$P_4 + [NO]^+[Al(OC(CF_3)_3)_4]^-$	2.5 equiv. of P_4, no X-Ray	29
$[Sb_8]^{2+}$	$[GaCl_4]^-$	Lewis	$SbCl_3 + [Ga]^+[GaCl_4]^-$ in $GaCl_3/C_6H_6$		403
$[Bi_2]^{4+}\cdot[Bi_9]^{5+}$	$[Ag_3Bi_3Br_{15}]^{3-}\cdot6[Br]^-$	Lewis, Ox	$Bi + BiBr_3 + Ag$	HTS (350°C)	430
$2[Bi_5]^+\cdot[Bi_6]^{2+}$	$2[IrBi_6Br_{12}]^-\cdot[IrBi_6Br_{13}]^{2-}$	Lewis, Ox	$Bi + Ir + BiBr_3$	HTS (1000°C)	431
$[Bi_5]^{3+}$	$[AlCl_4]^-$	Lewis, Ox	$Bi + BiCl_3 + AlCl_3$	HTS	432
$[Bi_5]^{3+}$	$[AlCl_4]^-$	Lewis, Ox	$Bi + BiCl_3 + [BMIM]Cl/AlCl_3$	Ionic liquid based synthesis	404
$[Bi_5]^{3+}$	$[AlX_4]^-$ (X = Br, I)	Lewis, Ox	$Bi + BiX_3 + AlX_3$	HTS (490°C (I), 520°C (Br))	433
$[Bi_5]^{3+}\cdot2SO_2$	$[AsF_6]^-$	Lewis, Ox	$Bi + AsF_5$ in SO_2	No X-Ray	196
$[Bi_8]^{2+}$	$[AlCl_4]^-$	Lewis, Ox	$Bi + BiCl_3 + AlCl_3$	HTS	434
$[Bi_8]^{2+}$	$[Ta_2O_2Br_7]^-$	Lewis, Ox	$Bi + BiBr_3 + TaBr_5$	HTS (570°C), traces of H_2O	435
$[Bi_9]^{5+}$	$4[BiCl_5]^{2-}\cdot[Bi_2Cl_8]^{2-}$	Lewis, Ox	$Bi + BiCl_3$	HTS (325°C), Bi_6Cl_7	436,236
$[Bi_9]^{5+}$	$[Bi]^+\cdot3[HfCl_6]^{2-}$	Lewis, Ox	$Bi + BiCl_3 + HfCl_4$	HTS	437
$[Bi_9]^{5+}$	$[Bi]^+\cdot3[NbCl_6]^{2-}$	Lewis, Ox	$Bi + BiCl_3 + NbCl_5$	HTS (550°C), Nb(V) to Nb(IV) reduction	435
$[Bi_9]^{5+}$	$[Sn_7Br_{24}]^{10-}$	Lewis, Ox	$Bi + BiBr_3 + Sn$	HTS (250°C), C_{4v} symmetric	438
Metal-nonmetal-cluster complexes					
$[Cu(P_4)_2]^+$	$[Al(OR^{PF})_4]^-$	Com	$CuI + [Ag]^+[Al(OR^{PF})_4]^- + P_4$		439
$[Cu(P_4)]^+$	$[GaCl_4]^-$	Com	$CuCl + GaCl_3 + P_4$		440
$[Ag(P_4)_2]^+$	$[Al(OR^{PF})_4]^-$	Com	$[Ag]^+[Al(OR^{PF})_4]^- + P_4$		72
$[Ag(P_4)]^+$	$[GaCl_4]^-$	Com	$AgCl + GaCl_3 + P_4$		440
$[Au(P_4)_2]^+$	$[GaCl_4]^-$	Com	$AuCl + GaCl_3 + P_4$		440
$[Cp^*M(dppe)(P_4)]^+$ (M = Fe, Ru)	$[BPh_4]^-$	Salt	$[Cp^*M(dppe)Cl] + P_4 + [Na]^+[BPh_4]^-$		441
$[CpOs(PPh_3)_2(P_4)]^+$	$[OTf]^-$	Salt	$[CpOs(PPh_3)_2Cl] + [Ag]^+[OTf]^-$		442
$[\{CpRu(PPh_3)_2\}_2(P_4)]^{2+}$	$[OTf]^-$	Com, Salt	$[CpRu(PPh_3)_2Cl] + P_4 + [Ag]^+[OTf]^-$		443
$[\{CpRu(PPh_3)_2\}\text{-}\{CpOs(PPh_3)_2\}(P_4)]^{2+}$	$[OTf]^-$	Com	$[CpOs(PPh_3)_2(P_4)]^+ + [\{CpRu(PPh_3)_2\}]^+$	Bridging end-on/end-on	442
$[Ag(As_4)_2]^+$	$[Al(OR^{PF})_4]^-$	Com	$[Ag]^+[Al(OR^{PF})_4]^- + As_4$		406
$[AuPPh_3(As_4)]^+$	$[Al(OR^{PF})_4]^-$	Com, Salt	$[Ag(As_4)_2]^+[Al(OR^{PF})_4]^- + AuPPh_3Cl$		406
$[Cp^*Ru\text{-}(dppe)(As_4)]^+$	$[Al(OR^{PF})_4]^-$	Com, Salt	$[Ag(As_4)_2]^+[Al(OR^{PF})_4]^- + Cp^*Ru\text{-}(dppe)Cl$		444
$[Ag(P_4S_3)_n]^+$ (n = 1, 2)	$[Al(OR^{PF})_4]^-$	Com	$[Ag]^+[Al(OR^{PF})_4]^- + P_4S_3$		445
$[Ag_2(P_4S_3)_6]^+$	$[Al(OR^{PF})_4]^-$	Com	$[Ag]^+[Al(OR^{PF})_4]^- + P_4S_3$		170
$[\{CpRu(PPh_3)_2\}_2(P_4S_3)]^{2+}$	$[OTf]^-$	Com, Salt	$[CpRu(PPh_3)_2Cl] + P_4S_3 + [Ag]^+[OTf]^-$		443
Clusters, Cluster-like and Catenated cations					
$[N_2Ph]^+$	$[BF_4]^-$	Other	$PhNH_2 + NaNO_2$ in $HCl_{(aq)}$ and $[Na]^+[BF_4]^-$	N-N triple bond	446

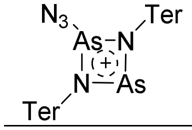
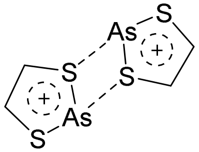
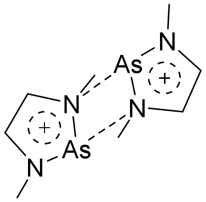
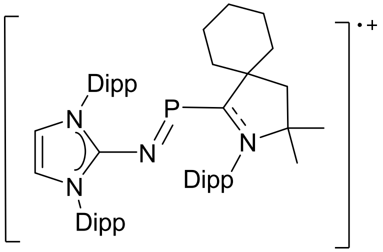
	$[BF_4]^-$	Other	$H_2NC_6(CF_3)_5 + NO^+[BF_4]^-$		447
$Mes{-}\overset{+}{N}{\equiv}N$	$[OsO_2(NO_3)_2(Mes)]^-$	Other	$[N_2Mes]^+[NO_3]^- + [OsO_2(NO_3)(Mes)]$		448
	$[GaCl_4]^-$	Other	$Hg(N_2(TMS)_3)_2 + [Ag]^+[GaCl_4]^-$ or $Bi(N_2(TMS)_3)_2 + GaCl_3 + Cl_2$	LTS (-80°C)	449
$Mes^*{-}\overset{+}{N}{\equiv}P$	$[AlCl_4]^-$	Lewis	Mes*-NPCl + $AlCl_3$	N-P triple bond,	408
	$[GaCl_4]^-$	Other	$[P(N^iPr_2)N_3]^+[GaCl_4]^- + PCy_3$		450
 R = ^{i}Pr, SiMe3	$[GaCl_4]^-$	Other	$[P(N^iPr_2)N_3]^+[GaCl_4]^- + P(NR_2)Cl_2$	N_2 as leaving group	450
	$[SbF_6]^-$	Salt	$[(^tBuIM)NPCl(C(PPh_3)_2)]^+[Cl]^-$ + $[Ag]^+[SbF_6]^-$	Dicationic Iminophosphorane	451
$[P_2Ph_5]^+$	$[OTf]^-$	Lewis	Ph_2PCl + TMSOTf + PPh_3	First homoleptic phosphine-phosphonium	452
$[P_2Me_6]^{2+}$	$[OTf]^-$	Lewis	P_2Me_4 + MeOTf		453
$[P_2Br_5]^+$	$[Al(OR^{PF})_4]^-$	Salt	$PBr_3 + [Ag]^+[Al(OR^{PF})_4]^-$		454
$[P_2I_5]^+$	$[AlI_4]^-$	Lewis	$PI_3 + AlI_3$		455

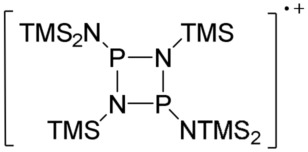
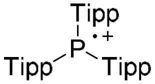
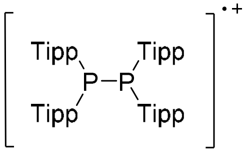
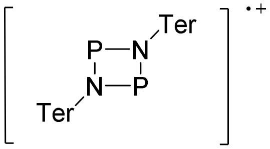
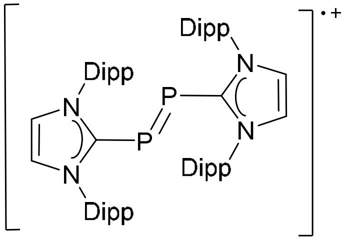
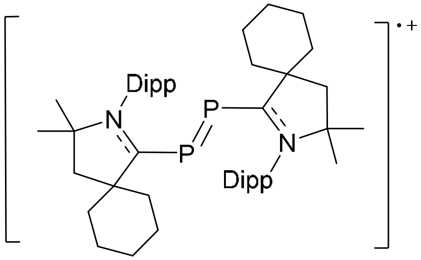
$[P_2I_5]^+$	$[Al(OR^{PF})_4]^-$	Salt	$PI_3 + [Ag]^+[Al(OR^{PF})_4]^-$		454
	$[AlCl_4]^-$	Lewis	$PPh_3 + PCl_3 + AlCl_3$	$[P(PPh_3)_2]^+$	422
	$[OTf]^-$	Lewis	$P_2Me_4 + PMe_2Cl + TMSOTf$	$[(PMe_2)_3]^+$	456
	$[AlCl_4]^-$	Prot	$[P(PPh_3)_2]^+[AlCl_4]^- + AlCl_3 + HCl$		457
$[P_3I_6]^+$	$[F(Al(OR^{PF})_3)_2]^-$	Salt	$P_4 + I_2 + [Ag]^+[Al(OR^{PF})_4]^-$	$[(PI_2)_3]^+$	458
$[PMe(AsMe_3)_2]^+$	$[OTf]^-$	Other	$MePCl_2 + AsMe_3 + TMSOTf$	$[PRL_2]^+$	459
$[P_4Ph_8]^{2+}$	$[OTf]^-$	Lewis	$PPhCl_2 + PPh_3 + TMSOTf$		460
$[P_4NO]^+$	$[Al(OR^{PF})_4]^-$	Other	$P_4 + [NO]^+[Al(OR^{PF})_4]^-$	Insertion in P_4, no X-Ray	78
	$[GaCl_4]^-$	Lewis	$ClP(PMes^*)_2PCl + GaCl_3$	Bicyclic phosphine-phosphonium	461
$[(PPh)_2(PnPh_3)_2]^{2+}$ (Pn = As, Sb)	$[AlCl_4]^-$	Lewis	$PPhCl_2 + PnPh_3 + AlCl_3$		462
$[P_5Br_2]^+$	$[Al(OR^{PF})_4]^-$	Lewis, Other	$P_4 + PBr_3 + [Ag]^+[Al(OR^{PF})_4]^-$	Insertion in P_4	463,454
$[P_5Ph_2]^+$, $[P_7Ph_6]^{3+}$	$[GaCl_4]^-$	Lewis, Other	$P_4 + Ph_2PCl + GaCl_3$	Different stoichiometries, insertion in P_4, HTS (60-70°C)	68
$[P_5RCl]^+$ (R = Me, Et, ^{i}Pr, Cy, Ph, C_6F_5)	$[GaCl_4]^-$	Lewis, Other	$P_4 + RPCl_2 + GaCl_3$	Insertion in P_4	464
$[P_5R_2]^+$ (R = Me, Et, ^{i}Pr, Cy, Mes, Dipp)	$[GaCl_4]^-$	Lewis, Other	$P_4 + R_2PCl + GaCl_3$	Insertion in P_4	465
$[P_5(NCy_2)Cl]^+$	$[GaCl_4]^-$	Lewis, Other	$P_4 + P(NCy_2)Cl_2 + GaCl_3$	Insertion in P_4	466
 X = Br, I	$[Al(OR^{PF})_4]^-$	Salt, Other	$P_4S_3 + PX_3 + [Ag]^+[Al(OR^{PF})_4]^-$	Initial Insertion in P_4S_3	134

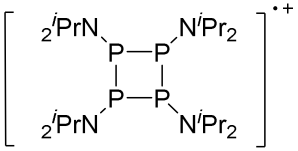
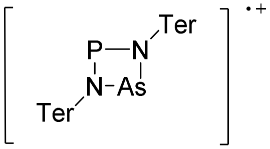
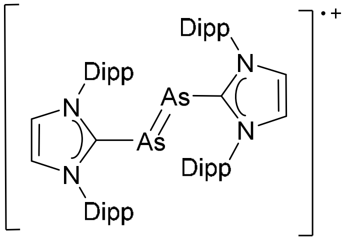
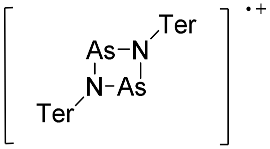
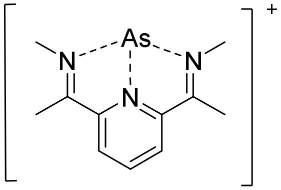
	$[AlCl_4]^-$	Other	$[P_4(AsPh_3)_2]^{2+}([AlCl_4]^-)_2 + PPh_3$	Ligand exchange	467
	$[AlCl_4]^-$	Other	$AsPh_3 + PCl_3 + AlCl_3$		467
	$[Al(OR^{PF})_4]^-$	Salt	$P_4S_3I_2 + [Ag]^+[Al(OR^{PF})_4]^-$		234
	$[OTf]^-$	Other	$(AsPh_3)(OTf)_2 + PCl_3 + Ph_3As$		468
	$[AlCl_4]^-$	Lewis, Other	$P_{(red)} + Se + SeCl_4 + BMImCl/AlCl_3$	Ionic liquid based synthesis, rhombohedral and orthorhombic modification	413
$[P_3Se_4]^+$	$[AlCl_4]^-$	Lewis, Other	$P_3Se_4 + Me_5C_6Br + AlCl_3$	In solution, orthorhombic modification	413
$[P_3Se_4]^+$	$[Ga_2Cl_7]^-$	Lewis, Other	$PCl_3 + SeTMS_2 + GaCl_3$	In solution	413
$[P_5Se_2Ph_2]^+$	$[GaCl_4]^-$	Ox	$[P_5Ph_2]^+[GaCl_4]^- + Se$	HTS (160°C)	465
$[P_5Se_2Cy_2]^+$	$[GaCl_4]^-$	Ox	$[P_5Cy_2]^+ + GaCl_3 + Se$	HTS (140°C)	465
$\text{Mes}^*\!-\!\overset{+}{N}\equiv As$	$[GaCl_4]^-$	Lewis	$Mes^*NAsCl + GaCl_3$	N-As triple bond	409
$[As_3N_3Ph_3Cl_2]^+$	$[GaCl_4]^-$	Lewis	$N_2As_2Ph_2Cl_2 + GaCl_3$	As_3N_3 ring	469
$[As_2Me_6]^{2+}$	$[OTf]^-$	Other	$Me_3As + PCl_3 + TMSOTf$		459
$[As_2Ph_6]^{2+}$	$[AlCl_4]^-$	Ox	$AsPh_3 + PCl_3 + AlCl_3$		467
	$[AsF_6]^-$	Ox	$As_4S_4 + AsF_5$ in SO_2		470
$[As_3S_4]^+$	$[SbF_6]^-$	Ox	$As_4S_4 + SbF_5$ in SO_2		470

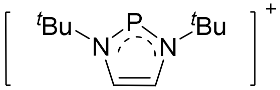
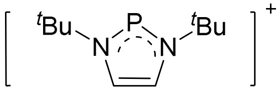
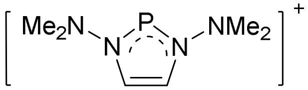
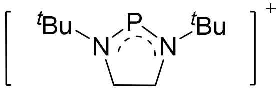
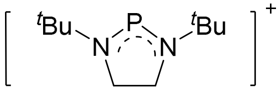
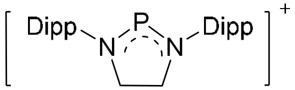
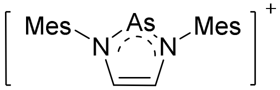
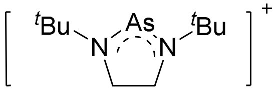
	$[AlCl_4]^-$	Ox, Lewis	As + $AsCl_3$ + S + $AlCl_3$	HTS (80°C)	471
	$[SbF_6]^-$	Ox	As + Se + SbF_5 in SO_2		470
$[As_3Se_4]^+$	$[AlCl_4]^-$	Ox, Lewis	As + $AsCl_3$ + Se + $AlCl_3$	HTS (80°C)	471
$([Sb_2Se_2]^+)_n$	$[AlCl_4]^-$	Ox	Sb + Se + BMImCl/$AlCl_3$	Ionothermal, HTS (160°C)	67
	$[AlCl_4]^-$	Ox, Others	Sb + Se + $SeCl_4$ + BMImCl/$AlCl_3$	Ionic liquid based synthesis	410
$([Sb_2Te_2]^+)_n$	$[AlCl_4]^-$	Ox, Lewis	Sb + Te + $SbCl_3$ + NaCl + $AlCl_3$	HTS (130°C), polymeric	15
$[Sb_7Te_8]^{5+}$	$3[Ga_2Cl_7]^-\cdot2[GaCl_4]^-$/ $2[Ga_2Cl_7]^-\cdot3[GaCl_4]^-$	Ox, Lewis	Sb + Te + $SbCl_3$ + $GaCl_3$	$AlCl_3$/$GaCl_3$ melt	411
	$[MCl_4]^-$ (M = Al, Ga)	Ox, Lewis	Sb + Te + $SbCl_3$ + MCl_3 + NaCl	$AlCl_3$/$GaCl_3$ melt	411
$[Bi_2X_4]^{2+}$(X = Cl, Br)	$[AlX_4]^-$	Lewis	BiX_3 + AlX_3		472
$[Bi_4OF_2Cl_6(C_6Me_6)_4]^{2+}$	$[Al(OR^{PF})_4]^-$	Other	$[Bi_5]^+[AsF_6]^-$ + $[Li]^+[Al(OR^{PF})_4]^-$ + C_6Me_6	Evidence for soluble $[Bi_n]^{x+}$ salts, partial decomposition of anion and solvent	405

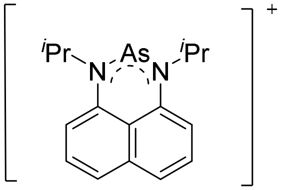
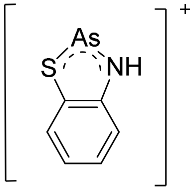
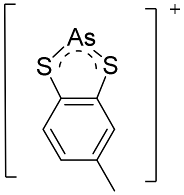
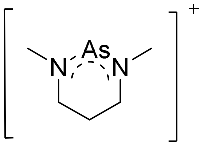
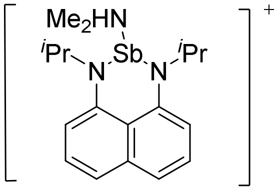
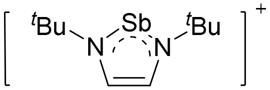
 Ch = S, Se	$[AlCl_4]^-$	Ox, Lewis	$Bi + BiCl_3 + Ch$ in $AlCl_3/NaCl$	HTS (130°C), heterocubane, Series $Bi_4Ch_4^{4+}$ (Ch = S, Se, Te) complete	414
	$[AlCl_4]^-$	Ox, Lewis	$Bi + BiCl_3 + Te$ in $AlCl_3/NaCl$	HTS (130°C), heterocubane	415
$[PdBi_{10}]^{4+}$	$([BiBr_4]^-)_\infty$	Ox	$Bi_2Pd + Bi + Br_2$	HTS (1000°C) $Pd@[Bi_{10}]^{4+}$	473
(4n+2)π-Cations					
	$[GaCl_4]^-$	Lewis	$ClP(\mu\text{-NTer})_2PCl + GaCl_3$	P_2N_2 ring	474
	$[N_3(GaCl_3)_2]^-$	Other	$[ClP(\mu\text{-NTer})_2P]^+[GaCl_4]^- + TMSN_3 + GaCl_3$	P_2N_2 ring	474
	$[GaCl_4]^-$	Other	$[Mes^*\text{-NAs}]^+[GaCl_4]^- + Ph_3CN_3$	Cycloaddition	409
	$[GaCl_4]^-$	Lewis	$ClAs(\mu\text{-NTer})_2AsCl + GaCl_3$	As_2N_2 ring	475
	$[OTf]^-$	Salt	$ClAs(\mu\text{-NTer})_2AsCl + [Ag]^+[OTf]^-$	As_2N_2 ring	475

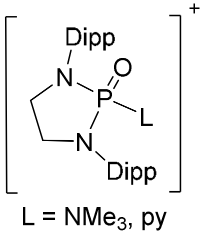
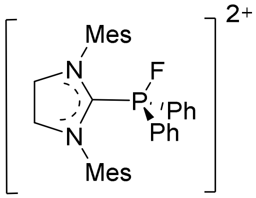
	$[N_3(GaCl_3)_2]^-$	Lewis	$[ClAs(\mu\text{-}NTer)_2As]^+[GaCl_4]^-$ + $TMSN_3$ + $GaCl_3$	As_2N_2 ring	475
$[As(\mu\text{-}NTer)_2As]^{2+}$	$[OTf]^-$	Salt	$ClAs(\mu\text{-}NTer)_2AsCl$ + $[Ag]^+[OTf]^-$	As_2N_2 ring, 4π system, 2 equiv. of $Ag^+[OTf]^-$	475
$[ClSb(\mu\text{-}NTer)_2Sb]^+$	$[GaCl_4]^-$	Lewis	$ClSb(\mu\text{-}NTer)_2SbCl$ + $GaCl_3$	Sb_2N_2 ring	476
$[Sb(\mu\text{-}NTer)_2Sb]^{2+}$	$[OTf]^-$	Salt	$ClSb(\mu\text{-}NTer)_2SbCl$ + $[Ag]^+[OTf]^-$	Sb_2N_2 ring, 4π system, 2 equiv. of $Ag^+[OTf]^-$	476
$[IBi(\mu\text{-}NTer)_2Bi]^+$	$[B(C_6F_5)_4]^-$	Salt	$IBi(\mu\text{-}NTer)_2BiI$ + $[Ag(Tol)_3]^+[B(C_6F_5)_4]^-$	Bi_2N_2 ring	476
$[Bi(\mu\text{-}NTer)_2Bi]^{2+}$	$[OTf]^-$	Salt	$ClBi(\mu\text{-}NTer)_2BiCl$ + $[Ag]^+[OTf]^-$	Bi_2N_2 ring, 4π system, 2 equiv. of $Ag^+[OTf]^-$	476
π*-π*-complexes					
	$[GaCl_4]^-$	Lewis	$AsS_2(CH)_2Cl$ + $GaCl_3$		416
	$[MCl_4]^-$ (M = Al, Ga)	Lewis	$As(NMe)_2(CH)_2Cl$ + MCl_3		416
Radicals					
	$[B(C_6F_5)_4]^-$	Ox	$[P(CN(Dipp)C_{10}H_{18})N(C(N(Dipp))_2C_2H_2)]$ + $[CPh_3]^+[B(C_6F_5)_4]^-$	$CN(Dipp)C_{10}H_{18}$ = CAAC, cyclic alkylaminocarbene	417

	$[SbF_6]^-$	Ox	$[(NTMS)_2(PNTMS_2)_2]$ + $[NO]^+[SbF_6]^-$		421
	$[X]^-$ = $[SbF_6]^-$, $[Al(OR^{PF})_4]^-$	Ox	$PTipp_3$ + $[Ag]^+[X]^-$		419
	$[Al(OR^{HT})_4]^-$	Ox	P_2Tipp_4 + $[Ag]^+[Al(OR^{HT})_4]^-$		420
	$[B(C_6F_5)_4]^-$	Ox	$[P_2(NTer)_2]$ + $[Ag(Tol)_3]^+[B(C_6F_5)_4]^-$		477
 Pn = P, As	$[B(C_6F_5)_4]^-$	Ox	$[P_2(C(N(Dipp))_2C_2H_2)_2]$ + $[CPh_3]^+[B(C_6F_5)_4]^-$	$C(N(Dipp))_2C_2H_2$ = NHC, N-heterocyclic carbene	208
	$[B(C_6F_5)_4]^-$	Ox	$[P_2(CN(Dipp)C_{10}H_{18})_2]$ + $[CPh_3]^+[B(C_6F_5)_4]^-$	$NC_{10}H_{18}$ = tetramethylamide	478

	$[Al(OR^{PF})_4]^-$	Ox	$[P_4(N^iPr_2)_4]$ + $[NO]^+[BF_4]^-$ + $[Li]^+[Al(OR^{PF})_4]^-$		421
	$[B(C_6F_5)_4]^-$	Ox	$[AsP(NTer)_2]$ + $[Ag(Tol)_3]^+[B(C_6F_5)_4]^-$		477
	$[GaCl_4]^-$	Ox	$[As_2(C(N(Dipp))_2C_2H_2)_2]$ + $GaCl_3$		418
	$[B(C_6F_5)_4]^-$	Ox	$[As_2(NTer)_2]$ + $[Ag(Tol)_3]^+[B(C_6F_5)_4]^-$		477
Oxidation state +I					
	$[SbCl_5·THF]^-$	Lewis	$AsCl_3$ +$SnCl_2$ + DppDIMPY	$[AsL_3]^+$, DppDIMPY = [α,α'-{2,6-$^iPr_2$PhN-C(Me)}$_2$(C_5H_3N)]	424
Oxidation state +III					
$[P(N^iPr_2)_2]^+$	$[GaCl_4]^-$	Lewis	$P(N^iPr_2)_2Cl$ + $GaCl_3$	$[PX_2]^+$	479,480
$[P(NCy_2)Cl]^+$	$[GaCl_4]^-$	Lewis	$P(NCy_2)Cl_2$ + $GaCl_3$	$[PX_2]^+$	466
$[P(N^iPr_2)Cl]^+$	$[GaCl_4]^-$	Lewis	$P(N^iPr_2)Cl_2$ + $GaCl_3$	$[PX_2]^+$	450
$[P(NTMS_2)Cl]^+$	$[GaCl_4]^-$	Lewis	$P(NTMS_2)Cl_2$ + $GaCl_3$	$[PX_2]^+$	481
$[P(N^iPr_2)N_3]^+$	$[GaCl_4]^-$	Other	$[P(N^iPr_2)Cl]^+[GaCl_4]^-$ + $TMSN_3$	$[PX_2]^+$	450

$[P(NTMS_2)X]^+$ (X = N_3, NCO, NCS)	$[GaCl_4]^-$	Other	$[P(NTMS_2)Cl]^+[GaCl_4]^-$ + TMSX	$[PX_2]^+$	481,482
$[P(NTMS_2)OTMS]^+$	$[GaCl_4]^-$	Other	$[P(NTMS_2)Cl]^+[GaCl_4]^-$ + TMSCNO	$[PX_2]^+$	482
$[PCp^*Cl]^+$	$[Cl(Al(OR^{PF})_3)_2]^-$	Lewis	PCp^*Cl_2 + $PhF\cdot Al(OR^{PF})_3$	$[PR_2]^+$	483
$[PCp^*_2]^+$	$[Cl(Al(OR^{PF})_3)_2]^-$	Lewis	PCp^*_2Cl + $PhF\cdot Al(OR^{PF})_3$	$[PR_2]^+$, Phosphocenium ion	483
$[AsCp^*Cl]^+$	$[Cl(Al(OR^{PF})_3]^-$	Lewis	$AsCp^*Cl_2$ + $PhF\cdot Al(OR^{PF})_3$	$[AsRX]^+$	483
$[SbCl_2(AsMe_3)]^+$	$[OTf]^-$	Lewis	$SbCl_3$ + $AsMe_3$ + TMSOTf	$[SbX_2L]^+$	484
$[SbPhCl(AsPh_3)]^+$	$[AlCl_4]^-$	Lewis	$SbPhCl_2$ + $AsPh_3$ + $AlCl_3$	$[SbRXL]^+$	484
$[BiPh(AsPh_3)]^{2+}$	$[OTf]^-$	Lewis	$BiCl_2Ph$ + $AsPh_3$ + TMSOTf	$[BiRL]^{2+}$	485
$[BiCl(SbPh_3)]^{2+}\cdot C_6H_6$	$[AlCl_4]^-$	Lewis	$BiCl_3$ + $AsPh_3$ + $AlCl_3$	$[BiXL]^{2+}$	485
$[BiCl_2(AsPh_3)_2]^+$	$[OTf]^-$	Lewis	$BiCl_3$ + $AsPh_3$ + TMSOTf	$[BiX_2L_2]^+$	484
$[BiCl_2(SbPh_3)_2]^+\cdot C_7H_8$	$[AlCl_4]^-$	Lewis	$BiCl_3$ + $SbPh_3$ + $AlCl_3$	$[BiX_2L]^+$	485
$[Bi(N_2TMS_3)_2]^+$	$[GaCl_4]^-$	Lewis	$Bi(N_2TMS_3)_2Cl$ + $GaCl_3$	$[BiX_2]^+$	486
	$[BF_4]^-$	Salt	$PCl(N^tBu)_2C_2H_2$ + $[Ag]^+[BF_4]^-$	P carbenoid	487
	$[PF_6]^-$	Salt	$PCl(N^tBu)_2C_2H_2$ + $[Ag]^+[PF_6]^-$	P carbenoid	488
	$[GaCl_4]^-$	Lewis	$PCl(NMe)_2C_2H_4$ + $GaCl_3$	P carbenoid	480
	$[GeCl_5]^-\cdot[Cl]^-$	Other	$Ge(N^tBu)_2C_2H_4$ + PCl_3	P carbenoid	489
	$[PF_6]^-$	Salt	$PCl(N^tBu)_2C_2H_4$ + $[Ag]^+[PF_6]^-$	P carbenoid	488
	$[GaCl_4]^-$	Lewis	$PCl(NDipp)_2C_2H_4$ + $GaCl_3$	P carbenoid	427
	$[SbCl_5\cdot THF]^-$	Lewis	$AsCl_3$ + $SnCl_2$ + $(MesN)_2C_2H_2$	As carbenoid	424
	$[GeCl_5]^-\cdot[Cl]^-$	Other	$Ge(N^tBu)_2C_2H_4$ + $AsCl_3$	As carbenoid	489

	$[GaCl_4]^-$	Lewis	$As(^iPrN)_2C_{10}H_6Cl + GaCl_3$	As carbenoid	490
	$[AlCl_4]^-$	Lewis	$AsCl(HN)SC_6H_4 + AlCl_3$	As carbenoid	491
	$[AlCl_4]^-$	Lewis	$AsClS_2C_6H_3CH_3 + AlCl_3$	As carbenoid	491
	$[GaCl_4]^-$	Lewis	$AsCl(NMe)_2C_3H_6 + GaCl_3$	As carbenoid	492
	$[OTf]^-$	Other	$Sb(^iPrN)_2C_{10}H_6(NMe_2) + HOTf$	Not planar through the ligand $NHMe_2$	490
	$[Sb_2Cl_8]^{2-}$	Lewis	$[Sb(^tBuN)_2C_2H_2]^+ + SbCl_3$	Sb carbenoid	493
Oxidation state +V					
$[NF_4]^+$	$[BF_4]^-$, $[SbF_6]^-$, $[Sb_2F_{11}]^-$	Lewis	$NF_3 + F_2 + BF_3$ or SbF_5		494
$[PF_4]^+$	$[Sb_3F_{16}]^-$	Lewis	$PF_5 + SbF_5$	No X-Ray	495
$[PCl_4]^+$	$[SnCl_6]^{2-}$	Lewis	$PCl_5 + SnCl_4$	For more structures see [496]	497

$[PBr_4]^+$	$[Al(OR^{PF})_4]^-$	Salt	$PBr_3 + Br_2 + [Ag]^+[Al(OR^{PF})_4]^-$		454
$[PI_4]^+$	$[AlCl_4]^-$	Lewis	$PI_3 + ICl + AlCl_3$ in CS_2		496
$[PI_4]^+$	$[AlBr_4]^-$	Lewis	$PI_3 + IBr + AlBr_3$ in CS_2		496
$[PI_4]^+$	$[AlI_4]^-$	Lewis	$PI_3 + I_2 + AlI_3$ in CS_2		498
$[PI_4]^+$	$[GaI_4]^-$	Lewis	$PI_3 + I_2 + GaI_3$ in CS_2		496
$[PI_4]^+$	$[Al(OR^{PF})_4]^-$	Salt	$PI_3 + I_2 + [Ag]^+[Al(OR^{PF})_4]^-$		454
$[AsCl_4]^+$	$[AsF_6]^-$	Lewis, Ox	$AsCl_3 + Cl_2 + AsF_5$		499
$[AsCl_4]^+$	$[As(OTeF_5)_6]^-$	Lewis, Ox	$AsCl_3 + ClOTeF_5 + As(OTeF_5)_5$		500
$[AsBr_4]^+$	$[Al(OR^{PF})_4]^-$	Salt	$AsBr_3 + Br_2 + [Ag]^+[Al(OR^{PF})_4]^-$		501
$[AsBr_4]^+$	$[FAs(OTeF_5)_5]^-$	Lewis, Ox	$AsBr_3 + BrOTeF_5 + AsF(OTeF_5)_4$		500
$[SbCl_4]^+$	$[Sb_2F_{11}]^-$	Lewis	$SbCl_5 + SbF_5$		502
$[SbCl_4]^+$	$[Sb(OTeF_5)_6]^-$	Ox	$Sb(OTeF_5)_3 + Cl_2$		503
$[SbBr_4]^+$	$[Sb(OTeF_5)_6]^-$	Ox	$Sb(OTeF_5)_3 + Br_2$		503
 L = NMe$_3$, py	$[GaCl_4]^-$	Ox	$[(CH_2)_2(NDipp)_2P]^+ + OL$	"PO^+" cation	427
	$[B(C_6F_5)_4]^-$	Lewis	$[(SIMes)PF_2Ph_2]^+ + [Et_3Si(Tol)]^+[B(C_6F_5)_4]^-$	„$PFPh_2^{2+}$“ cation	428
$[Ph_3Pn]^{2+}$ (Pn = Sb, Bi)	$[OTf]^-$	Salt	$Ph_3PnCl_2 + [Ag]^+[OTf]^-$	Strong contact to the anion	426
Protonated cations					
$[H_2N_3]^+$	$[SbF_6]^-$	Prot	$HN_3 + HF/SbF_5$		310
$[P(OH)_4]^+$	$[SbF_6]^-$	Prot	$H_3PO_4 + HF/SbF_5$		429

* Classification according to the introduction: Lewis = Lewis acid halogen bond heterolysis , Ox = Oxidation, Com = Complexation reaction, Prot = Protonation, Other = All other reactions not classified; ** HTS = High temperature synthesis.

Group 16 Cations

Hundreds of chalcogen cations are known to the literature (See **Table 9** for reviews). The relatively strong Ch-Ch- and Ch-X-single bonds (Ch = S, Se, Te; X = F, Cl, Br, I) led to a great diversity of reactive compounds, which include homo- and heteropolyatomic clusters, radical cations and a large number of different $[ChX_3]^+$ structures for instance. To avoid the formation of the more stable neutral compounds, weakly coordinating anions are needed to stabilize the reactive chalcogen cations.

Table 9. Review articles including cationic group 16 compounds.

Year	Title	Ref
2000	Recent advances in the understanding of the syntheses, structures, bonding and energetics of the homopolyatomic cations of Groups 16 and 17	504
2003	Homoatomic Sulfur Cations	505
2004	Cages and Clusters of the Chalcogens	506
2006	Synthesis, reactions and structures of telluronium salts	507
2011	Homo- and heteroatomic polycations of groups 15 and 16. Recent advances in synthesis and isolation using room temperature ionic liquids	66
2013	Catenated Sulfur Compounds	508
2013	Catenated Compounds – Group 16 (Se, Te)	509
2013	Recent advances in the syntheses of homopolyatomic cations of the non-metallic elements C, N, P, S, Cl, Br, I and Xe	11
2013	$RCNSSS^+$: A novel class of stable sulfur rich radical cations	510
2015	Coordination chemistry of homoatomic ligands of bismuth, selenium and tellurium	399,400

Homopolyatomic Cations: The first observation of homopolyatomic cations were the colored solutions of elemental sulfur, selenium and tellurium in sulfuric acid in the 18th and 19th century. Over the next centuries, the nature of these solutions stayed unclear and it was not before the middle of the 20th century that the use of superacidic media and better analytical methods made it possible to characterize the responsible species. Since then, starting with $[O_2]^+[PtF_6]^-$ in 1962,[511] the crystal structures of a multitude of different homopolyatomic chalcogen cations were measured in the last 50 years (**Figure 82**). All of them have more or less weakly coordinating anions as counter ions. In some cases, cationic clusters with unusual bonding situations including trans-annular interactions and negative hyperconjugation were found that presented quite a challenge for theory (e.g. the $[S_8]^{2+}$ dication).[11,504,512] The cations were mostly synthesized under superacidic conditions or through solid state or solvothermal reactions at higher temperature. Either the elemental chalcogen is directly oxidized with strong oxidants like MF_5 (M = As, Sb) or WCl_6 or a combination of the elemental chalcogen, chalcogen halides ChX_4 (e.g. $SeCl_4$, $TeBr_4$) and a strong Lewis acid undergo a synproportionation.

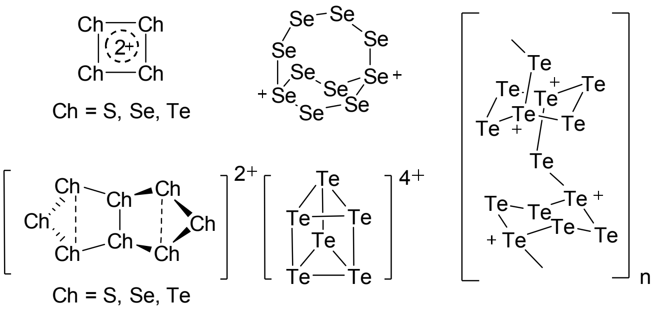


Figure 82. Selected examples for homopolyatomic chalcogen cations.

Metal-Chalcogen Complexes: The use of very weakly coordinated metal salts M[WCA] (e.g. $M^+ = Cu^+$, Ag^+) made it possible to obtain complexes with very weak ligands like the elemental modifications of the chalcogen elements. Stable, metastable and hitherto unknown modifications were prepared, for example $[Cu(S_{12})(S_8)]^+$,[513] $[Cu_2Se_{19}]^{2+}$ (**Figure 83**)[50] and $[Ag_2Se_6]^{2+}$ (**Figure 84**).[514] In all such complexes, extensive charge delocalization from the metal cation to the chalcogen ring took place as evidenced by cation-anion contacts as well as accompanying quantum chemical calculations.

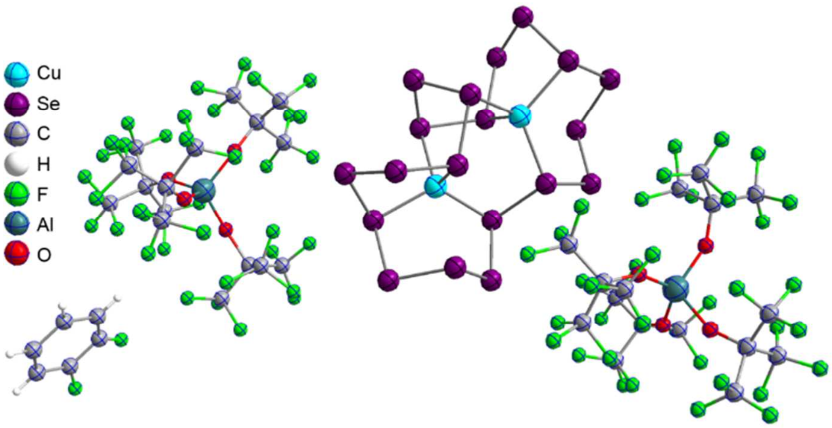


Figure 83. Molecular structure of $[Cu_2Se_{19}]^{2+}([Al(OC(CF_3)_3)_4]^-)_2\cdot C_6F_4H_2$. a) J. Schaefer, A. Steffani, D. A. Plattner, I. Krossing, *Angew. Chem., Int. Ed. Engl.* 2012, *51*, 6009–6012, *Angew. Chem.* 2012, *124*, 6112–6115. Data from this Reference were used to draw this figure.

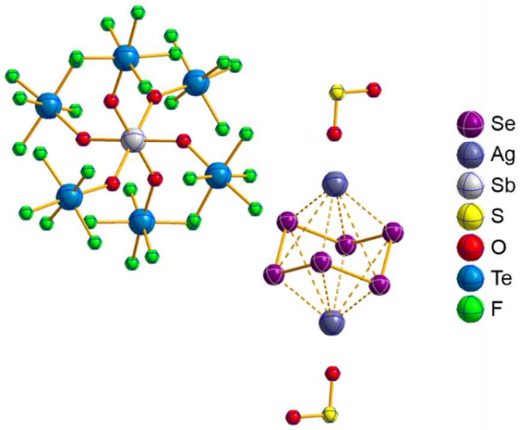


Figure 84. Molecular structure of $[(SO_2)_2Ag_2(Se_6)]^{2+}([Sb(OTeF_5)_6]^-)_2$. D. Aris, J. Beck, A. Decken, I. Dionne, I. Krossing, J. Passmore, E. Rivard, F. Steden, X. Wang, *Phosphorus, Sulfur, and Silicon and the Related*

Elements **2004**, *179*, 859–863. Data from this Reference were used to draw this figure. One anion of the formula unit and the disorder of the anion and SO_2 molecules were omitted for clarity.

Clusters/Cluster-like Cations: Chalcogens have a strong tendency to form clusters. There are examples for chains, rings and cages with almost every combination of the groups 15 and 16 (**Figure 85**). The clusters often have delocalized charges, positive and negative hyperconjugation, or show pseudo-aromaticity (**Figure 86**) or π*-π*-interactions (**Figure 87**). The clusters were often synthesized through direct oxidation of neutral clusters like S_4N_4 or mixtures of the elements (e.g. Se and Te) with strong oxidants like MF_5 in SO_2. $[NS]^+$, a useful starting material for the syntheses of further rPBC, can be obtained by halide abstraction from trichlorocyclotrithiazene $(NSCl)_3$ with $[Ag]^+[WCA]^-$.[515]

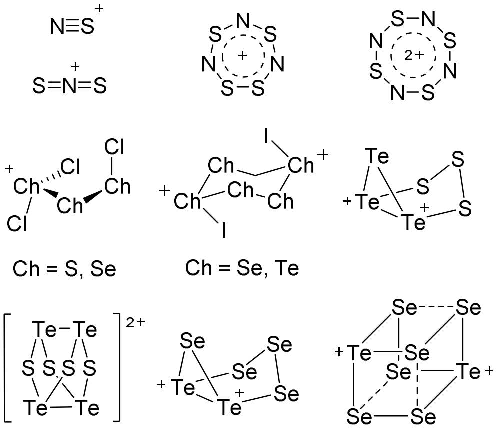


Figure 85. Selected examples for cationic chalcogen clusters or cluster-like structures.

(4n+2)π-Cations: Some planar cationic conjugated π-systems containing chalcogen atoms can be described as (pseudo-)aromatic systems. The four-membered rings are related to the homopolyatmic cations Ch_4^{2+} and were synthesized through direct oxidation of mixtures of the elemental chalcogens instead of the pure elements. The five-membered rings were obtained by cycloadditions of $[NS]^+$ and $[NS_2]^+$ [516] or in case of the selenium containing rings with Se, $[Se_8]^{2+}$ or EtSeCl and $[NS]^+$ as starting materials.[517–519] $[S_4N_3]^+$, a 10π-system, was synthesized through the reaction of S_4N_4 with Se_2Cl_2 and is stabilized by the polymeric $([SeCl_5]^-)_\infty$ anion.[520]

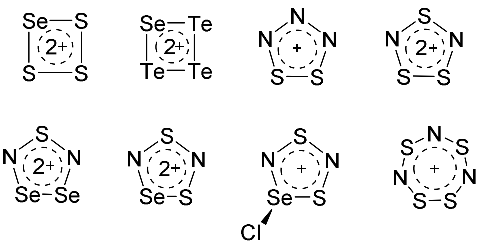


Figure 86. Heteroatomic cationic aromatic (6π) systems containing chalcogen atoms. ($S_4N_3^+$ is a 10π system).

π*-π*-Complexes: The chalcogen cations containing π*-π*-interactions can be described as dimers of chalcogen radicals, whose half-occupied interacting orbitals have π*-character. The two $[Ch_2I_4]^{2+}$

cations (Ch = S, Se) have a very similar structure, but include different orbital interactions. In case of $[S_2I_4]^{2+}$ two 2e4c-bonds were formed through the π* of the diatomic molecules ($([I_2\cdots S_2\cdots I_2]^{2+})$).[521] In $[Se_2I_4]^{2+}$ the two delocalized π* orbitals of the "monomer" $[SeI_2]^{\cdot+}$ are overlapping.[522] In the last 10 years, chalcogen systems, which are analogous to the $[I_4]^{2+}$ cation were characterized by scXRD. The isolobality of $[Ch_2R_2]^{+\cdot}$ and $[X_2]^{+\cdot}$ leads to the same rectangular structural motif with two long π^*-π^*- and two short σ- interactions. Overall those cations are typically diamagnetic in the solid state.

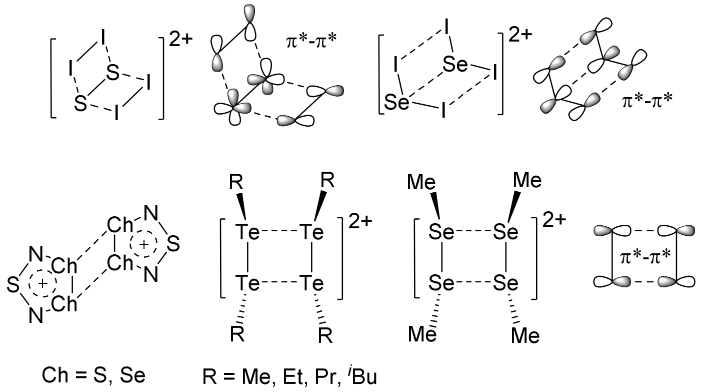


Figure 87. Selected chalogen cations containing different π^*-π^*-interactions.

Radical Cations: The chalcogen elements have a rich radical cation chemistry. Most of the cations contain (pseudo-)aromatic systems or Ch-Ch fragments, over which the unpaired electron is delocalized. Strong one-electron oxidants like $[NO]^+$ or XeF_2 combined with a Lewis acid were frequently used to synthesize the cations. There are also examples of diradicals like $(CNS_3^{\cdot+})_2$, obtained by the reaction of homopolytomic sulfur cations (a formal $[S_3]^+$ equivalent) and dicyanogen.[523,524] We also refer the reader to a recently published comprehensive review about $[RCNSSS]^{\cdot+}$ radical cations and their properties.[510]

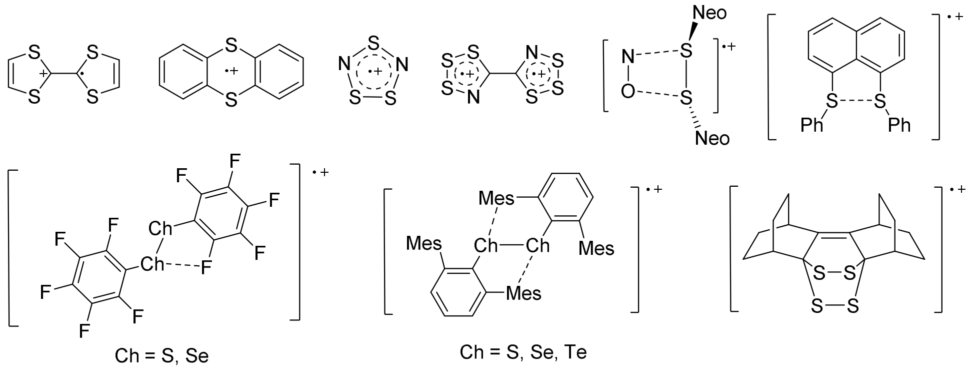


Figure 88. Selected chalcogen radical cations, which were stabilized by WCAs.

Oxidation State +II: Chalcogen cations $[RCh]^+$ in the formal oxidation state +II are only known in combination with stabilizing donor ligands. It was for example possible to stabilize the formal selenenium cation $[RSe]^+$ with the two amine-arms of a pincer ligand[525] (**Figure 89**). Two different

Te(II) cations with the strong donors DMAP and the carbene ^{i}PrIM as ligands (**Figure 89**) were synthesized with the useful starting material $[(Dipp_2BIAN)Te]^{2+}([OTf]^{-})_2$, a base stabilized "Te(OTf)$_2$", which was presented in 2009 and can also be understood as a tellurium analogue of a carbene.[526] The thi-, selen- and tellur-irenium cations (in the figure drawn as coordination complexes of $[RCh]^{+}$ ions) were all synthesized with starting materials that contain Ch-Ch bonds like Me_2S_2 [82] or $[Se_3Me_3]^{+}$ [527] or already oxidized chalcogens like $[PhTe]^{+}[SbF_6]^{-}$ [527] and alkynes.

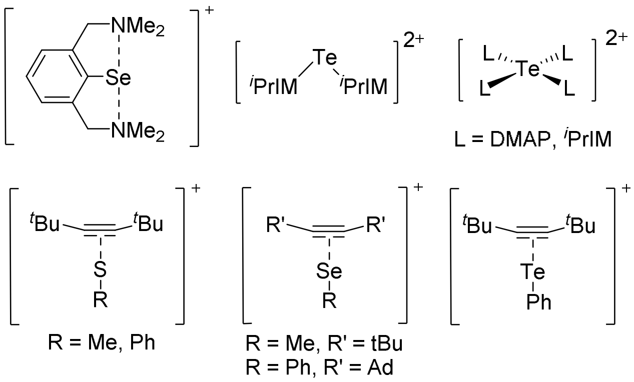


Figure 89. Selected chalcogen cations with chalcogen atoms in the formal oxidation state of +II.

Another example of ligand-stabilized chalcogen cations are the N-heterocyclic carbenoidic rings $[R_2C_2N_2Ch]^{2+}$ (Ch = S, Se, Te), which are formally 1,4-diaza-1,3-butadiene complexes of a chalcogen cation in oxidation state +II, but the delocalization of the positive charge supports a description as a chalcogen in oxidation state +IV.[528] The carbene-analogues were prepared through complexation of an in situ generated Ch^{2+} dication, which can be obtained through halide abstraction from SCl_2,[529] $SeCl_4$[530] or $(Dipp_2BIAN)TeI_2$[526] ($Dipp_2BIAN$ = 1,4-(2,6-diisopropyl)phenyl-bis(arylimino)-acenaphthene).

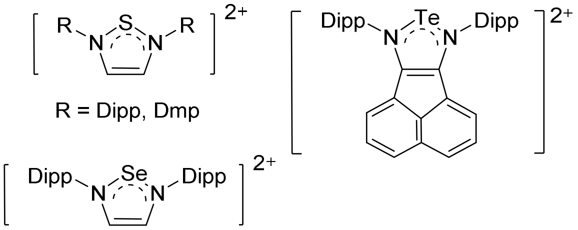


Figure 90. Carbene-analogous chalcogen dications.

Oxidation State +IV: The $[ChX_3]^{+}$ cations were one of first structurally characterized reactive chalcogen cations (**Figure 91**). The first experiments mainly on $[TeCl_3]^{+}$ were published already in the 1950s.[531] Now, a multitude of crystal structures can be found in the literature. Due to the relatively simple vibrational spectra of the four-atomic molecules, they can serve as a probe for the coordination power of the anion. The stronger the secondary interaction is, the weaker are the intramolecular Ch-X bonds and thus they get red-shifted.[532] There are also over 60 crystal structures of triorganyltelluronium $[TeR_3]^+$ cations with different anions. We decided only to list the "classics" $[TePh_3]^+$ 533 and $[Te(C_6F_5)_3]^+$ 534 and to refer to a recently published review about the chemistry and structures of these cations.[507] Some newer examples of compounds with chalcogen atoms in oxidation state +IV are the triazidetelluronium cation $[Te(N_3)_3]^+$ 535 and a fluoride bridged version of $[TeCl_3]^+$.[28]

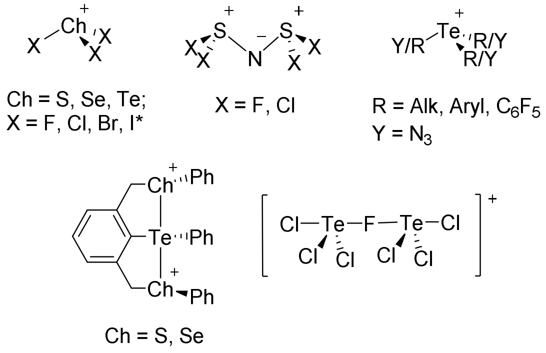


Figure 91. Chalcogen cations with chalcogen atoms in oxidation state +IV. *Every combination but $[SI_3]^+$ is known.

Oxidation State +VI: To our knowledge, the only chalcogen cation with a chalcogen atom in oxidation state +VI is $[TePh_5]^+$. It was obtained through halide abstraction from $TePh_5Cl$ with silver triflate and crystalized with the classical WCAs $[B(C_6F_5)_4]^-$ 533 and $[B(Ar^{CF3})_4]^-$.[536]

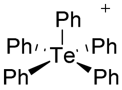


Figure 92. $[TePh_5]^+$, a cation with a chalcogen atom in oxidation state +VI.

Protonated chalcogen cations: The use of super-acidic conditions, makes it possible to obtain the protonated forms of very weakly basic molecules like trifluorosulfonic acid (**Figure 93**).[537] In some cases, it is not possible to isolate the neutral form of a molecule, but the conjugated positively charged acid (e.g. carbonic acid[538]). We decided to list the protonated carbonic acid together with the sulphur species like protonated sulphuric acid in this chapter.[539]

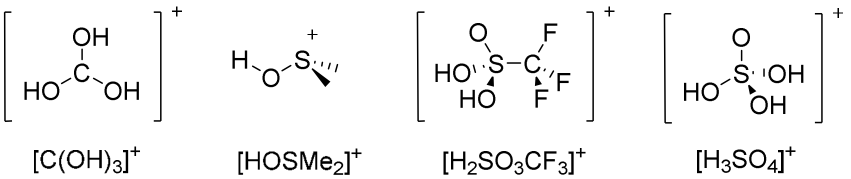


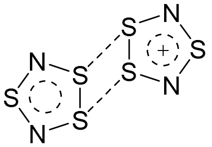
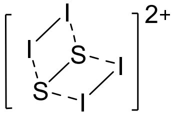
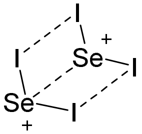
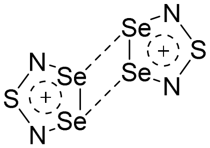
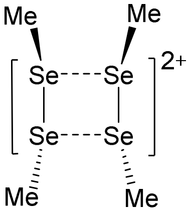
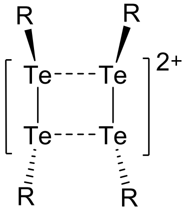
Figure 93. Examples for protonated molecules obtained under superacidic contitions.

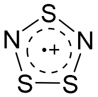
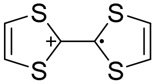
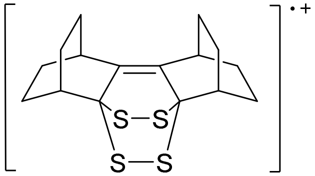
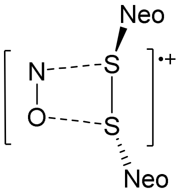
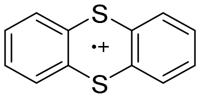
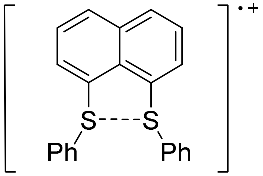
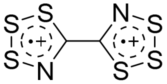
Table 10. Overview on structurally characterized chalcogen cations.

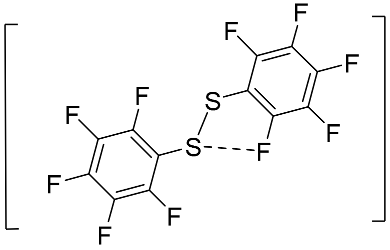
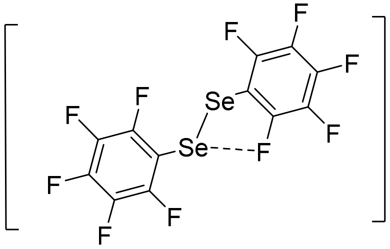
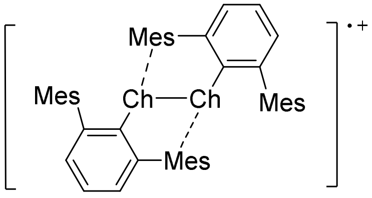
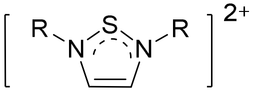
Cation	Anion	Class.*	Synthesis	Comment**	Ref.
Homopolyatomic Cations					
$[O_2]^+$	$[PtF_6]^-$	Ox	$O_2 + PtF_6$		511
$[O_2]^+$	$[PtF_6]^-$	Ox	$O_2 + PtF_6$	Neutron Diffraction	540
$[S_4]^{2+}$	$[AsF_6]^-$	Ox	$S + AsF_5$ in SO_2		541
$[S_4]^{2+} \cdot 4[S_7I]^+$	$[AsF_6]^-$	Ox, Lewis	$S + I_2 + AsF_5$ in SO_2		542,541
$[S_4]^{2+}$	$[Sb_9F_{39}]^{2-}$ (≙ $[(SbF_6)_5(Sb_2F_4)(Sb_2F_5)]^{2-}$)	Ox	$S + SbF_5$ in SO_2	Traces of Br_2 were added	543
$[S_4]^{2+} \cdot AsF_3$	$[AsF_6]^-$	Ox	$S + AsF_5 + AsF_3$ in HF	Traces of Br_2 were added	544
$[S_8]^{2+}$	$[AsF_6]^-$	Ox	$S + HF/AsF_5$		545
$[S_8]^{2+}$	$[SbF_6]^- \cdot [Sb_3F_{14}]^-$ (≙ $[(SbF_6)_2(SbF_2)]^-$)	Ox	$S + SbF_5$ in SO_2		543
$[S_8]^{2+}$	$[AsF_6]^-$	Ox	$[S_8]^{2+}([AsF_6]^-)_2$ in SO_2/ SO_2ClF		73
$[S_{19}]^{2+}$	$[AsF_6]^-$	Ox	$S + AsF_5$ in SO_2/ SO_2ClF		546
$[S_{19}]^{2+}$	$[SbF_6]^-$	Ox	$S + SbF_5$ in SO_2		543
$[Se_4]^{2+}$	$[AlCl_4]^-$	Lewis, Ox	$Se + SeCl_4 + AlCl_3$		547
$[Se_4]^{2+}$	$[MCl_6]^{2-}$ (M = Zr, Hf)	Lewis, Ox	$Se + SeCl_4 + MCl_4$	HTS (130°C)	235
$[Se_4]^{2+}$	$[SbF_6]^- \cdot [Sb_4F_{11}]^-$ (≙ $[(SbF_6)_2(Sb_2F_5)_2]^-$)	Ox	$Se + SbF_5$ in SO_2		548
$[Se_4]^{2+}$	$[Sb_9F_{39}]^{2-}$ (≙ $[(SbF_6)_5(Sb_2F_4)(Sb_2F_5)]^{2-}$)	Ox	$S + Se + SbF_5$ in SO_2		547
$[Se_4]^{2+}$	$[MoOCl_4]^-$	Ox	$Se + MoOCl_4$	HTS (190°C)	549
$[Se_4]^{2+}$	$[Mo_2O_2Cl_8]^- \cdot [MCl_6]^-$ (M = Zr, Hf)	Lewis, Ox	$[Se_4]^{2+}[Mo_2O_2Cl_8]^{2-} + [Se_4]^{2+}[MCl_6]^{2-}$ or Se, $SeCl_4 + MoOCl_4 + MCl_4$	HTS (120°C)	550
$[Se_8]^{2+}$	$[AlCl_4]^-$	Lewis, Ox	$Se + SeCl_4 + AlCl_3$	Crystals from vapour-phase transport	551
$[Se_8]^{2+} \cdot [Te_6]^{4+} \cdot SO_2$	$[AsF_6]^-$	Ox	$Se + Te + AsF_5$ in SO_2		552
$[Se_{10}]^{2+}$	$[SbF_6]^-$	Ox	$Se + SbF_5$ in SO_2		553
$[Se_{10}]^{2+}$	$[SO_3F]^-$	Ox	$Se + AsF_5$ in SO_2		554
$[Se_{10}]^{2+}$	$[Bi_4Cl_{14}]^-$	Lewis, Ox	$Se + SeCl_4 + BiCl_3$	HTS (90°C)	555
$[Se_{17}]^{2+}$	$[WCl_6]^-$	Ox	$Se + WCl_6$		556
$[Se_{17}]^{2+}$	$[NbCl_6]^-$	Lewis, Ox	$Se + SeCl_4 + NbCl_5$ in $SnCl_4$	Solvothermal (150°C)	557
$[Se_{17}]^{2+}$	$[TaBr_6]^-$	Lewis, Ox	$Se + SeBr_4 + TaBr_5$ in $SiBr_4$	Solvothermal (150°C)	
$[Te_4]^{2+}$	$[AlCl_4]^-$ $[Al_2Cl_7]^-$	Lewis, Ox	$Te + TeCl_4 + AlCl_3$	HTS (250°C)	558
$[Te_4]^{2+}$	$[SbF_6]^-$	Ox	$Te + SbF_5$ in SO_2	Germanium was added to obtain mixed cations	547

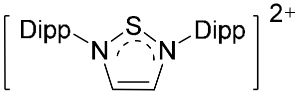
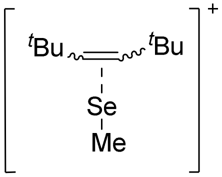
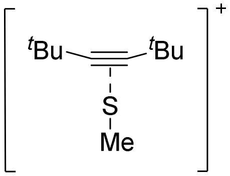
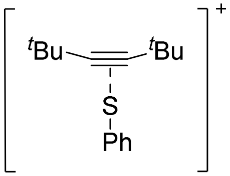
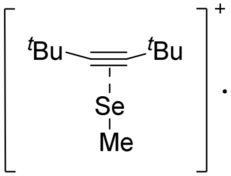
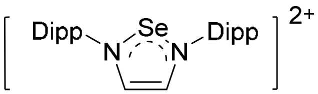
$[Te_4]^{2+}$	$[WCl_6]^{-}$	Ox	Te + WCl_6	HTS (190°C)	559
$[Te_4]^{2+}$	$[WCl_6]^{-}$	Ox	Te + WCl_6	Traces of Br_2 were added, β-mod.	560
$[Te_4]^{2+}$	$[Zr_2Br_{10}]^{2-}$	Lewis, Ox	Te_2Br + $ZrBr_4$	HTS (210°C)	561
$[Te_4]^{2+}$	$[HfCl_6]^{-}$	Lewis, Ox	Te + $TeCl_4$ + $HfCl_4$	HTS (200°C)	235
$[Te_4]^{2+}$	$[MCl_6]^{-}$ (M = Nb, Ta), $[TaBr_6]^{-}$, $[Ta_2Cl_{10}O]^{2-}$	Lewis, Ox	Te + $TeCl_4$ + MCl_5	HTS (170°C)	562
$[Te_4]^{2+}$	$[Bi_6Cl_{10}]^{2-}$ $[Bi_2Br_8]^{2-}$	Lewis, Ox	Te + TeX_4 + BiX_3 (X = Cl, Br)	HTS (170°C)	563
$[Te_4]^{2+}$	$[Nb_2Cl_{10}O]^{2-}$	Lewis, Ox	Te + $TeCl_4$ + $NbCl_5$ + $NbOCl_3$	HTS (200°C)	564
$[Te_4]^{2+}$	$[MoCl_4O]^{-}$	Ox	Te + $MoOCl_4$	HTS (250°C)	565
$(Te_{10}{}^{2+})_n \cdot Te_4{}^{2+}$	$[Bi_4Cl_{16}]^{2-}$	Lewis, Ox	Te + $TeCl_4$ + $BiCl_3$	HTS (150°C)	566
$[Te_6]^{2+}$	$[MCl_6]^{2-}$ (M = Zr, Hf)	Lewis, Ox	Te + $TeCl_4$ + MCl_4	HTS (220°C)	103
$[Te_6]^{2+}$	$[WCl_4O]^{-}$	Ox	Te + $WOCl_4$	HTS (150°C)	567
$[Te_6]^{2+}$	$[NbCl_4O]^{-}$	Lewis, Ox	Te + $TeCl_4$ + $NbOCl_3$	HTS (200°C)	568
$[Te_6]^{4+} \cdot 2AsF_3$	$[AsF_6]^{-}$	Ox	Te + AsF_5 in SO_2		569
$(Te_7{}^{2+})_n$	$[AsF_6]^{-}$	Other	$[Te_4]^{2+}([AsF_6]^{-})_2$ + $Fe(CO)_5$ in SO_2	Reduction of $Te_4{}^{2+}$	570
$(Te_7{}^{2+})_n$	$[Be_2Cl_6]^{2-}$	Lewis, Ox	Te + $TeCl_4$ + $BeCl_2$	HTS (250°C)	566
$(Te_7{}^{2+})_n$	$[WBr_4O]^{-} \cdot [Br]^{-}$	Ox	Te + $WOBr_4/WBr_5$	HTS (230°C)	571
$(Te_7{}^{2+})_n$	$[WCl_4O]^{-} \cdot [Cl]^{-}$	Ox	Te + $WOCl_4/WCl_5$	HTS (150°C)	572
$(Te_7{}^{2+})_n$	$[NbCl_4O]^{-} \cdot [Cl]^{-}$	Ox	Te + $TeCl_4$ + $NbOCl_3$	HTS (225°C)	101
$(Te_7{}^{2+})_n$	$[NbBr_4O]^{-} \cdot [Br]^{-}$	Ox	Te_2Br + $NbOBr_3$	HTS (220°C)	101
$[Te_8]^{2+}$	$[WCl_6]^{-}$	Ox	Te + WCl_6	HTS (200°C)	573
$[Te_8]^{2+}$	$[ReCl_6]^{2-}$	Lewis, Ox	Te + $TeCl_4$ + $ReCl_4$	HTS (230°C)	574
$[Te_8]^{2+}$	$[Bi_4Cl_{14}]^{2-}$	Lewis, Ox	Te + $TeCl_4$ + $BiCl_3$	HTS (160°C)	575
$[Te_8]^{2+}$	$[U_2Br_{10}]^{2-}$	Lewis, Ox	Te + $TeBr_4$ + UBr_5 in $SiBr_4$	Solvothermal 200°C	576
$[Te_8]^{2+}$	$[Ta_4O_4Cl_{16}]^{4-}$	Lewis, Ox	Te + $TeCl_4$ + $TaCl_5$ + $TaOCl_3$ + $[BMIM]^{+}Cl^{-}$	Ionic liquid based synthesis	577
$[Te_8]^{4+}$	$([VCl_4O]^{2-})_n$	Ox	Te + $VOCl_3$	HTS (270°C), Cubic	578
Metal-nonmetal-cluster complexes					
$[Cu(S_{12})(S_8)]^{+}$	$[Al(OR^{PF})_4]^{-}$	Com	$[Cu]^{+}$ + S		513,579
$[Cu(S_{12})(CH_2Cl_2)]^{+}$	$[Al(OR^{PF})_4]^{-}$	Com	$[Cu]^{+}$ + S		513,579
$[Ag(S_8)_2]^{+}$	$[Al(OR^{PF})_4]^{-}$	Com	$[Ag]^{+}$ + S		580
$[Cu_2Se_{19}]^{2+}$	$[Al(OR^{PF})_4]^{-}$	Com	$[Cu]^{+}$ + $Se_{(red)}$		50
$([Ag_2(Se_6)]^{2+})_{\infty}$	$[AsF_6]^{-}$	Com	$[Ag]^{+}$ + Se		514
$[Ag(Se_6)]^{+}$	$[Ag_2(SbF_6)_3]^{-}$	Com	$[Ag]^{+}$ + Se		514
$[Ag_2(Se_6)(SO_2)_2]^{2+}$	$[Sb(OTeF_5)_6]^{-}$	Com	$[Ag]^{+}$ + $Se_{(grey)}$		514
$[Ag_2(Se_6)(SO_2)_4]^{2+}$	$[Al(OR^{PF})_4]^{-}$	Com	$[Ag]^{+}$ + $Se_{(grey)}$		581
$[Ag_2Se_{12}]^{2+}$	$[FAl(OC(C_5F_{10})(C_6F_5))_3]^{-}$, $[Al(OR^{PF})_4]^{-}$)	Com	$[Ag]^{+}$ + $Se_{(red)}$		582,176
Clusters/Cluster-like					

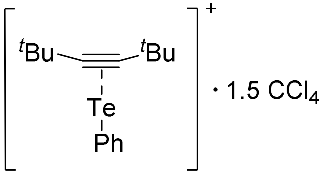
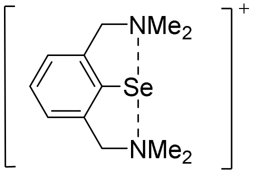
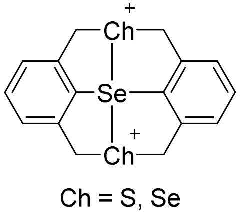
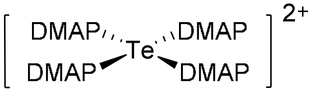
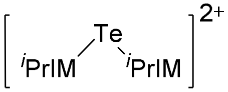
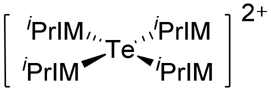
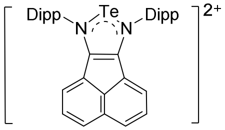
NS^+	$[AlCl_4]^+$	Lewis	$(NSCl)_3 + AlCl_3$		518
$[NS_2]^+$	$[AlCl_4]^+$	Other	$S_4N_4 + AlCl_3$		583
$[S_4N_4]^{2+}$	$[SbCl_6]^-$,	Ox	$S_4N_4/S_3N_3Cl_3 + SbCl_5$ in SO_2		584
$[S_4N_4]^{2+}$	$[Sb_3F_{14}]^- \cdot [SbF_6]^-$	Ox	$S_4N_4 + SbF_5$ in SO_2		584
$[S_5N_5]^+$	$[SbCl_6]^-$	Lewis	$S_3N_3Cl_3 + SbCl_5$ in $SOCl_2$		585
$[S_3Cl_3]^+$	$[AsF_6]^-$	Other	$[SCl_3]^+[AsF_6]^- + S_8$ in SO_2		586
$[(S_2N_2C)_2]^{2+}$	$[SbF_6]^-$, $[Sb_2F_{11}]^-$	Other	$[NS_2]^+[AsF_6]^- + (CN)_2$ in SO_2		587
$[S_4Te_4]^{2+} \cdot SO_2$	$[AsF_6]^-$	Ox	Te + Sn + AsF_5 in SO_2		588
$[S_3Te_3]^{2+}$	$[AsF_6]^-$	Ox	S + Te + AsF_5 in SO_2		589
$[Se_3Cl_3]^+$	$[AsF_6]^-$	Other	$[SeCl_3]^+[AsF_6]^-$ + Se in SO_2		586
$[Se_6Ph_2]^{2+} \cdot 2SO_2$	$[AsF_6]^-$	Other	$[Se_4]^{2+}([AsF_6]^-)_2 + Ph_2Se_2$		590
$[Se_6I_2]^{2+} \cdot 2SO_2$	$[AsF_6]^-$	Ox	Te + I_2 + AsF_5 in SO_2 or $[SeI_3]^+[AsF_6]^-{}_2 + [Se_8]^{2+}([AsF_6]^-)_2$		591
$[Te_6I_2]^{2+}$	$[WCl_6]^-$	Ox	Te + I_2 + WCl_6	HTS (150°C)	567
$([Te_{15}X_4]^{2+})_n$	$([MOX_4]^-)_n$ (M = Mo, X = Cl, Br; M = W, X = Br)	Other	$Te_2Br + MoOBr_3$, $TeCl_4 + MoNCl_2/ MoOCl_3$, Te + $WBr_5/WOBr_3$		592
$[Se_4Te_2]^{2+}$	$[MF_6]^-$ (M = As, Sb)	Ox	Se + Te + MF_5 in SO_2		589
$[Se_4Te_3]^{2+}$	$[MOCl_4]^-$	Ox	Se + $[Te_6]^{2+}([MOCl_4]^-)_2$	HTS (190°C)	593
$[Se_6Te_2]^{2+} \cdot [Se_8Te_2]^{2+} \cdot 2SO_2$	$[AsF_6]^-$	Ox	S + Se + Te + AsF_5 in SO_2	Heterocubane	594
$[Se_8Te_2]^{2+}$	$[MF_6]^-$ (M = As, Sb)	Ox	Se + Te + MF_5 in SO_2	Isostructural to $Se_{10}{}^{2+}$	594
$[Se_8Te_2]^{2+} \cdot SO_2$	$[AsF_6]^-$	Ox	Te + $[Se_8]^{2+}([AsF_6]^-)_2$ in SO_2		595
(4n+2)π-Cations					
$[S_2N_3]^+$	$[Hg_2Cl_6]^{2-}$	Lewis	NSCl + $HgCl_2$		596
$[S_3N_2]^{2+}$	$[MF_6]^-$ (M = As, Sb)	Other	$[SN]^+[MF_6]^- + [S_2N]^+[MF_6]^-$ in SO_2	Cycloaddition	516
$[S_4N_3]^+$	$([SeCl_5]^-)_\infty$	Ox	$S_4N_4 + Se_2Cl_2$ in $SOCl_2$	10π-aromatic	520
$[S_3Se]^{2+}$	$[Sb_3F_{16}]^- \cdot 3[SbF_6]^-$	Ox	S + Se +SbF_5 in SO_2	Traces of Br_2 were added, contains disordered mixture of $[S_xSe_{x-4}]^{2+}$	597
$[SSe_2N_2]^{2+}$	$[AsF_6]^-$	Ox	$[(SSe_2N_2)_2]^{2+}([AsF_6]^-)_2 + AsF_5$ in SO_2		598
$[S_2SeN_2]^{2+}$	$[AsF_6]^-$	Other	$[NS]^+[AsF_6]^- + [Se_8]^{2+}[AsF_6]^-$		517
$[S_2SeN_2Cl]^+$	$[AlCl_4]^-$	Other	$[NS]^+[AlCl_4]^-$ + Se/EtSeCl		519,518
$[Se_2Te_2]^{2+}$	$[Sb_3F_{14}]^{3-} \cdot [SbF_6]^-$	Ox	Se + Te +SbF_5 in SO_2		599
$[SeTe_3]^{2+}$	$[Sb_3F_{14}]^{3-} \cdot [SbF_6]^-$	Ox	Se + Te +SbF_5 in SO_2	Contains disordered mixture of $[SeTe_3]^{2+}$, $[Te_4]^{2+}$ and $[Se_2Te_2]^{2+}$	599
π*-π*-complexes					

	$[AsF_6]^-$	Ox	$S_4N_4 + AsF_5$ in SO_2	600
$[S_6N_4]^{2+}$	$[S_2O_2F]^-$, $[SO_3F]^-$	Ox	$S_4N_4 + HSO_3F$ in SO_2	601
	$[AsF_6]^-$	Ox	$S + I_2 + AsF_5$ in SO_2	521
	$[Sb_2F_{11}]^-$	Ox	$Se + [I_2]^+[Sb_2F_{11}]^-$ in SO_2	522
	$[MF_6]^-$ (M = As, Sb)	Other	$S_4N_4 + [Se_4]^{2+}([MF_6]^-)_2$ in SO_2	602
	$[BF_4]^-$	Ox	$Me_2Se_2 + XeF_2 + BF_3{\cdot}OEt_2$	82
$[(MeSe)_4]^{2+}$	$[OTf]^-$	Ox	$Et_2Te_2 + [NO]^+[OTf]^-$	603
 R = Me, Et, Pr, ^{i}Bu	$[OTf]^-$	Ox	$Et_2Te_2 + [NO]^+[OTf]^-$	82,603

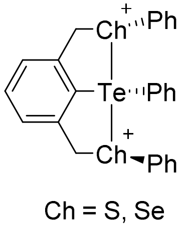
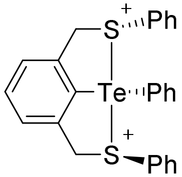
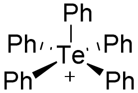
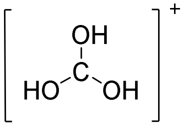
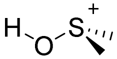
Radicals					
	$[AsF_6]^-$	Ox	$S_4N_4 + [Te_4]^{2+}([AsF_6]^-)_2$ in SO_2		601
 · 0.5 EtCN	$[NTf_2]^-$	Ox	TTF + 0.5 XeF_2 + $TMSNTf_2$	TTF = Tetrathiafulvalene	82
	$[SbCl_6]^-$	Ox	$(C_8H_{10})_2S_2 + SbCl_5$	Strong transannular interactions	604
	$[OTf]^-$	Ox	$(NeoS)_2 + NO^+$	Diorgano disulfide–nitrosonium adduct	605
 · 0.5 Et_2O	$[FAl(OR^{PF})_3]^-$	Ox	$C_{12}H_8S_2 + XeF_2 + Al(OC(CF_3)_3)_3$	$C_{12}H_8S_2$ = Thianthrene	82
	$[Al(OR^{PF})_4]^-$	Ox	1,8-$(SPh)_2$Nap + NO^+	S-S-3e-σ-bond Nap = Naphthalene	606
	$[AsF_6]^-$	Ox	S + AsF_5 + $(CN)_2$ in SO_2	Traces of Br_2 were added	523
$(CNS_3^{\cdot+})_2$	$[SbF_6]^-$, $[Sb_2F_{11}]^-$	Ox	S + SbF_5 + $(CN)_2$ in SO_2	Traces of Br_2 were added	524

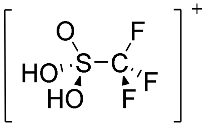
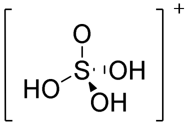
	$[Sb_2F_{11}]^-$	Ox	$(C_6F_5S)_2 + SbF_5$		607
	$[As_2F_{11}]^-$	Ox	$(C_6F_5Se)_2 + AsF_5$		607
 Ch = S, Se, Te	$[SbF_6]^-$	Ox	$(2,6\text{-}Mes_2C_6H_3E)_2 + NO^+$		607
Oxidation state +II					
$[Me_2S\text{-}SMe]^+$	$[SbCl_6]^-$	–	–		608
$[MeS\text{-}S(Me)\text{-}SMe]^+$	$[SbCl_6]^-$	Ox, Lewis	$S_2Me_2 + SbCl_5$	$= [S_3Me_3]^+$	608
 R = Dipp, Dmp	$[OTf]^-$	Com	$S(OTf)_2 + (NR)_2C_2H_2$	Sulfur carbenoid, Oxidation state unclear	529

	$[B(C_6F_5)_4]^-$	Other	$[S(NDipp)_2C_2H_2]^{2+}$ $([OTf]^-)_2$ + $[K]^+[B(C_6F_5)_4]^-$	Sulfur carbenoid, Salt metathesis, Oxidation state unclear	529
cis/trans- 	$[X]^-$ = $[SbCl_6]^-$, $[BF_4]^-$	Other	$[S_3Me_3]^+[X]^-$ + $C_2H_2{}^{t}Bu_2$	Thiiranium ion	609
	$[X]^-$ = $[BF_4]^-$ $[PF_6]^-$	Other	$[S_3Me_3]^+[X]^-$ + $C_2{}^{t}Bu_2$	Thiirenium ion	609
$[MeSC_2{}^{t}Bu_2]^+\cdot CH_2Cl_2$	$[CHB_{11}Cl_{11}]^-$	Ox	Me_2S_2 + $C_2{}^{t}Bu_2$ + XeF_2 + $Me_3Si[CHB_{11}Cl_{11}]$		82
	$[B(C_6F_5)_4]^-$	Ox	Ph_2S_2 + $C_2{}^{t}Bu_2$ + XeF_2 + $[Me_3Si(Tol)]^+[B(C_6F_5)_4]^-$	Thiirenium ion	82
$[MeSe\text{-}Se(Me)\text{-}SeMe]^+$	$[SbCl_6]^-$	Ox, Lewis	Se_2Me_2 + $SbCl_5$	= $[Se_3Me_3]^+$	608
 · $0.5\ CH_2Cl_2$	$[SbCl_6]^-$	Other	$[Se_3Me_3]^+[SbCl_6]^-$ + $C_2{}^{t}Bu_2$	Selenirenium ion	527
$[PhSeC_2Ad_2]^+\cdot CH_2Cl_2$	$[SbCl_6]^-$	Other	$[PhSe]^+[SbCl_6]^-$ + C_2Ad_2		527
	$[SnCl_6]^{2-}$	Ox, Lewis	$(NDipp)_2C_2H_2$ + $SnCl_2$ + $SeCl_4$	Selenium carbeniod	530

	$[SbF_6]^-$	Other	$[PhTe]^+[SbF_6]^- + C_2{}^tBu_2$	Tellurirenium ion	527
	$[PF_6]^-$	Other	$C_6H_3(CH_2NMe_2)_2SeMe$ + tBuOCl + $[K]^+[PF_6]^-$		525
	$[PF_6]^-$	Ox	$(C_6H_3(CH_2)_2Ch)_2Se + [NO]^+[PF_6]^-$		610
	$[OTf]^-$	Other	$[(Dipp_2BIAN)Te]^{2+}$ $([OTf]^-)_2$ + DMAP	Ligand exchange	526
	$[OTf]^-$	Other	$[(Dipp_2BIAN)Te]^{2+}$ $([OTf]^-)_2 + 2\ {}^iPrIM$	Ligand exchange, anions coordinating	526
	$[OTf]^-$	Other	$[(Dipp_2BIAN)Te]^{2+}$ $([OTf]^-)_2 + {}^iPrIM$	Ligand exchange, 4 equivalents of ^{i}PrIM	526
	$[OTf]^-$	Hal	$(Dipp_2BIAN)TeI_2 + [Ag]^+[OTf]^-$	Tellurium carbenoid, $Dipp_2BIAN$ = 1,4-(2,6-diisopropyl) phenyl-bis (arylimino) acenaphthene	526
Oxidation state +IV					
$[SF_3]^+$	$[BF_4]^-$	Lewis	$SF_4 + BF_3$	Crystals through sublimation	611
$[SF_3]^+$	$[GeF_6]^{2-}$	Lewis	$SF_4 + GeF_4$		612
$[SCl_3]^+$	$[ICl_4]^-$	Ox, Lewis	$S + Cl_2 + I_2$		613

$[SCl_3]^+$	$[ICl_4]^-$	Ox, Lewis	$S + Cl_2 + I_2$	Second modification	614
$[SCl_3]^+$	$[UCl_6]^-$	Lewis	$SOCl_2 + UCl_5$		615
$[SCl_3]^+$	$[AlCl_4]^-$	Lewis	$SCl_4 + AlCl_3$		616
$[SCl_3]^+$	$[SbCl_6]^-$	Ox, Lewis	$As_4S_4 + SbCl_5$ in SO_2		532
$[SCl_3]^+$	$[MoOCl_4]$	Ox	$S + MOCl_4$	HTS (100°C), Large excess of ICl_3 was added	617
$[SBr_{1.2}Cl_{1.8}]^+$	$[SbCl_6]^-$	Ox, Lewis	$S + Br_2 + SbCl_5$ in SO_2	Attempt to prepare $[SBr_3]^+[SbCl_6]^-$	532
$[SBr_3]^+$	$[AsF_6]^-$	Lewis	$S + Br_2 + AsF_5$ in SO_2		618,619
$[(SX_2)_2N]^+$ (X = F, Cl)	$[AsF_6]^-$	Ox	$[S_2N]^+[AsF_6]^- + X_2$ in SO_2		620
$[SeF_3]^+$	$[NbF_6]^-$, $[Nb_2F_{11}]^-$, $[TaF_6]^-$	Lewis	$SeF_4 + NbF_5$	First structure with a $[ChX_3]^+$ cation (Ch = S, Se, Te; X = F, Cl, Br, I)	621
$[SeCl_3]^+$	$[AlCl_4]^-$	Lewis	$SeCl_4 + AlCl_3$ in SO_2Cl_2		622
$[SeCl_3]^+$	$[SbCl_6]^-$	Ox, Lewis	$As + Se + SbCl_5$, or $SeCl_4 + SbCl_5$ in SO_2	melt	532
$[SeCl_3]^+$	$[MoOCl_4]^-$	Others	$[Se_4]^{2+}[MoOCl_4]^{2-}$ in $SOCl_2$	Decomposition at 150°C, β-modification	623
$[SeCl_3]^+$	$[AuCl_4]^-$	Lewis	$SeCl_4 + AuCl_3$		624
$[SeBr_3]^+$	$[AsF_6]^-$	Ox, Lewis	$Se + Br_2 + AsF_5$ in SO_2	Small amount of AsF_3 was added	625
$[SeBr_3]^+$	$[SbF_6]^-$	Ox, Lewis	$[Se_4]^{2+}([SbF_6]^-)_2 + Br_2 + AsF_5$ in SO_2		625
$[SeBr_3]^+$	$[AlBr_4]^-$	Lewis	$SeBr_4 + AlBr_3$	HTS (150°C)	626
$[SeI_3]^+$	$[AsF_6]^-$	Ox, Lewis	$[Se_4]^{2+}([SbF_6]^-)_2 + I_2$ in AsF_3		618,619
$[SeI_3]^+$	$[SbF_6]^-$	Ox, Lewis	$Se + I_2 + SbF_5$ in SO_2		
$[TeF_3]^+$	$[Sb_2F_{11}]^-$	Lewis	$TeF_4 + SbF_5$		627
$[TeF_3]^+$	$[SO_4]^{2-}$	Ox, Lewis	$Te + Br_2 + AsF_5$ in SO_2		532
$[TeCl_3]^+$	$[AlCl_4]^-$	Lewis	$TeCl_4 + AlCl_3$	monoclinic	628
$[TeCl_3]^+$	$[AlCl_4]^-$	Lewis	$S_7TeCl_2 + AlCl_3$	$TeCl_3[AlCl_4]$ (triclinic)	532
$[TeCl_3]^+$	$[AsF_6]^-$	Lewis	$TeCl_4 + AsF_5$		532
$[TeCl_3]^+$	$[SbF_6]^-$	Lewis	$TeF_4 + SbF_5$ in CH_2Cl_2	Solvent decomposition	532
$[TeCl_3]^+$	$[AuCl_4]^-$	Lewis	$TeCl_4 + AuCl_3$		629
$[TeCl_3]^+$	$[MoCl_4O]^-$	Lewis	$TeCl_4 + MoOCl_3$	HTS (180°C)	630
$[TeCl_3]^+$	$[MoCl_6]^{2-}$	Lewis	$TeCl_4 + MoCl_4$	HTS (195°C)	631
$[TeCl_3]^+$	$[Re_2Cl_6]^-$	Lewis, Ox	$Te + TeCl_4 + ReCl_5$	HTS (150°C), β-modification	631
$[TeCl_3]^+$	$[MoCl_6]^{2-}\cdot[Cl]^-$	Lewis	$TeCl_4 + MoCl_4$	HTS (300°C)	632
$[TeCl_3]^+$	$[MCl_6]^-$ (M = Nb, Ta)	Lewis	$TeCl_4 + MCl_5$	α- and β- modification	633
$[TeCl_3]^+$	$[WCl_6]^-$	Lewis	$TeCl_4 + WCl_6$		633
$[TeBr_3]^+$	$[AsF_6]^-$	Ox, Lewis	$Te + Br_2 + AsF_5$ in SO_2		625
$[TeBr_3]^+\cdot½ Br_2$	$[AuBr_4]^-$	Ox, Lewis	$Te + Au + Br_2$	HTS (160°C)	634
$[TeBr_3]^+$	$[Zr_2Br_9]^-$	Other	$[Te_4]^{2+}[Zr_2Br_{10}]^-$	Decomposition above 250 °C	561
$[TeBr_3]^+$	$[MBr_6]^-$ (M = Ta, W)	Lewis	$TeBr_4 + MBr_5$		633
$[TeI_3]^+$	$[AsF_6]^-$	Ox, Lewis	$Te + I_2 + AsF_5$ in SO_2		635

$[TeI_3]^+$	$[SbF_6]^-$	Ox, Lewis	Te + I_2 + SbF_5 in SO_2		619,618
$[TeI_3]^+$	$[AlI_4]^-$	Lewis, Ox	Te + I_2 + AlI_3	HTS (150°C)	626
$[TeI_3]^+$	$[MI_4]^-$, (M = Ga, In)	Lewis, Ox	Te + M + I_2	HTS (350°C)	636
$[TeI_3]^+\cdot$½ SO_2	$[AsF_6]^-$	Ox, Lewis	Te + I_2 + AsF_5 in SO_2	Hemisolvate of $[TeI_3]^+[AsF_6]^-$	637
$[TeI_3]^+$	$[Al(OR^{PF})_4]^-$	Salt	TeX_4 + $[Ag]^+[Al(OR^{PF})_4]^-$	Good solubility	638
$[TePh_3]^+$	$[B(C_6F_5)_4]^-$	Other	$[TePh_5]^+[B(C_6F_5)_4]^-$	Thermal decomposition at 150°C	533
$[Te(C_6F_5)_3]^+$	$[OTf]^-$	Other	$Te(C_6F_5)_4$ + TMSOTf		534
$[Te(N_3)_3]^+$	$[SbF_6]^-$	Ox	$Te_4^{2+}([SbF_6]^-)_2$ + KN_3 in SO_2	Side products may be explosive!	535
$[F(TeCl_3)_2]^+$	$[Sb(OTeF_5)_6]^-$	Ox, Lewis	$TeBr_4$ + $[Ag]^+[Sb(OTeF_5)_6]^-$ in SO_2ClF		28
	$[BF_4]^-$	Ox	$(C_6H_3(CH_2ChPh)_2)TePh$ + $[NO]^+[BF_4]^-$		639
	$[OTf]^-$	Ox	$(C_6H_3(CH_2SPh)_2)TePh$ + ${}^tBuOCl$ + $O(Tf)_2$		639
Oxidation state +VI					
	$[B(C_6F_5)_4]^-$	Hal	$TePh_5Cl$ + $[Ag]^+[OTf]^-$ + $Li^+[B(C_6F_5)_4]^-$		533
$[TePh_5]^+$	$[ClO_4]^-$	Hal	$TePh_5Cl$ + $[Ag]^+[ClO_4]^-$		536
$[TePh_5]^+\cdot$ MeCN	$[B(Ar^{CF3})_4]^-$	Hal	$TePh_5Cl$ + $[Ag]^+[OTf]^-$ + $[B(Ar^{CF3})_4]^-$		536
Protonated cations					
	$[AsF_6]^-$	Prot	$OC(OTMS)_2$ + HF/AsF_5		538
	$[Ge_3F_{16}]^{4-}$	Prot	Me_2SO + HF/GeF_4		640

	$[SbF_6]^-$	Prot	OTf_2 + HF/SbF_5	537
	$[SbF_6]^-$	Prot	$SO_2(OTMS)_2$ + HF/SbF_5	539

* Classification according to the introduction (**Table 2**): , Com = complexation reaction Lewis = Lewis acid halogen bond heterolysis, Prot = Protonation, Ox = Oxidation, Other = All other reactions not classified; ** HTS = High Temperature synthesis.

Group 17 Cations

The electronegative halogen atoms are strongly oxidizing and have high ionization energies as well as electron affinities. This makes halogen cations good electrophiles, which need very oxidation-resistant WCAs to be stabilized in condensed phases. Concerning the synthesis of these highly reactive compounds, there are many similarities to the noble gas cations. Almost every halogen cation, for which a crystal structure is known, was synthesized though a halide abstraction by a strong Lewis acid like MF_5 (M = As, Sb). The starting materials are normally neutral interhalogen compounds like ClF_3, BrF_5, IF_7, I_2Cl_6, or IBr, and the majority of the obtained cations contains halogen atoms in oxidation state +III, +V and +VII.

Table 11. Review articles including cationic group 17 compounds.

Year	Title	Ref
2000	Recent advances in the understanding of the syntheses, structures, bonding and energetics of the homopolyatomic cations of Groups 16 and 17	504
2008	Polyvalent perfluoroorgano- and selected polyfluoroorgano-halogen(III and V) compounds	641
2013	Recent advances in the syntheses of homopolyatomic cations of the non-metallic elements C, N, P, S, Cl, Br, I and Xe	11

Fluorine Cations

Because of the high electronegativity and ionization potential of fluorine, it would be very difficult to oxidize it and obtain actual fluorine cations in the condensed phase. By contrast, in the gas phase this is possible.[642] Some bulk cationic compounds contain fluorine, but it is very unlikely that the positive charge is actually localized on the fluorine atom. Such compounds like for example the in **Figure 94** shown compound that was published as a formal disilylfluoronium ion are discussed in the chapters of the element, which has a larger positive charge density (here silicon).[643]

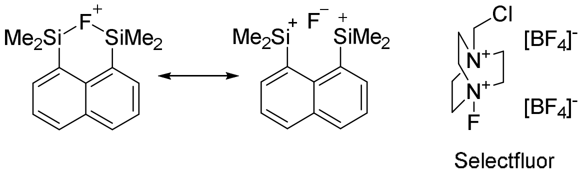


Figure 94. Left: Formal Disilylfluoronium ion that bears a larger positive charge density at the silicon atoms. Therefore, it is discussed with the silylium cations in the section on group 14 rPBC. Right: The Selectfluor Reagent.

It should be mentioned that also electrophilic “F^+-“ or “N-F-“ reagents like “Selectfluor” belong to this class of compounds that are very useful for organic transformations and compatible with solvents like CH_2Cl_2.[644]

Chlorine, Bromine and Iodine Cations

Homopolyatomic Cations: Two homopolyatomic chlorine cations are known in the solid state and its crystal structures of $[Cl_3]^+$ and $[Cl_4]^+$ were published in 1999[42]and 2000.[645] $[Cl_2]^+$, which would be the lighter homologue to the known $[Br_2]^+$ and $[I_2]^+$, was only detected in the gas phase. $[Cl_3]^+$ can be synthesized through a reaction of ClF with AsF_5, with the adduct $^{\delta+}Cl\text{-}F^{\delta-}\rightarrow AsF_5$ as intermediate. This leads to a more activated ClF with a more positively charged chlorine atom and results in the formation of $[Cl_2F]^+[AsF_6]^-$, which can be described as a formal "Cl^+" stabilized by a second equivalent of ClF. When elemental chlorine is used instead of a second equivalent of ClF, $[Cl_3]^+$ is formed. $[Cl_4]^+$, which is a homopolyatomic cation but also a π^*-π^*-complex (see below: π^*-π^*-Complexes of Group 17) can be obtained by direct oxidation of chlorine with the strong one-electron oxidant IrF_6. For bromine, three cations are known. Of those, $[Br_2]^+$ was one of the first homopolyatomic cations of the non-metals for which the crystal structure was determined. It was already in 1968 that Edwards et al. stabilized it with the very good $[Sb_3F_{16}]^-$ WCA. The structures of the other two known cations $[Br_3]^+$ and $[Br_5]^+$ were measured relatively late in 1991. $[Br_5]^+$ can be synthesized by oxidation of elemental bromine with the strong oxidant $[XeF]^+$ [211] and the only measurable crystals of a $[Br_3]^+$ salt were obtained from a 20 year old $[BrF_2]^+[AsF_6]^-$ solution.[646] Iodine has five known cations. $[I_2]^+$, $[I_3]^+$ and $[I_5]^+$ are isostructural to the lighter homologues and can all be obtained by oxidation from I_2 with the strong Lewis acids MF_5 (M = As, Sb). $[I_4]^{2+}$ was synthesized through the entropically unfavorable dimerization of the paramagnetic $[I_2]^{+\cdot}$ radical cation at low temperature and can be described as an rectangular planar diamagnetic π^*-π^*-complex (see below: π^*-π^*-Complexes of Group 17).

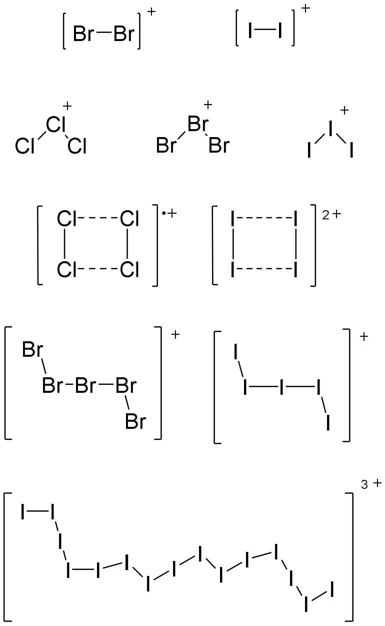


Figure 95. Structurally characterized homopolyatomic cation of chlorine, bromine and iodine.

Metal-Halogen Complexes: The very weak coordination power of the neutral dihalogen molecules X_2 (F_2, Cl_2, Br_2, I_2) made it very difficult to obtain metal-halogen-complexes. Only for diiodine, which is the strongest donor, it was possible to get polymeric $[\{Ag(I_2)\}_n]^{n+}$ cations through the reaction of

$[Ag]^+[MF_6]^-$ (M = As, Sb) and I_2 in liquid SO_2.[647] Also one example of a neutral complex with diiodine as ligand is known: $[Rh_2(O_2CCF_3)_4(I_2)]\cdot I_2$.[648] Dibromine and dichlorine complexes remained unknown. However, very recently,[649] the use of the very weakly coordinating solvent perfluorohexane and one of the weakest anions $[Al(OR^{PF})_4]^-$ led to the isolation of the first dichlorine and dibromine complexes $[Ag(X_2)]^+$ (X = Cl, Br, also I) (**Figure 96**). Moreover, diiodine turned out to have a rich coordination chemistry and formed three further structures with Ag_2I_2-moiety as well as isolated $[Ag_2(I_2)_4]^{2+}$ as well as $[Ag_2(I_2)_6]^{2+}$ dications well separated from the counterion (**Figure 96**). It should be noted that the $[Ag(X_2)]^+$ cations are structurally related to the $[X_3]^+$ cations and the polymeric $[\{Ag(I_2)\}_n]^{n+}$ cations bear some similarity to $[I_5]^+$.

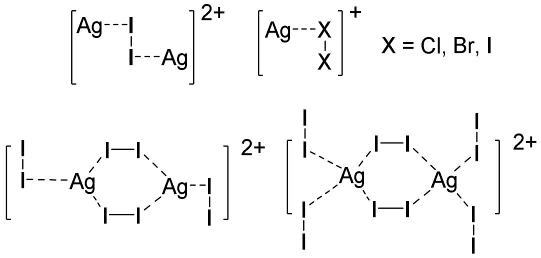


Figure 96. Structurally characterized metal complexes with dihalogen molecules as ligands.

π*-π*-Complexes: The three halogen containing cations that can be described as π*-π* complexes, can be understood as adduct of two homonuclear diatomic (radical) cations. According to its synthesis from chlorine and $[O_2]^+[SbF_6]^-$, $[Cl_2O_2]^{+\cdot}$ can be described as complex of the paramagnetic $[O_2]^{+\cdot}$ cation with Cl_2. For $[Cl_4]^{+\cdot}$, which is made from Cl_2 and the strong oxidant IrF_6, an initially formed paramagnetic $[Cl_2]^{+\cdot}$ could react with another equivalent of Cl_2. In the case of $[I_4]^{2+}$, which was obtained from an $[I_2]^{+\cdot}$ solution at low temperature, a dimerization of the two paramagnetic $[I_2]^{+\cdot}$ units to give the $[I_4]^{2+}$ dimer is obvious. All three syntheses have in common that at least one molecule with a half-filled π* orbital as HOMO is involved, for $[I_4]^{2+}$ even both "starting materials". The formed π*-π* interaction includes two quarter bonds for $[Cl_2O_2]^{+\cdot}$ (243/241 pm, Σ v. d. W. radii: 327 pm) and $[Cl_4]^{+\cdot}$ (293 pm, Σ v. d. W. radii: 350 pm) and two half bonds for $[I_4]^{2+}$, where the interaction leads to 2e-4c π*-π* bond (328 pm, Σ v. d. W. radii: 396 pm, **Figure 97**).[504,11]

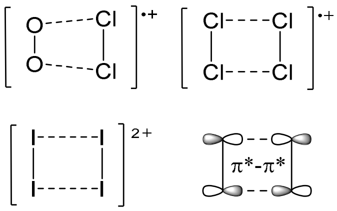
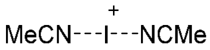


Figure 97. Structurally characterized halogen cations, which include π*-π*-interactions. Bond lengths: $[Cl_2O_2]^+$: O-O 121, Cl···O 241/243, Cl-Cl 191; $[Cl_4]^+$: Cl-Cl 194, Cl···Cl 293; $[I_4]^{2+}$: I-I 258, I···I 328 [pm].

Oxidation State +I: The isolated halogens X in this oxidation state would either correspond to a triplet state X^+ or the triplet dimer $[X{=}X]^{2+}$ – isoelectronic to the dichalcogens O_2 to Te_2. Neither the monomer, nor the dimer cation are hitherto known in condensed phase. Only one cation type with a formal oxidation state of +I is known: $[I(Donor)_2]^+$, in which the electrophilicity of I^+ is dampened by coordination of neutral donor molecules. Thus, $[I_3]^+[AsF_6]^-$ reacted with acetonitrile to form the structurally characterized salt $[I(NCMe)_2]^+[AsF_6]^-$ (**Figure 98**).[650] The closely related $[I(py)_2]^+[BF_4]^-$ is a useful reagent in organic chemistry.[651] For the latter it is disputable, if this is better assigned as being a pyridinium cation.



$$\mathrm{MeCN{-}{-}{-}\overset{+}{I}{-}{-}{-}NCMe}$$

Figure 98. $[I(NCMe)_2]^+$ cation in $[I(NCMe)_2][AsF_6]$ with iodine in the formal oxidation state +I.[650]

Oxidation State +III: The known interhalonium cations with the central halogen atoms in oxidation state +III are $[ClF_2]^+$, $[BrF_2]^+$, $[ICl_2]^+$, $[IBrCl]^+$ and $[IBr_2]^+$ (**Figure 99**). All were synthesized by halide abstraction from a neutral interhalogen. Others, like $[Cl_2F]^+$ and $[IF_2]^+$ are also accessible, but no crystal structures are known.[652] The cations $[I_3Cl_2]^+$ and $[I_3Br_2]^+$ can also be understood as interhalonium compounds with two iodine atoms in oxidation state +III and one in –I and are in some way the lighter homologues of the homopolyatomic cation I_5^+.[653–655] Two recently published examples are the dialkyl chloronium cations $[ClR_2]^+$ (R = Me, Et), which were synthesized through alkylation of chloromethane and –ethane, both stabilized by the very good carborate WCA $[CHB_{11}Cl_{11}]^-$ (**Figure 100**). The superacid $H(CHB_{11}Cl_{11})$ was used to generate ion-like methyl and ethyl cations "R^+" by protonation of the chloroalkanes RCl, which than react with a second equivalent of RCl to the chloronium cations.[656]

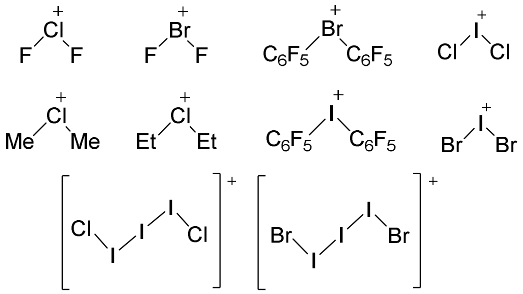


Figure 99. Structurally characterized halonium cations.

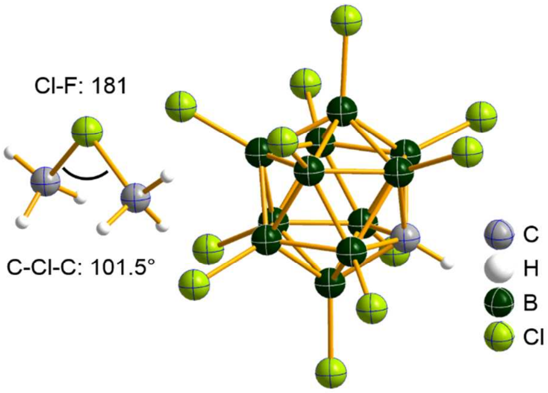


Figure 100. Molecular structure of $[ClMe_2]^+[CHB_{11}Cl_{11}]^-$. E. S. Stoyanov, I. V. Stoyanova, F. S. Tham, C. A. Reed, *Journal of the American Chemical Society* **2010**, *132*, 4062–4063. Data from this Reference were used to draw this figure. Bond lengths in [pm].

In case of bromine and iodine, also some new examples were synthesized during the last 20 years. The stable cyclic bromonium and iodonium ions of sterically hindered olefins (**Figure 101**) were stabilized by the $[OTf]^-$ anion and can be seen as stable intermediates of the halogenation of olefins.[657]

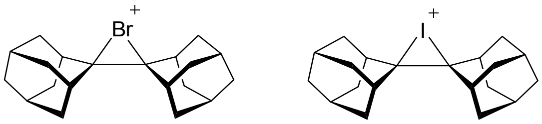


Figure 101. Stable $[OTf]^-$ salts of cyclic Bromonium and Iodonium Ions. [657]

Oxidation state +V: There are also some examples of cations in oxidation state +V. Besides the classical $[XF_4]^+$ cations (X = Cl, Br, I), the two oxocations $[ClO_2]^+$ and $[BrO_2]^+$ as well as since 2008 also one example of a cation with a X^V-carbon bond were structurally characterized. This electrophilic $[IF_2(C_6F_5)_2]^+$ cation was synthesized as $[BF_4]^-$ salt through halide abstraction and ligand exchange from $C_6F_5IF_4$ and $C_6F_5BF_2$.[658] Examples without crystal structures include $[OClF_2]^+$ [659] and $[OBrF_2]^+$. [660]

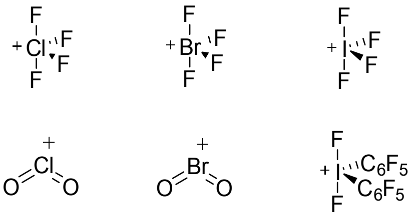


Figure 102. Structurally characterized halogen cations with halogen atoms in oxidation state +V. [658,661–663]

Oxidation State +VII: In 2004, with the octahedral complexes of the series $[XF_6]^+$ (X = Cl, Br, I) the first structures of cations with oxidation state +VII were published (**Figure 103**). All three cations were crystallized with the anion $[Sb_2F_{11}]^-$ and have very weak contact to the anion (**Figure 104**). It is also possible to obtain the $[AsF_6]^-$ and $[SbF_6]^-$ salts, but the differentiation between the octahedral $[XF_6]^+$ and $[MF_6]^-$ would not be easily done by X-ray crystallography (e.g., for $[BrF_6]^+[AsF_6]^-$ or $[IF_6]^+[SbF_6]^-$).

The use of $[Sb_2F_{11}]^-$ allowed for a clear differentiation between cations and anions [661]

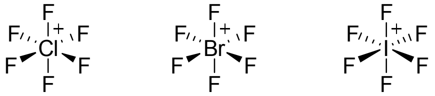


Figure 103. Structurally characterized halogen cations with halogen atoms in oxidation state +VII.[661]

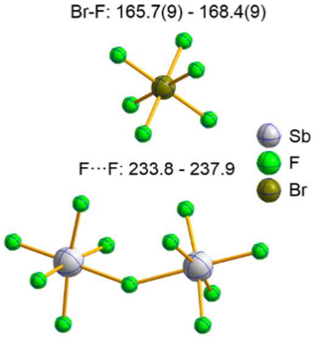
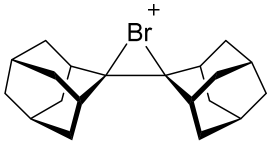
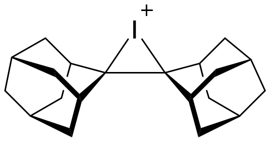


Figure 104. Molecular structure of $[BrF_6]^+[Sb_2F_{11}]^-$. J. F. Lehmann, G. J. Schrobilgen, K. O. Christe, A. Kornath, R. J. Suontamo, *Inorg. Chem.* **2004**, *43*, 6905–6921. Data from this Reference were used to draw this figure. Bond lengths in [pm].

Table 12. Overview on all structurally characterized halogen cations.

Cation	Anion	Class.*	Synthesis	Comment	Ref.
Homopolyatomic Cations					
$[Cl_3]^+$	$[AsF_6]^-$	Lewis	$[Cl_2F]^+[AsF_6]^- + Cl_2 + AsF_5$		42
$[Cl_3]^+$	$[X]^- = [SbF_6]^-, [Sb_2F_{11}]^-, [Sb_3F_{16}]^-$	Other	$[Cl_2O_2]^+[X]^- + Cl_2$ in HF at RT		42
$[Br_2]^+$	$[Sb_3F_{16}]^-$	Ox	Br_2+ $HSO_3F/SbF_5/3SO_3$		664
$[Br_3]^+$	$[AsF_6]^-$	Other	$[BrF_2]^+[AsF_6]^-$ decomposition	Store $[BrF_2]^+[AsF_6]^-$ for 20 years (!)	646
$[Br_5]^+$	$[MF_6]^-$ (M = As, Sb)	Ox	$[XeF]^+[MF_6]^- + Br_2$		211
$[I_2]^+$	$[Sb_2F_{11}]^-$	Ox	$I_2 + SbF_5$		15
$[I_3]^+$	$[AsF_6]^-$	Ox	$I_2 + AsF_5$		15
$[I_5]^+$	$[AsF_6]^-$	Ox	$I_2 + AsF_5$		665
$[I_{15}]^{3+}$	$[SbF_6]^-$	Ox	$I_2 + SbF_5$		15
Metal-nonmetal-cluster complexes					
$[Ag(Cl_2)]^+$	$[Al(OR^{PF})_4]^-$	Com	$[Ag]^+[Al(OR^{PF})_4]^- + Cl_2$	Only stable at low temperature	
$[Ag(Br_2)]^+$	$[Al(OR^{PF})_4]^-$	Com	$[Ag]^+[Al(OR^{PF})_4]^- + Br_2$		
$[Ag_2(I_2)_x]^{2+}$ (x = 1, 4, 6)	$[Al(OR^{PF})_4]^-$	Com	$[Ag]^+[Al(OR^{PF})_4]^- + I_2$		
$[Ag(I_2)]_n^{n+}$	$[MF_6]^-$ (M = Sb, As)	Com	$[Ag]^+[MF_6]^- + I_2$	First complex with halogen as donor	647
π*-π*-complexes					
$[Cl_4]^+$	$[IrF_6]^-$	Ox	$Cl_2 + IrF_6$	Radical, homo-polyatomic cation	645
$[Cl_2O_2]^+$	$[X\ ]^- = [SbF_6]^-, [Sb_2F_{11}]^-$	Com	$[O_2]^+ + Cl_2$		42
$[I_4]^{2+}$	$[MF_6]^-$ (M = As, Sb), and $[Sb_3F_{14}]^-/[SbF_6]^-$	Com	$2\ [I_2]^+$	Also homopoly-atomic cation	666
Oxidation state +I					
$[I(NCMe)_2]^+$	$[AsF_6]^-$	Other	$[I_3]^+$ + MeCN	I_3^+ as I^+ donor	650
Oxidation state +III					
$[ClF_2]^+$	$[AsF_6]^-$	Lewis	$ClF_3 + AsF_5$		667
$[ClF_2]^+$	$[SbF_6]^-$	Lewis	$ClF_3 + SbF_5$		668
$[ClF_2]^+$	$[RuF_6]^-$	Lewis	$ClF_3 + RuF_5$		669
$[ClMe_2]^+$ $[ClEt_2]^+$	$[CHB_{11}Cl_{11}]^-$	Prot	$H(CHB_{11}Cl_{11})$+ RCl (R = Me, Et)	Protonation of RCl	656
$[BrF_2]^+$	$[SbF_6]^-$	Lewis	$BrF_3 + SbF_5$		670
$[Br(C_6F_5)_2]^+$	$[BF_4]^-$	Lewis	$BrF_3 + (C_6F_5)_2BF$		671
	$[OTf]^-$	Lewis	Olef. + Br_2 +MeOTf $C_{20}H_{28}$ = Adamantylideneadamantane	Stable Bromonium Ion	657
$[ICl_2]^+$	$[SbF_6]^-$	Lewis	$I_2Cl_6 + SbF_5$		672
$[IBr_2]^+$	$[Sb_2F_{11}]^-$	Lewis	$IBr + SbF_5$		673

$[IBr_{0.75}Cl_{1.25}]^+$	$[SbCl_6]^-$	Lewis	$IBr + Cl_2 + SbF_5$		673
$[I_3Cl_2]^+$	$[X]^- = [SbCl_6]^-, [AlCl_4]^-$	Lewis, Other	$I_2 + SbCl_5$		654,655,653
$[I_3Br_2]^+$	$[SbCl_6]^-$	Lewis, Other	$I_2 + SbCl_5$		654
$[I(C_6F_5)R]^+$	$[BF_4]^-$	Lewis	$I(C_6F_5)F_2 + RBF_2$ R = C_6H_5, *o*-C_6H_4F, *m*-C_6H_4F, *p*-C_6H_4F, 2,4,6-$C_6H_2F_3$, C_6F_5	Strong interactions with the anions	674
	$[OTf]^-$	Lewis	Olef. + I_2 + Ag[OTf] $C_{20}H_{28}$ = Adamantylideneadamantane	Stable Iodonium Ion	657
Oxidation state +V					
$[ClF_4]^+$	$[SbF_6]^-$	Lewis	$ClF_5 + SbF_5$		662
$[ClO_2]^+$	$[SbF_6]^-$	Lewis	ClO_2F + HF/SbF_5		675
$[ClO_2]^+$	$[Sb_2F_{11}]^-$	Lewis	$ClO_2F + 2\ SbF_5$	Also an oxidation product of $[ClF_2]^+$	676
$[ClO_2]^+$	$[X]^- = [BF_4]^-, [GeF_5]^-$	Lewis	$ClO_2F + BF_3, GeF_4$		612,677
$[ClO_2]^+$	$[ClO_4]^-$	Ox	$ClO_2 + O_3$	Cl_2O_6	678
$[ClO_2]^+$	$[RuF_6]^-$	Lewis Ox	$ClO_2F + 2\ RuF_5$ ClF_3 + HF/RuO_4		669
$[BrF_4]^+$	$[Sb_2F_{11}]^-$	Lewis	$BrF_5 + 2\ SbF_5$		679,663
$[BrO_2]^+$	$[SbF_6]^-$	Lewis Other	$BrO_3F + SbF_5$	Reduction of Br^{VII}	675
$[IF_4]^+$	$[SbF_6]^-$	Lewis	IF_5 in HF/SbF_5		680,663
$[IF_4]^+$	$[Sb_2F_{11}]^-$	Lewis	IF_5 + 2 HF/SbF_5		681,663
$[I(C_6F_5)_2F_2]^+$	$[BF_4]^-$	Lewis	$C_6F_5IF_4 + C_6F_5BF_2$		658
Oxidation state +VII					
$[ClF_6]^+$	$[Sb_2F_{11}]^-$	Ox, Lewis	$ClF_5 + F_2 + SbF_5$		661
$[BrF_6]^+$	$[Sb_2F_{11}]^-$	Ox, Lewis	$BrF_5 + F_2 + SbF_5$		661
$[IF_6]^+$	$[Sb_2F_{11}]^-$	Lewis	$IF_7 + SbF_5$		661

* Classification according to the introduction (**Table 2**): Lewis = Lewis acid halogen bond heterolysis, Ox = Oxidation, Com = Complexation reaction, Other = All other reactions not classified.

Group 18 Cations

Due to the high ionization potential of the noble gases, their cations all need weakly coordinating and very oxidation resistant anions to be stabilized. The history of noble gas compounds started in the early 1960s, when Bartlett obtained „$[Xe]^+[PtF_6]^-$“ from a reaction of $[O_2]^+[PtF_6]^-$ and xenon – the noble gas with the lowest ionization potential. Over the next decades the composition of this product stayed unclear. In 2000 a very comprehensive review about the nature of the product was published with the result that it is very likely a $[XeF]^+$ salt of a polymeric (weakly coordinating) $[PtF_5]_n$ anion.[682] All of the hitherto known and structurally characterized noble gas cations are included with **Table 13**.

Krypton Cations

The only other noble gas besides xenon, for which cations are known, is krypton. The oxidation state +II is the only one known yet. The diversity of the amount of compounds and the number of hitherto realized Kr-X bonds is much smaller. Only two different fluorine-containing cations are known ($[KrF]^+$ and $[Kr_2F_3]^+$) and some nitrile complexes, which can be described as Kr-N compounds. $[KrF]^+$ is a very strong oxidative fluorinating reagent[683] and made is possible to synthesize $[XeF_5]^+$ from Xe,[684] $[ClF_6]^+$ from ClF_5,[685] $[BrF_6]^+$ from BrF_5[686] and $[O_2]^+$ from O_2.[687] There are only seven crystal structures of krypton cations in the literature and five of them with the classical $[AsF_6]^-$ and $[SbF_6]^-$ anions.

Xenon Cations

The lower ionization potential calls for a richer chemistry of xenon. Thus, since the birth of noble gas chemistry, a multitude of different xenon cations containing the element in the oxidation state II, IV and VI were synthesized.

Homopolyatomic Cations: The two known homopolyatomic cations are $[Xe_2]^+$ and $[Xe_4]^+$. It was only possible to obtain a crystal structure from $[Xe_2]^+$, but because of its importance $[Xe_4]^+$, which was assigned based on spectroscopic and computational evidence as being stable at higher Xe pressure, is also mentioned.

Fluoroxenon Cations and Related: The majority of such cations include Xe-F bonds ($[XeF_m]^+$, m = 1, 3, 5; $[Xe_2F_n]^+$, n = 3, 11, **Figure 105**), but over the decades a lot of different cations with Xe-X (X = F, Cl, O, N, C) bonds were obtained and are included with **Table 13** and in part also with **Figure 106**. Some of them were already published in the late sixties,[688–690] but also recently with $[XeF]^+[SbF_6]^-$ and $[XeF_3]^+[SbF_6]^-$ some new structures were presented[691,692] and in 2015 the crystal structures of $[XeF_5]^+$ with the classical WCAs $[SbF_6]^-$ and $[Sb_2F_{11}]^-$ were measured for the first time,[693] which shows that the investigation of xenon cations is still in progress.

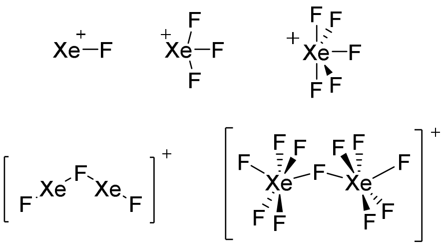


Figure 105. Fluoroxenon cations.

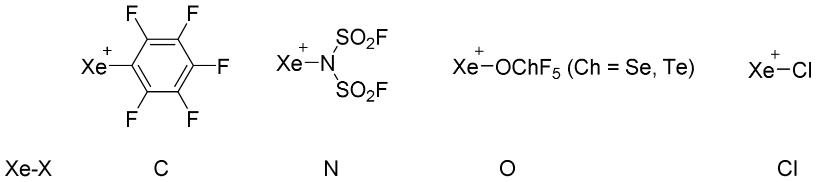


Figure 106. Examples of Xe-X bonds (X = C, Cl, N, O) in cations.

Most of the syntheses use Lewis acids to abstract fluoride from the neutral xenon fluoride (XeF_2, XeF_4, XeF_6). Most structures contain the conjugated weakly coordinating anions of these Lewis acids ($[MF_6]^-$, M = As, Sb, Au, Ru). Another mentionable approach is the reaction of XeF_2 with the Lewis acid $B(C_6F_5)_3$, which led to the $F_5C_6Xe^+$ cation containing the first Xe-C bond and the unsymmetric anion $[(F_5C_6)_2BF_2]^-$.[694] Through the use of the dioxydifluoride XeO_2F_2 as starting material, it was also possible to obtain the mixed cation $[XeO_2F]^+$ or the fluoride bridged $[F(XeO_2F)_2]^+$.[695]

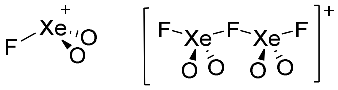


Figure 107. Examples of Xe-O-F cations.

Metal-Xenon Complexes: There are also some examples of metal-xenon complexes (M = Au^I, Au^{II}, Au^{III} and Hg^{II}), which can be described as part of the stabilization of modifications of main group elements as metal complexes ($[M_m(E_n)]^+$). Formally, Xe is isoelectronic to iodide I^-, and thus complex formation appeared to be difficult, but feasible. The syntheses proceed under the superacidic conditions of the systems HF/MF_5 (M = As, Sb). In case of these compounds, the role of the anions can be described as unreactive, but not really weakly coordinating. Most of them have relatively short contacts to the anions (shorter than the sum of the van-der-Waals-radii) and show typical coordination spheres with the anions included (e.g. square planar *trans*-$Au^{II}Xe_2(SbF_6)_2$) (Figure 108).[696]

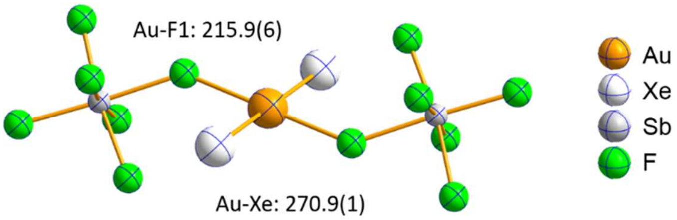


Figure 108. Molecular structure of *trans*-Au^{II}Xe$_2$(SbF$_6$)$_2$. T. Drews, S. Seidel, K. Seppelt, *Angew. Chem.* **2002**, *114*, 470–473, *Angew. Chem. Int. Ed.* **2002**, *41*, 454–456. Data from this Reference were used to draw this figure.

Only the [AuXe$_4$]$^{2+}$ dication exists in a truly ionic structure with two [Sb$_2$F$_{11}$]$^-$ counterions in the lattice.

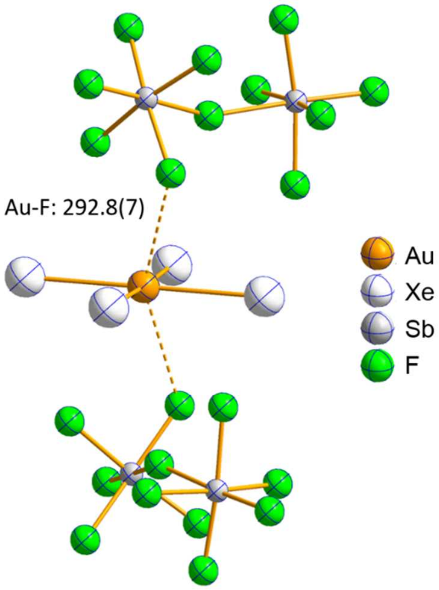


Figure 109. Molecular structure of tetragonal [Au^{II}Xe$_4$]$^{2+}$([Sb$_2$F$_{11}$]$^-$)$_2$. T. Drews, S. Seidel, K. Seppelt, *Angew. Chem.* 2002, *114*, 470–473, *Angew. Chem. Int. Ed.* 2002, *41*, 454–456. Data from this Reference were used to draw this figure.

Table 13. Cationic noble gas compounds with weakly coordinating anions

Cation	Anion	Class.*	Synthesis	Comment	Ref.
Homopolyatomic Cations					
$[Xe_2]^+$	$[Sb_4F_{21}]^-$	Lewis	$[XeF]^+$/Xe + SbF_5	First homopoly-atomic cation	27
$[Xe_4]^+$	$[Sb_xF_{5x+1}]^-$	Lewis	$[XeF]^+[Sb_2F_{11}]^-$, SbF_5 + Xe	No X-Ray	697
Metal-nonmetal-cluster complexes					
$[AuXe_4]^{2+}$	$[Sb_2F_{11}]^-$	Lewis, Com	AuF_3, Xe in HF/SbF_5	First xenon metal complex, gold(II) 2 modifications: triclinic and tetragonal	698,696
[*trans*-$AuXe_2]^{2+}$	$[SbF_6]^-$	Com	$HAuCl_4$, XeF_2, Xe in HF/SbF_5	gold(II)	696
[*cis*-$AuXe_2]^{2+}$	$[Sb_2F_{11}]^-$	Com	$[AuXe_4]^{2+}([Sb_2F_{11}]^-)_2$ – Xe at RT	gold(II)	696
[*trans*-$AuXe_2F]^{2+}$	$[SbF_6]^-$ + $[Sb_2F_{11}]^-$	Com	Au, XeF_2, Xe in HF/SbF_5	gold(III)	696
$[Au_2Xe_2F]^{3+}$	$[SbF_6]^-$	Com	Au, XeF_2, Xe in HF/SbF_5	gold(II)	696
$[(F_3As)AuXe]^+$	$[Sb_2F_{11}]^-$	Com	AuF_3, Xe, AsF_3 in HF/SbF_5		699
$[HgXe]^{2+}$	$[SbF_6]^-$ + $[Sb_2F_{11}]^-$	Com	HgF_2, Xe in HF/SbF_5		699
Oxidation state +II					
$[KrF]^+$	$[MF_6]^-$ (M = As, Sb, Bi)	Lewis	$KrF_2 + MF_5$	First krypton cation	700
$[KrF]^+$	$[AuF_6]^-$	Lewis	KrF_2 + Au		683
$[Kr_2F_3]^+\cdot KrF_2$, $[Kr_2F_3]^+\cdot{}^1/_2KrF_2$, $[Kr_2F_3]^+\cdot[KrF]^+$	$[SbF_6]^-$ $[SbF_6]^-$ $[AsF_6]^-$	Lewis	$KrF_2 + MF_5$		700
$[XeF]^+$	$[Sb_2F_{11}]^-$	Lewis	XeF_2 + 2 SbF_5		688
$[XeF]^+$	$[RuF_6]^-$	Lewis	$XeF_2 + RuF_5$		701
$[XeF]^+$	$[AsF_6]^-$	Lewis	$XeF_2 + AsF_5$		702
$[XeF]^+$	$[N(SO_2F)_2]^-$	Lewis	$XeF_2 + HN(SO_2F)_2$	First Xe-N bond, strong interaction with the anion	703
$[XeF]^+\cdot HF$	$[Sb_2F_{11}]^-$	Lewis	XeF_2 + 2 SbF_5		27
$[XeF]^+$	$[X]^-$ = $[AsF_6]^-$, $[SbF_6]^-$, $[Sb_2F_{11}]^-$, $[BiF_6]^-$, $[Bi_2F_{11}]^-$	Lewis	XeF_2 + AsF_5, SbF_5, BiF_5	Better structures for $[XeF]^+[X]^-$: $[X]^{-=}$ $[MF_6]^-$, $[SbF_6]^-$, $[Sb_2F_{11}]^-$	692
$[Xe_2F_3]^+$	$[AsF_6]^-$	Lewis	2 XeF_2 + AsF_5	Monoclinic structure	704,705
$[Xe_2F_3]^+$	$[AuF_6]^-$	Lewis	$XeF_2 + AuF_5$		687
$[Xe_2F_3]^+$	$[MF_6]^-$ (M = As, Sb)	Com	$[XeF]^+$ as starting material	$[Xe_2F_3]^+[AsF_6]^-$ trigonal structure	706
$[Xe(N(SO_2F)_2)]^+$	$[Sb_3F_{16}]^-$	Lewis	3 step synthesis with AsF_5 and SbF_5		707
$[XeC_6F_5]^+$	$[(F_5C_6)_2BF_2]^-$	Lewis	$XeF_2 + B(C_6F_5)_3$	First Xe-C bond	694
$[(MeCN)XeC_6F_5]^+$ $[XeC_6F_5]^+$	$[BX]^-$ (X = CF_3, C_6F_5) $[BX]^-$ (X = CF_3, CN)	Lewis, Com	$XeF_2 + C_6F_5BF_2$	Salt metatheses with $[XeC_6F_5]^+[BF_4]^-$	708
$[(C_6F_5Xe)_2Cl]^+$	$[AsF_6]^-$	Other	$XeC_6F_5{}^+$ + TMSCl	First Xe-Cl bond	709
$[XeOChF_5]^+$ (Ch = Se, Te)	$[AsF_6]^-$	Lewis	$FXeOChF_5 + AsF_5$	First Xe-O bond	710
$[XeOTeF_5]^+\cdot SO_2ClF$	$[Sb(OTeF_5)_6]^-$	Other	$Xe(OTeF_5)_2 + Sb(OTeF_3)_3$	$OTeF_5{}^-$ abstraction	711

$[XeCl]^+$	$[Sb_2F_{11}]^-$	Other	$[XeF]^+ + [Cl]^-$	Ligand exchange	712
$[XeN(H)TeF_5]^+$	$[AsF_6]^-$	Lewis	$[F_5TeNH_3]^+[AsF_6]^- + XeF_2$	First Xe-N(sp^3) bond	713
$[(F_3SN)XeF]^+$	$[AsF_6]^-$	Com	$F_3SN + [XeF]^+$	First Xe-N(sp) bond	714
$[XeNSF_4]^+$	$[AsF_6]^-$	Other	In solid state and HF/BrF_5 solution	rearrangement of $[F_3SNXeF]^+[AsF_6]^-$	715
$[(F_3SN)XeNSF_4]^+$	$[AsF_6]^-$	Com	$[F_3SNXeF]^+ + F_3SN$		716
$[Xe_3OF_3]^+$	$[MF_6]^-$ (M = As, Sb)	Other	$H_2O + XeF_2/[XeF]^+$	Hydrolysis to XeFOH followed by a reaction with $[Xe_2F_3]^+$	717
Oxidation state +IV					
$[XeF_3]^+$	$[Sb_2F_{11}]^-$	Lewis	$XeF_4 + 2\ SbF_5$		718
$[XeF_3]^+$	$[BiF_6]^-$	Lewis	$XeF_4 + BiF_5$		719
$[XeF_3]^+$	$[Sb_2F_{11}]^-$	Lewis	$XeF_4 + SbF_5$	better structure	692
$[XeF_3]^+\cdot HF$ $[H_5F_4]^+\cdot 2([XeF_3]^+\cdot HF)$ $[XeF_3]^+$	$[Sb_2F_{11}]^-$ $[SbF_6]\cdot 2[Sb_2F_{11}]^-$ $[SbF_6]^-$	Lewis	$XeOF_2\cdot xHF + HF/SbF_5$		720
Oxidation state +VI					
$[XeF_5]^+$	$[PtF_6]^-$	Lewis	$XeF_6 + PtF_5$	First xenon cation structure	690,689
$[XeF_5]^+$	$[AsF_6]^-$	Lewis	$XeF_6 + AsF_5$		705
$[XeF_5]^+$	$[SbF_6]^-$	Ox	$[XeF]^+[SbF_6]^- + F_2$ in aHF		693
$[XeF_5]^+$	$[Sb_2F_{11}]^-$	Other	$[XeF_5]^+[SbF_6]^-$	Crystals from a O_2SbF_6/XeF_5SbF_6 mixture	693
$[XeF_5]^+$	$[RuF_6]^-$	Lewis	$XeF_6 + RuF_5$		701
$[XeF_5]^+$	$[PdF_6]^{2-}$	Lewis	$2\ XeF_6 + PdF_4$		721
$[XeF_5]^+$	$[Ti_4F_{19}]^{3-}$	Lewis	$XeF_6 + TiF_4$	XeF_6 from XeF_2, F_2 and UV radiation	722
$[XeF_5]^+$	$[\textit{m}\text{-}F(OsO_3F_2)_2]^-$ $[OsO_3F_2]^-$	Lewis	$XeF_6 + (OsO_3F_2)_\infty$		691
$[XeF_5]^+$	$[Cu(SbF_6)_3]^-$	Other	$[XeF_5]^+[SbF_6]^- + [Cu]^+[SbF_6]^-$ in aHF	Anion exchange	43
$[XeF_5]^+$	$[AgF_4]^-$	Lewis	$AgF_2 + KrF_2 + XeF_6$ in aHF		723
$[XeF_5]^+$	$[AuF_4]^-$	Lewis	$XeF_6 + BrF_3\ AuF_3$		723
$[XeF_5]^+\cdot XeF_2\cdot$ $[XeF_5]^+\cdot 2\ XeF_2$ $[XeF_5]^+\cdot ½\ XeF_2$	$[AsF_6]^-$ $[AsF_6]^-$ $[AsF_6]^-$	Com	$XeF_2 + [XeF_5]^+[AsF_6]^-$		724
$[XeF_5]^+\cdot XeOF_4$	$[SbF_6]^-$	Lewis	$XeF_6 + [H_3O]^+[SbF_6]^-$		695
$[XeF_5]^+\cdot NO_2^+$	$[SbF_6]^-$	Other	$[XeF_5]^+[SbF_6]^- + [NO_2]^+[SbF_6]^-$		43
$[Xe_2F_{11}]^+$	$[AuF_6]^-$	Lewis	$2\ XeF_6 + AuF_5$		725
$[Xe_2F_{11}]^+$	$[OsO_3F_2]^-$	Lewis	$XeF_6 + (OsO_3F_2)_\infty$		691
$[XeO_2F]^+$ $[F(XeO_2F)_2]^+$	$[MF_6]^-$ (M = As, Sb) $[AsF_6]^-$	Lewis	$XeO_2F_2 + MF_5$ (M = As, Sb)	α- and β-modification of $[XeO_2F]^+[SbF_6]^-$	695

* Classification according to the introduction (Table 2): Lewis = Lewis acid halogen bond heterolysis, Com = Complexation reaction, Other = All other reactions not classified.

Conclusion

Sparked by the availability of new WCAs and new WCA starting materials in combination with novel concepts like FLP and others, the number of rPBC exploded over the last one to two decades. Noteworthy additions were found for each p-block element and, despite their quite high moisture and air sensitivity, true applications of rPBC salts emerged.

Where will this lead to over the next one or two decades…? To our understanding the blue sky synthesis of rPBC salts barely accessible with good / novel WCAs in combination with suitable media will continue to function as an “eye-opener” of what is possible. Many surprising discoveries will force us to sharpen our use of bonding concepts or lead to novel applications. It is often the combination of structural knowledge (“Wow, this crazy cation is stable…? I would have never thought so.”) that leads to the right moment of wonder and then inspiration (“Hm, if this cation is really straight forward accessible, one could use its electrophilic / acidic / oxidizing / activating properties in application XY”). In the 21st century, it is our duty as creative scientists to use this potential from fundamentals to the first application. Do not hesitate to really seek for application of your rPBC salt, as rarely others will pick up on these ideas, since the activation barrier for synthesizing a to this application group unknown rPBC is simply too high. So do not give up until you have demonstrated a possible application – yourself or through collaborations – to a level that others will continue. And on the other hand this compilation of rPBC should encourage application based groups to identify interesting cations that may have an application. Contact the people, the chances are very good that through an informal collaboration showing a proof-of-principle new and relevant application areas may be developed.

In this respect, we are looking forward to all the scientific creativity that is breaking loose, and to realize what potentially could be done with the rPBC. This is an integral element of innovation and the justification for preparing blue sky or simply beautiful and esoteric compounds.

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