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Donor-Acceptor Bonding in Novel Low-Coordinated Compounds of Boron and Group-14 Atoms C - Sn

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Abstract. A summary of theoretical and experimental work in the area of low-coordinated compounds of boron and group-14 atoms C - Sn in the last decade is presented. The focus of the account lies on molecules EL_2, E_2L_2 and E_3L_3 which possess dative bonds between one, two or three atoms E and σ-donor ligands L that stabilize the atoms E through L→E donor-acceptor interactions. The interplay between theory and experiment provides detailed insight into the bonding situation of the molecules, which serves as guideline for the synthesis of molecules that possess unusual bonding motifs.

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1. Introduction

This review summarizes recent theoretical and associated experimental work in the area of low-valent main group complexes that have one, two or three boron atoms or group-14 elements C - Sn as central moieties that are stabilized by σ-donor ligands. The molecules that are described in this review have mostly the general formula EL_2, E_2L_2 and E_3L_3 where E_3 is a cyclic fragment. The characteristic feature of the molecules is the occurrence of dative bonds L→E instead of electron-sharing bonds R-E, which is a very helpful model for understanding the geometries and reactivities that are experimentally observed. Donor-acceptor complexes of low-valent main group compounds are presently a very active field of experimental and theoretical research that is rapidly growing. Our report does not strive after a comprehensive coverage of the whole field. Rather, we focus on the interplay of theory and experiment and the mutually stimulating effect on calculated and observed results on the scientific progress. We emphasise the relevance of chemical bonding models derived from quantum chemical calculations. Theoretical work does not only supply accurate numbers with the help of powerful computers and sophisticated software, which are available these days. Calculated data may also be used as input for modern methods of bonding analysis that have been developed in the recent past.[1] The famous request of Charles Coulson to his fellow theoreticians from 1960 "Give us insight, not numbers"[2] may now be answered with the expression "We give insight and numbers".

The timewise coverage of this review is restricted to the last ten years, i.e. only work that was published since 2005 is considered unless it is cited for historical reasons. The topic restriction on compounds of boron and group-14 atoms C – Sn does not mean that there has been no progress for other main-group elements in the chemistry of low-valent donor-stabilized compounds in recent years. On the contrary, there was a stormy development in neighbouring fields which could easily fill a whole volume of this journal. For example, complexes of alkaline and earth-alkaline atoms have seen much progress[3] and also the field of low-valent coordination chemistry of nitrogen[4] and heavier atoms P - Bi[5] experienced rapid growth where some spectacular molecules could be isolated. We rather focus on the elements B and C - Sn, because our own research is active mainly in these fields. We consider the reports that are discussed here as examples of the fruitful interplay of modern computational and experimental studies characteristic for present day chemistry. It is our intention to write a summary of theoretical and experimental research, which is more a stimulant for future experimental studies than a historical account of achievements. A purely theoretical work, which covers the bonding aspects of the molecules, was published by us in 2014.[6] A review article which covers experimental and theoretical work on complexes of mono- and diatomic species EL_2 and E_2L_2 where E are elements of groups 13 - 16 until 2013 has been presented by Wilson and Dutton.[7] Experimental work in the field of carbene-stabilized main-group species was summarized by Wang and Robinson.[8] We would be very happy if our paper inspires experimentalists toward new reactions.

2. Single-Centre Complexes of Group-14 Atoms C - Sn

In 2005, Petz and co-workers reported the isolation and structural characterization of the CO_2 and CS_2 adducts with carbodiphosphorane (CDP) $C(PPh_3)_2$ from which the first one is shown in Figure 1.[9] The central C-C distances C1-C2 are between a single and double bond. The analysis of the bonding situation showed that the molecules are best described in terms of donor-acceptor complexes between CX_2 (X = O, S) and CDP. The surprising finding was, that $C(PPh_3)_2$ is a double Lewis base with a π- and a σ-lone pair orbital that are localized at the central carbon atom as HOMO (Highest Occupied Molecular Orbital) and HOMO-1. An appropriate description with Lewis structures is $(Ph_3P)_2C\rightrightarrows CX_2$.

Figure 1

Double Lewis bases were unknown at that time and the bonding situation in CDP became the focus of intensive theoretical studies that have recently been reviewed.[10] The electronic structure was analysed with a variety of modern methods of quantum chemistry. The conclusion was, that the best description of the chemical bonds at the central carbon atom of CDP is given in terms of donor-acceptor interactions between a carbon atom in the excited singlet (^1D) state and two phosphine ligands PPh_3 as donors.[11] The carbon atom retains its valence electrons as two (σ- and π-) lone pairs and has the electronic reference configuration $2s^2 2p_x^2 2p_y^0 2p_z^0$. The bonding model was generalized to other ligands L that bind as σ-donors to carbon in the oxidation state C(0) in the complexes CL_2 sketched as $L\rightarrow C\leftarrow L$.[12] The dominant orbital interactions are sketched in Figure 2 where the electronic reference configuration of carbon(0) with respect to the molecular plane is $C(2s^2\ 2p_{\pi\perp}^2 2p_{\sigma}^0 2p_{\pi\parallel}^0)$. The vacant $2p_{\sigma}^0$ and $2p_{\pi\parallel}^0$ AOs of carbon serve as acceptor orbitals for the donation of the σ (+,+)

and $\pi_{\|}$ (+,-) combination of the ligand orbitals.[13] Further details of the donor-acceptor interactions and the bonding analysis are discussed in the literature.[6]

Figure 2

The peculiar donor strength of CDP had already been observed in earlier experimental studies by Schmidbauer[14] and by Kaska[15] who ascribed the reactivity to a dominant resonance structure, which has two negative charges at the central carbon atom. The proposal of dative bonding in CDP as a new concept was the topic of a healthy controversy[16] which helped to scrutinize the donor-acceptor model in further studies. However, there is one case of clear overlooking of earlier theoretical work, which suggested dative bonding in CDP and related compounds. The bonding model L→C←L with two lone pairs at carbon was already introduced in 1980 by Yuri Varshavsky who used the model to describe chemical bonding in various carbon complexes.[17] The paper appeared in Russian and it was unknown to us and apparently not widely known in the community. Yuri Varshavsky contacted one of us (GF) in 2012 and pointed out that he had made similar suggestions in his 1980 publication as in our original work that appeared after 2005. An English version of the original Russian paper has now been placed online by the author.[18]

The electronic structure at the divalent C(0) atom of CL_2 which has two lone pairs is clearly different from the divalent C(II) atom of carbenes CR_2 that have only one lone pair. Theoretical studies showed that the occurrence of a second lone pair in CL_2 leads to significantly higher second proton affinities (PAs) than in CR_2.[19] The name "carbone" was coined for divalent C(0) compounds CL_2 which underlines the character of a naked carbon atom in the molecule.[20] The different chemical properties of carbenes and carbones also showed up in the calculated stability of carbon complexes with two main group and TM Lewis acids.[12b] Recent theoretical studies explored the different reactivities of carbon(II) and carbon(0) compounds and the stabilization of cyclic and acylic C(0) species.[21]

The value of the donor-acceptor model for carbones CL_2 became evident by explaining the bent equilibrium structure of carbon suboxide C_3O_2 which is usually described as cumulene with double bonds O=C=C=C=O. The latter model does not account for the bending angle of 156° at the central carbon atom.[22] The deviation from a linear geometry is straightforwardly explained when the molecule is considered as dicarbonyl complex of carbon atom OC→C←CO.[12a] The larger bending angle compared with CDP in $Ph_3P \rightarrow C \leftarrow PPh_3$ (136°) comes from the stronger π-backdonation in the carbonyl complex which is well known from transition metal (TM) complexes.[23] The analogy of carbon complexes with TM complexes led to the theoretical prediction of carbodicarbenes $C(NHC)_2$ with N-heterocyclic carbenes (NHC) as donor ligands.[24] Experimental studies suggested that phosphines PR_3 and NHC have similar properties as mainly σ-donors.[25] Calculations showed that the bonding angle at carbon(0) in NHC→C←NHC should be ~138° , very similar as in $Ph_3P \rightarrow C \leftarrow PPh_3$.[24a] The prediction was quickly verified by the first synthesis and structural characterization of the benzoannelated carbodicarbene $C(NHC^{Bz})_2$ by Bertrand and co-workers shown in Figure 3.[26] The bending angle in $C(NHC^{Bz})_2$ is 134.8° which is close to the calculated value for $C(NHC^{Me})_2$. Fürstner *et al.* reported at the same time about complexes carrying $C(NHC)_2$ as ligands.[27] The latter group synthesized later a series of mixed carbones with one phosphine and various other ligands $C(PPh_3)(L)$ where L is CO, CNPh, PPh_3 or a cyclic or acyclic carbene CR_2 with different substituents R.[28]

Figure 3

The chemistry of carbodicarbenes (CDCs) $R_2C \rightarrow C \leftarrow CR_2$ (which were sometimes termed "bent allenes")[29] with cyclic and acyclic carbene ligands has received much attention by synthetic chemists in recent years who showed that CDCs exhibit particular reactivities that clearly distinguish them from carbenes.[30,31] Several groups utilized the peculiar bonding properties of CDCs as ligands for a range of catalytic reactions such as hydrogenation of inert olefins[30a], C-C cross-coupling reactions[31b], intermolecular hydroamination[30c] and hydroheteroarylation[30b]. Very recently, the group of Ong reported a facile synthesis of unsymmetrical CDCs CL^1L^2 where L^1 and L^2 are different NHC ligands. [31a]

There are three noteworthy observations demonstrating the different reactivities of carbones CL_2 and carbenes CR_2. Two cases involve the parent carbone $C(PPh_3)_2$[32] (see Scheme 1 for an overview) while the other one concerns the benzoannelated CDP $C(NHC^{Bz})_2$.[26] In 2009, Petz and co-workers reacted $C(PPh_3)_2$ with excess diborane B_2H_6.[33] The reaction proceeds with fast formation of the mono adduct $(PPh_3)_2C \rightarrow BH_3$ stabilized by tetrahydrofurane (THF). Further reaction of the precipitate which is likely a mixture of several compounds yielded the bisadduct $[(PPh_3)_2C \rightrightarrows B_2H_4(\mu\text{-}H)]^+$ (Figure 4a) as salt with the counter anion $[B_2H_7]^-$ presumably via the initial formation of the neutral bisadduct

$(PPh_3)_2C\rightrightarrows(BH_3)_2$.[33] This was the first example of a complex where a carbone binds two main group Lewis acids other than H^+ or CH_3^+. Related adducts with two Lewis acids E were previously realized in the cations $([H_2C(PPh_3)_2]^{2+}$,[34] $[Ag\{HC(PPh_3)_2\}_2]^{3+}$,[11] $[HMeC(PPh_3)_2]^{2+}$[35] and in $Cl_2Au_2[\mu\text{-}C(PPh_3)_2]$.[36]

Figure 4, Scheme 1

The second example was reported in 2011, when Alcarazo and co-workers[37] treated the mono adduct $(PPh_3)_2C\rightarrow BH_3$ with the strong base $B(C_6F_5)_3$ which abstracts a hydride anion from the complex and gave the unusual cation $[(PPh_3)_2C\rightrightarrows BH_2]^+$ (Figure 4b) which could be isolated and structurally characterized by x-ray analysis. A quantum chemical bonding analysis nicely showed that the borinium cation BH_2^+ which has vacant σ and π orbital is stabilized through double donation of the carbone.[37] The authors reacted also the carbene adduct $NHC\rightarrow BH_3$ with the strong base $B(C_6F_5)_3$ and obtained the cation $[NHC\text{-}BH_2(\mu\text{-}H)BH_2\text{-}NHC]^+$ (Scheme 1b). This is a striking demonstration of the different reactivities of a carbone and a carbene. Very recently, Ong and co-workers studied the reaction of the benzoannelated CDC $C(NHC^{Bz})_2$ with $BH_3{\bullet}THF$ which gave a surprising product.[31c] Unlike the CDP adducts $L_2C\rightarrow BH_3$ and $[L_2C\rightrightarrows BH_2]^+$ where L = PPh_3, they directly obtained the dication $[L\rightarrow(BH)\leftarrow L]^{2+}$ (L = $C(NHC^{Bz})_2$) where the CDC ligands formally donate six electrons to the BH^{2+} moiety. The bonding analysis shows that there are two σ bonds which come from the $(NHC^{Bz})_2C\rightarrow(BH^{2+})\leftarrow C(NHC^{Bz})_2$ σ-donation and an allenic type π bond from the π-donation. The analogous reaction with $AlCl_3$ gives only the classical adduct $(NHC^{Bz})_2C\rightarrow AlCl_3$.[31c]

The relationship between carbodicarbenes $R_2C\rightarrow C\leftarrow CR_2$ and allenes $R_2C{=}C{=}CR_2$ and the different bonding situations becomes obvious when amino substituted systems where R = NX_2 (X = alkyl) are considered. The parent allene $H_2C{=}C{=}CH_2$ shows the typical features of a tetravalent C(IV) species with linear arrangement of the carbon atoms and where the central carbon atom has rather large bending potential and a comparatively low proton affinity (PA) of 182.4 kcal/mol.[24a] In contrast, the tetraaminoallene (TAA) $(Me_2N)_2C{=}C{=}C(NMe_2)_2$ has a very shallow bending potential and a much higher PA of 282.5 kcal/mol and even a second PA of 151.6 kcal/mol not much lower than the first PA of $H_2C{=}C{=}CH_2$. The latter parent compound has a negative second PA. A rather large first PA (268.2 kcal/mol) and second PA (175.8 kcal/mol) was also calculated for the ethyl derivative $(Et_2N)_2C{=}C{=}C(NEt_2)_2$ which exhibits a bending angle of 169.5° for the central CCC moiety.[24a] The calculated data suggest that the bonding situation in the TAAs may be described with dative bonds $(X_2N)_2C{\rightarrow}C{\leftarrow}C(NX_2)_2$ where the central carbon atom possesses two electron lone pairs. This is in agreement with earlier experimental observations by Viehe *et al.* who found that $(Me_2N)_2C{=}C{=}C(NMe_2)_2$ reacts "extremely readily and in good yields" with CO_2 and CS_2 giving the adducts $[(Me_2N)_2C]_2C{\rightrightarrows}CX_2$ (Scheme 2a).[38] The related reaction of CDP which gives the complexes $(Ph_3P)_2C{\rightrightarrows}CX_2$ (Scheme 2b) was the starting point for identifying carbones CL_2 as a unique class of carbon bases.[9] Since $(Me_2N)_2C{=}C{=}C(NMe_2)_2$ has a linear geometry where the lone-pair orbitals at the central carbon atom are not obvious, the term "hidden carbone" was coined for TAAs.[12a] A possibly "hidden carbone" character of carbon compounds was the topic of recent theoretical studies by Phukan and coworkers.[39]

Scheme 2

The carbone character of TAAs was recognized by Fürstner who reacted $(Me_2N)_2C{=}C{=}C(NMe_2)_2$ with $[AuCl(PPh_3)]$ in the presence of $NaSbF_5$ as halide scavenger.[27] They isolated the adduct $[(Me_2N)_2C]_2C{\rightarrow}Au(PPh_3)^+(SbF_5)^-$ in 72% yield. Attempts of dimetallation of $(Me_2N)_2C{=}C{=}C(NMe_2)_2$ failed, which was explained with the shape of the amino groups. Double protonation at the central carbon atom which leads to the dication $[(Me_2N)_2C]_2C(H^+)_2$ was possible.[28]

The experimental studies of carbodicarbenes suggest that carbones are a third major class of two-coordinated carbon bases besides NHCs which were developed by Arduengo[40,41] and the cyclic alkyl-amino carbenes (cAACs) that were introduced by Bertrand in 2005[42] and possess particular bonding properties to be utilized in chemical reactions. NHCs are known to be strong σ-donors and relatively weak π-acceptors. CAACs are even stronger nucleophilic (σ-donors) but also more electrophilic (π-acceptors) than NHCs.[42b] Carbones are double (σ- and π-) donors which makes them clearly different from carbenes. The chemistry of NHCs and cAACs is the focus of many experimental studies while the properties of carbones for organic synthesis and catalysis are less explored. We think that the unique bonding properties particularly of CDCs make carbones promising compounds for experimental work.

The extension of the chemistry of carbones CL_2 to heavier group-14 tetrylones EL_2 (E = Si - Pb) is a topic which is presently under extensive experimental investigation. The names silylones (SiL_2), germylones (GeL_2), stannylones (SnL_2) and plumbylones (PbL_2) where suggested in 2009 at a time when none of these species were known.[43] Theoretical studies had shown that the heavier homologues of carbones have similar structures and electronic properties and that they are best described in terms of dative bonds L→E←L.[44] This shed new light on experimental work that was published in the years 2003 – 2005 and reported about compounds that were introduced as the first silicon and germanium homologues of allenes which could become isolated.[45] However, the molecular structures have cyclic end groups and possess bent geometries and the planes of the substituents are twisted (Figure 5a). Classical carbenes possess a linear backbone $R_2C=C=CR_2$ where the terminal groups are orthogonal to each other. The structural features resemble more carbodicarbenes (Figure 5b) where the cyclic end groups do not have nitrogen atoms in α-position like CDCs. A re-evaluation of the bonding situation in the "trisilaallene" and "trigermaallene" suggested that the molecules should not be described with electron-sharing bonds $R_2E=E=ER_2$ but with dative bonds $R_2E \rightarrow E \leftarrow ER_2$.[44a,b] A theoretical study which applied topographical mapping of the molecular electrostatic potential of related two-coordinated Si and Ge compounds suggested that the molecules should be considered as Si(0) and Ge(0) species.[46] We want to point out that the dichotomy of E-E versus E→E bonds leads to a straightforward explanation of the unusual structures of E_2H_2 (E = Si – Pb) where none of them has the linear triply bonded form of acetylene $HC \equiv CH$.[47]

Figure 5

Recent experimental studies led to successful isolation of genuine silylones and germylones by the groups of Roesky and Driess.[48,49] Both groups employed N-heterocyclic carbenes as ligand for the synthesis of L_2E compounds (Figure 6). Roesky used Bertrand's cAAC carbene[42] and he reported the x-ray structure of $Si(cAAC)_2$ in 2013.[48] Driess employed a bidentate carbene ligand where two NHC donors are connected by a methylene bridge in $[(NHC\text{-}CH_2\text{-}NHC)E]$.[49] A recent theoretical study revealed that the bidentate NHC ligand is a stronger π-acceptor than two separated NHC donors. It was shown that the strength of the L←E→L π-backdonation of the carbene ligands has the trend $(cAAC)_2 >$ $NHC\text{-}CH_2\text{-}NHC >$ $(NHC)_2$.[50] Other silylones SiL_2 and germylones GeL_2 are experimentally not know so far. We know no report about stannylones and plumbylones. It does not take much fantasy that the situation may change in the near future.

Figure 6

3. Single-Centre Complexes of Boron

The extension of the bonding situation of carbones CL_2 to isoelectronic boron homologues $(BH)L_2$ is in an infant stadium where only very few examples of stable molecules have been reported so far. One reason is the much higher promotion energy of BH to reach the electronic reference state for the dative bonding with two σ donor ligands. Figure 7 shows schematically the bonding situation between carbon in the ^1D state and two ligands L and the related $^1\Delta$ state of BH. The B-H bond takes the position of the σ lone pair at carbon but the excitation from the X $^1\Sigma_g$ ground state where the electron lone pair occupies a σ orbital to the $^1\Delta$ state with an occupied p(π) lone pair orbital is much higher (139.1 kcal/mol) than the $^3P \rightarrow {}^1D$ promotion energy of carbon (29.1 kcal/mol). Dative bonds to BH must be very strong in order to overcome the large excitation energy in order to yield a stable complex L→(BH)←L.

Figure 7

Figure 7 also shows the calculated interaction energy ΔE_{int} between the ligands and the central species where $C(^1D)$ and $BH(^1\Delta)$ are in the excited reference state and the bond dissociation energy D_e for the fragmentation reactions towards the ground state.[51] The species $BH(^1\Delta)$ is an intrinsically stronger Lewis acid than $C(^1D)$ but the higher excitation energy makes the borylene complexes energetically less stable than particular carbone. The best chances are given for the carbene complex $(BH)(NHC)_2$. Bertrand employed the stronger π acceptor cAAC and succeeded in 2011 in the isolation of the first main group borylene complex[52] $(BH)(cAAC)_2$.[53] Figure 8 shows the structures and most important bond lengths and angles of the complex, its radical cation $[(BH)(cAAC)_2]^{+\bullet}$ and the protonated $(BH_2)^+(cAAC)_2$. The HOMO is energetically very high lying (ε = -3.34 eV) and it is easy to remove an electron or to add a proton. The calculated proton affinity of the complex of 264.8 kcal/mol is much higher than that of free BH, which is only 204.6 kcal/mol. The shape of the HOMO indicates a high degree of cAAC←(BH)→cAAC π-backdonation. An energy decomposition analysis shows that the cAAC←(BH)→cAAC π-backdonation is significantly stronger than in NHC←(BH)→NHC which in turn is clearly stronger than in the carbones cAAC←C→cAAC and NHC←C→NHC.[51]

Figure 8

There are two more recent reports about substituted homologues of the borylene complex $(BR)L_2$ that are stable under normal laboratory conditions. One was reported by Kinjo who synthesized a complex where phenylborylene is stabilized by two oxazol-2-ylidene ligands (Figure 9a),[54] which is another borylene complex with two carbene ligands. The other example is the dicarbonyl complex $(BR)(CO)_2$ that is shown in Figure 9b and was very recently reported by Braunschweig.[55] The data in Figure 7 suggest that the carbonyl ligands bind weaker to BH than cAAC. An energy decomposition analysis also showed that CO is only a slightly weaker π acceptor in borylene complexes $(BH)L_2$ than cAAC which might be important for the stabilization.[51] The very bulky terphenyl group in Braunschweig's dicarbonyl complex may protect the borylene fragment from electrophilic attack. Borylene complexes $(BR)L_2$ are isoelectronic to amines and are strong bases. The first report in Braunschweig's paper on $(RB)(CO)_2$ lets one expect that the molecule behaves similarly as transition metal complexes which is a novel finding.[55]

Figure 9

There is one more boron compound that is related to carbones. The anion $[B(CO)_2]^-$ which is isoelectronic to $C(CO)_2$ has recently been isolated in a low-temperature matrix.[56] The molecule exhibits unlike carbon suboxide a linear geometry which can was explained with the stronger π-backdonation of B^- over C. A detailed bonding analysis suggested that the anion possesses dative bonds and should be described as a complex $OC{\rightarrow}B^{(-)}{\leftarrow}CO$ which exhibits strong π backdonation $OC{\leftarrow}B^{(-)}{\rightarrow}CO$.

The field of heavier group-13 homologues of borylene complexes $(ER)L_2$ (E = Al – Tl) is essentially a terra incognita. The heavier homologue of the dicarbonyl anion $[Al(CO)_2]^-$ has a strongly bent geometry and has been synthesized in an inert low-temperature matrix.[57] There are no reports known to us about neutral homologues of the borylene complexes.

4. Two-Centre Complexes of Group-14 Elements C_2 – Sn_2

In 2008, Robinson and co-workers reported the isolation of the complex $NHC{\rightarrow}Si_2{\leftarrow}NHC$ where diatomic silicon is stabilized by two NHC ligands.[58] The authors wrote in their abstract "*Dative, or nonoxidative, ligand coordination is common in transition metal complexes; however, this bonding motif is rare in compounds of main group elements in the formal oxidation state of zero."* This statement did hold at the time when the paper was written, but it was also a time when it was discovered that many carbon compounds such as carbodiphosphorane $C(PPh_3)_2$ are actually C(0) species which led to the synthesis of other complexes CL_2.[6,12,24] The preparation of $Si_2(NHC)_2$ clearly paved the way toward further exploration of low-valent main group compounds. One year later in 2009, the analogous germanium complex $Ge_2(NHC)_2$ was isolated by Jones *et al.*[59] It took three more years before the synthesis of the tin adduct $Sn_2(NHC)_2$ was reported by the same group.[60] The lead homologue has not been isolated so far, which may be due to the experimental difficulties which are associated with the synthesis when the group-14 atom becomes heavier. At present there seem to be no other ligand stabilized complexes E_2L_2 which could be isolated besides the NHC species.

Figure 10

All three complexes $E_2(NHC)_2$ (E = Si – Sn) have an antiperiplanar arrangement of the NHC ligands at the diatomic moiety E_2 (Figure 10). This can be explained with the nature of the donor-acceptor interactions in $NHC \rightarrow E_2 \leftarrow NHC$ when the electronic reference state of E_2 in the complexes is considered.[50,59,60] Figure 11 shows schematically the molecular orbitals (MOs) of the diatomic molecules. The electronic ground state of E_2 is the $X^3\Sigma_g^-$ triplet state (Figure 11a), which is not suitable for dative bonding. The correct reference state is the excited $^1\Delta_g$ state (Figure 11b) which is between 18.8 kcal/mol (E = Si) and 15.6 kcal/mol (E = Sn) higher in energy than the ground state.[61] Quantum chemical calculations showed that the $X^3\Sigma_g^- \rightarrow {}^1\Delta_g$ excitation energy is compensated by the strong donor-acceptor interactions in the complexes. The theoretically predicted bond dissociation energies for the reaction $E_2(NHC)_2 \rightarrow E_2(X^3\Sigma_g^-) + 2\,NHC$ are D_e = 92.8 kcal/mol (E = Si), D_e = 75.6 kcal/mol (E = Ge) and D_e = 61.9 kcal/mol (E = Sn), Figures 11c,d show that the vacant $1\pi_u$' and $1\pi_g$' MOs of E_2 are perfectly suited for dative bonding when the ligands are arranged in a an antiperiplanar way. For a more detailed analysis of the bonding situation, we refer to the literature. [50,59,60]

Figure 11

The extension of the series of $E_2(NHC)_2$ to the carbon analogue has been an area of intensive investigations in recent years. In 2012, Dutton and co-workers suggested that the compounds $C_2(NHC)_2$ might be a viable target for synthesis.[62] They also calculated $C_2(PR_3)_2$ with R = Me, Ph which exhibit a *trans*-bent structure similar with rather acute bond angles C-C-P of 116° (R = Me) and 125° (R = Ph). The calculations of $C_2(NHC^R)_2$ with different substituents at nitrogen predicted a nearly linear arrangement with angles NHC-C-C between 173° for R = Me and 179° when R = H. The ligand exchange reactions $C_2(PR_3)_2 + 2\ NHC^R \rightarrow C_2(NHC^R)_2 + 2\ PR_3$ showed that the carbene stabilized systems are much lower in energy by as much as 64 kcal/mol (R = Me) than the phosphine complexes. The authors proposed that $C_2(NHC^R)_2$ might therefore become isolated.[62] Experimental attempts to synthesize the latter compounds did not succeed so far. Instead, the carbene homologues $C_2(cAAC^R)_2$ with different groups R could be prepared by two groups in 2014.[63,64] The x-ray analysis showed that the molecules have a nearly linear arrangement of the four central carbon atoms with bending angles close to 180° (Figure 12). It is interesting that the molecules can easily be ionized to the radical cations $[C_2(cAAC^R)_2]^{+\bullet}$ and even to the dication $[C_2(cAAC^R)_2]^{2+}$ whose geometries were determined by x-ray crystallography and also showed a nearly linear structure of the central C_4 unit. [63,64]

Figure 12

Dutton *et al.* recently reinvestigated their unsuccessful attempts to synthesize $C_2(NHC^R)_2$ in the light of the successful isolation of $C_2(cAAC^R)_2$.[65] The crucial finding is shown in Figure 13. The attempted deprotonation of $[C_2H_2(NHC^R)_2]^{2+}$ turned into a reduction which gave the neutral species $C_2H_2(NHC^R)_2$ instead of $C_2(NHC^R)_2$. The deprotonation route had been successfully employed by Bertrand in the synthesis of the first carbodicarbene $C(NHC)_2$[26] but it failed for the preparation of $C_2(NHC^R)_2$. The authors cited the higher first and particularly the second proton affinity of $C_2(NHC^R)_2$ as a possible reason for the outcome of the reaction.[65] They also mention the small HOMO-LUMO gap of $C_2(NHC^R)_2$ which is much smaller than in $C_2(cAAC^R)_2$ as reason for the contrasting behaviour.

Figure 13

The question arises whether the dicarbon species $C_2(cAAC)_2$ and $C_2(NHC)_2$ may be considered as cumulenes L=C=C=L or as donor-acceptor complexes L→CC←L which was found as appropriate description for the heavier group species with *trans*-bent geometry. The nearly linear geometry of the central C_4 moiety of the isolated species $C_2(cAAC^R)_2$ and $C_2(NHC^R)_2$ suggests that they may rather be considered as cumulenes and so were they named by the authors who synthesized them.[63,64]

Figure 14

Dutton and co-workers showed in their theoretical study that the dicarbon species may also be discussed in terms of donor-acceptor interaction when the highly excited $(2)^1\Delta_g$ state (Figure 14c), which has the valence electron configuration $(1\sigma_g^+)^2,(1\sigma_u^+)^0,(1\pi_u)^2,(1\pi_u')^2,(2\sigma_g^+)^0,(1\pi_g)^2,(1\pi_g')^0$, is used as reference state.[65] Figure 14a shows the orbital scheme for C_2 which has a $X^1\Sigma_g^+$ ground state. The excited $(1)^1\Delta_g$ state (Figure 14b) has vacant $1\pi_u$' and $1\pi_g$' MOs which would lead to complexes L→CC←L in a *trans*-bent arrangement. A linear structure requires two empty σ MOs as acceptor orbitals which are available in the $(2)^1\Delta_g$ state. An energy decomposition analysis showed that the linear structures $C_2(cAAC)_2$ and $C_2(NHC)_2$ may straightforwardly be explained in terms of dative bonds. It does not mean that the description as cumulenes is wrong. Bonding models are not wrong or right, they are more or less useful. They are fictions that were designed in order to convey quantum theoretical information about chemical bonding into a picture which is accessible to human perception. Future studies of the chemical reactivities of the molecules will show which model is more useful to explain experimental observation. Dutton and co-workers reported the calculated bond dissociation energies for the reactions $C_2L_2 \rightarrow C_2 + 2$ L. The calculations predict rather large values of $D_e = 180.8$ kcal/mol for L = NHC^{Me} and $D_e = 238.4$ kcal/mol for L = $cAAC^{Me}$.[65]

The above results suggest that carbene ligands such as NHC and cAAC are particularly useful to stabilize diatomic molecules E_2. A theoretical study by Wilson, Couchman and Dutton compared the donor strength of NHC with phosphines PR_3 (R = H, Me, Ph) in complexes E_2L_2 for atoms E of group 14 (C - Pb) and group 15 (N - Bi).[66] In all cases the NHC complexes were found to be more stable than the phosphine adducts.

5. Two-Centre Complexes of Boron

In 2011, a theoretical paper was published about complexes of group-13 diatomic molecules E_2 (E = B – In) which are stabilized by two NHC ligands.[67] Figure 15 shows the theoretically predicted geometries of the molecules $E_2(NHC)_2$. None of the molecules was experimentally known at that time. It becomes obvious that the heavier systems with E = Al – In have antiperiplanar arrangements of the ligands like the group-14 homologues where E = Si – Sn. In contrast, the boron compound $B_2(NHC)_2$ has a linear structure where the calculated boron-boron distance is very short (1.470 Å). The theoretically predicted bond length is in accord with a standard value for a B≡B triple bond (1.46 Å).[68] The related molecule $B_2(CO)_2$ had earlier been prepared in a low-temperature matrix.[69] The comparison of the vibrational spectrum with calculated values revealed that the molecule is a dicarbonyl complex OC→B≡B←CO which has a boron-boron triple bond with an interatomic distance of 1.459 Å.[69,70] The isoelectronic dianion $[B_2(BO)_2]^{2-}$ was studied theoretically and the anion $[B_2(BO)_2]^-$ was observed in the gas phase.[71]

Figure 15

The linear structure of $B_2(NHC)_2$ requires two vacant σ MOs of B_2 as acceptor orbitals for donor-acceptor interactions NHC→B≡B←NHC. Figure 16 shows the MO diagram of B_2 with (a) the $X^3\Sigma_g^-$ ground state and (b) the highly excited $(3)^1\Sigma_g^+$ state which enables σ-donation of the ligand orbitals into (c) the $1\sigma_u$ MO (+,- donation) and (d) the $2\sigma_g$ MO (+,+ donation). The calculations suggest that the dative bonds NHC→B≡B←NHC which are enhanced by NHC←B≡B→NHC π-backdonation from the $1\pi_u/1\pi_u$' MOs are very strong. The theoretical bond dissociation energy of D_e = 187.7 kcal/mol (Figure 16e) gives an average value of 94 kcal/mol for each NHC-boron bond. This is even higher than the calculated BDE for the carbonyl complex OC→B≡B←CO for where an average value of D_e = 78 kcal/mol was found.[70] Since bulky ligands at the nitrogen atoms of NHC may shield the B_2 triple bond from electrophilic attack, the complex $B_2(NHC)_2$ was clearly a target for synthesis.

Figure 16

The first synthesis of a molecule with a B≡B triple bond that is stable under ambient temperature was achieved by Braunschweig and co-workers in 2012 who isolated $B_2(NHC^R)_2$

where R is a bulky aryl group (Figure 17a).[72] The experimental distances of the B-B bond (1.449 Å) and the B-C bonds (1.487 – 1.495 Å) and the linear structure of the central moiety are in perfect agreement with the calculated values. Two related complexes $B_2(L)_2$ where L is a saturated NHC^{sat} (Figure 17b) and a cAAC ligand (Figure 17c) have been isolated very recently by the same group.[73] The experimentally observed bond lengthening of the boron-boron bond can nicely be explained with the increase of the $L \leftarrow B \equiv B \rightarrow L$ π-backdonation which has the trend NHC < NHC^{sat} < cAAC. Theoretical studies of $B_2(PMe_3)_2$ suggest that the phosphine ligands are more weakly bonded (D_e = 131.0 kcal/mol) than $B_2(NHC^{Me})_2$ (D_e = 187.7 kcal/mol) but the average bond strength of 65.6 kcal/mol is still rather high.[74] With very bulky phosphines PR_3 it is feasible that $B_2(PR_3)_2$, which would additionally be stabilized by dispersion interactions, could be isolated at normal conditions as well.

Figure 17

The assignment of a boron-boron triple bond to $B_2(NHC^R)_2$ has been challenged with arguments which are based on experimental values.[75] It was shown in a reply that the rationale in the paper is faulty and that the arguments which are used rest on unfounded assumptions.[76] Further experimental studies clearly support the notion of a triple bond in the diboron NHC complex.[77]

6. Three-Centre Cyclic Complexes of Boron and Silicon

The extension of experimental work one- and two centre adducts to three-centre cyclic complexes E_3L_3 where each main-group atoms E is stabilized by a σ-donor ligand L is presently in a status nascendi. While this review is written, two papers are in print which report about experimentally observed boron complexes $[B_3L_3]^+$ (L = N_2, CO)[78] and a silicon adduct Si_3L_3 (L = cAAC)[79] that open the door to another field of low-coordinated main-group compounds.

Figure 18, Table 1

Figure 18a shows the theoretically predicted geometries of the two cation complexes of boron $[B_3(NN)_3]^+$ and $[B_3(CO)_3]^+$, which were identified in the gas phase. The cyclic B_3^+ moiety is the smallest experimentally observed 2π aromate.[78] Figure 18b displays the HOMO of $[B_3(NN)_3]^+$ and that of naked B_3^+ which shows that the delocalized π orbital of the triboron core moiety is only slightly extended to the N_2 ligands. The shape of the LUMO of B_3^+ is perfectly suited for $L \rightarrow B_3^+$ σ donation from the lone-pair orbitals of N_2 and CO to the boron cation. The results of an energy decomposition analysis (EDA)[80] of $[B_3(NN)_3]^+$ and $[B_3(CO)_3]^+$ suggest that the $L \rightarrow B_3^+$ σ donation is clearly more important than the $L \leftarrow B_3^+$ π backdonation. Table 1 gives the numerical results of the interactions in the complexes $[B_3L_3]^+$ between one ligand L and the remaining fragment $[B_3L_2]^+$. The out-of-plane $L \leftarrow [B_3L_2]^+$ $\pi_\perp$-backdonation of the HOMO is even weaker than the in-plane $L \leftarrow [B_3L_2]^+$ $\pi_\parallel$-backdonation. The dominant orbital term is the $L \rightarrow [B_3L_2]^+$ σ-donation. Table 1 shows also the shape of the HOMO of N_2 and the LUMO of $[B_3(NN)_2]^+$ which give rise to the $N_2 \rightarrow [B_3(NN)_2]^+$ σ-donation. The associated charge flow $\Delta\rho_1$ nicely illustrates the change in the electronic structure which comes from the orbital interaction. The results which are shown in Table 1 demonstrate the potential of modern methods of bonding analysis. More details about the method are found in the literature.[80,81]

The calculations of $[B_3L_3]^+$ at the CCSD(T)/cc-pVTZ level give rather high bond dissociation energies of the three ligands which amount to D_o = 115.0 kcal/mol for L = N_2 and 183.6 kcal/mol for L = CO (Figure 18a). This gives an average BDE of 61 kcal/mol for one CO ligand. It is conceivable that more strongly bonded ligands which provide steric protection might lead to compounds that are stable under ambient temperature. A theoretical study by Tai and Nguyen predict an average BDE of the NHC ligands in $[B_3(NHC)_3]^+$ of D_e = 99.1 kcal/mol.[82] Note that the isolation of NHC→B≡B←NHC in 2012[72] came after the observation of OC→B≡B←CO in a low-temperature matrix 2002.[69]

Scheme 3

Scheme 3 schematically displays the bonding situation in the cation complexes $[E_3L_3]^+$ which have dative bonds and the dianions $[E_3R_3]^{2-}$ that nicely show the different types of bonding. The dianions of the heaver group-13 atoms gallium and aluminum where R is a bulky aryl group are well known species.[83] Very recently, the boron homologue $[B_3(NCy)_3]^{2-}$ (Cy = *cyclo*-C_6H_{11}) became isolated.[84] It is interesting that the eight-electron cation B_3^+ and the eleven-electron dianion B_3^{2-} exhibit the same 2π aromaticity. Unlike the cation $[E_3L_3]^+$, the dianion $[E_3R_3]^{2-}$ possess electron-sharing bonds E-R and thus, they are not considered here.

The most recent achievement in the field of three-centre cyclic complexes E_3L_3 is the synthesis of the triatomic silicon(0) complex $Si_3(cAAC)_3$ whose structure was determined by x-ray analysis.[79] The molecule was obtained by reacting the complex cAAC→$SiCl_4$ with KC_8 at low temperature in THF solution (reaction 1). It is interesting that the related reaction of the complex NHC→$SiCl_4$ which was reported in 2008 gives the two-centre complex $Si_2(NHC)_2$ (reaction 2).[58]

$$3\ \text{cAAC}\rightarrow\text{SiCl}_4 + 12\ \text{KC}_8 \rightarrow \text{Si}_3(\text{cAAC})_3 \qquad (1)$$

$$2\ \text{NHC}\rightarrow\text{SiCl}_4 + 8\ \text{KC}_8 \rightarrow \text{Si}_2(\text{NHC})_2 \qquad (2)$$

Figure 19

Figure 19a shows the geometry of the molecule and the most important bond lengths and angles. The Si_3 ring has pyramidally coordinated silicon atoms where two cAAC ligands are on the same side of the ring while the third ligand is at the opposite side. This explains why there are two identical Si-Si bonds (2.398 Å) and one shorter Si-Si distance (2.369 Å) which are slightly longer than a Si-Si single bond (2.32 Å).[85] The analysis of the bonding situation showed that the silicon atoms have a π-type lone-pair orbital which makes the Si_3 ring a formal 6π aromate.[79] The interactions of the π electrons are destabilizing, because all π valence orbitals of Si_3 are occupied. Inspection of the bonding orbitals of the cAAC-Si bonds showed that the π orbitals of silicon are strongly engaged in cAAC←Si π backdonation which leads to nearly unpolar π bonds. The cAAC-Si bonds have significant double bond character which consists of cAAC→Si σ donation and cAAC←Si π backdonation. This is indicated in the schematic presentation of the bonding situation in Figure 19b.

7. Concluding Remarks

The research described in this short review highlights the progress that has been made in the last decade in the chemistry of low-coordinated boron and group-14 atoms carbon, silicon, germanium and tin. Spectacular progress has particularly been made for boron and silicon compounds, where molecular architectures were experimentally realized that were not known until recently. This is schematically shown in Figure 20.

Figure 20

The synthesis of molecules with boron-boron triple bonds, tri-coordinated boron compounds with lone-pairs at boron and three-membered cyclic species of boron and silicon are remarkable highlights of synthetic main-group chemistry. The model of dative bonding and the use of modern quantum chemical methods are powerful tools for finding new molecules that possess unusual bonds. The knowledge that has been gained through the interplay of theoretical and experimental research provides a basis for further studies, which will definitely see more progress in the upcoming years. The combination of sophisticated experimental techniques in the hand of inventive chemists who team up with knowledgeable theoreticians is a guarantee for more breakthroughs to come.

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turned out that this does not hold for carbones CL_2 with real ligands L and that the appropriate configuration for the carbon(0) atom is $C(2s^2\ 2p_{\pi\perp}^2 2p_\sigma^0 2p_{\pi\parallel}^0)$.

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Captions and Legends

Scheme 1. Display of the experimentally observed different reactivities of a carbone CL_2 and a carbene CR_2. (a) Addition of B_2H_6 to $C(PPh_3)_2$ yields first the mono adduct $(PPh_3)_2C{\rightarrow}BH_3$. Further reaction with excess B_2H_6 yields to bis-adduct $[(PPh_3)_2C{\rightrightarrows}B_2H_4(\mu\text{-}H)]^+$ (top)[33] while treatment with the strong Lewis acid $B(C_6F_5)_3$ gives the borinium cation complex $[(PPh_3)_2C{\rightrightarrows}BH_2]^+$ (bottom).[37] (b) Addition of B_2H_6 to NHC also yields first the mono adduct $NHC{\rightarrow}BH_3$. Further reaction with excess B_2H_6 does not take place while treatment with the strong Lewis acid $B(C_6F_5)_3$ gives the hydrogen bridged cation $[NHC\text{-}BH_2(\mu\text{-}H)BH_2\text{-}NHC]^+$.[37]

Scheme 2. Schematic view of the experimentally observed addition of CX_2 (X = O, S) to (a) linear tetraaminoallenes[38] and (b) bent carbodiphosphorane[9] which demonstrates the similar chemical reactivity of the two compound classes.

Scheme 3. Schematic represenation of the bonding situation in (a) cation complexes $[E_3L_3]^+$ which have L→E dative bonds and (b) in dianions $[E_3R_3]^{2-}$ which have E-R electron-sharing bonds.

Figure 1. Geometry of the complex $(Ph_3P)_2C{\rightrightarrows}CO_2$. Calculated bond lengths in Å, angles in degree. Experimental values are given in parentheses. The values are taken from ref. 9.

Figure 2. Schematic representation of the donor-acceptor interactions L→C←L in carbones CL_2 between two σ-donor ligands L and carbon atom in the ^1D state with the electron configuration $2s^2 2p_{\pi\perp}^2 2p_{\sigma}^0 2p_{\pi\parallel}^0$. The vacant $2p_{\sigma}^0$ and $2p_{\pi\parallel}^0$ AOs of carbon serve as acceptor orbitals for the donation of the +,+(σ) and +,-($\pi_\parallel$) combination of the ligand orbitals.

Figure 3. Geometry of the first isolated carbodicarbene $C(NHC)_2$. Calculated (experimental) bond angle in degree. The data are taken from refs. 24b (calc.) and 26 (exper.).

Figure 4. Experimental geometries of the complexes (a) $[(PPh_3)_2C{\rightrightarrows}B_2H_4(\mu\text{-}H)]^+$ and (b) $[(PPh_3)_2C{\rightrightarrows}BH_2]^+$. The bond lengths (Å) and bond angles (degree) are taken from refs. 33 and 37.

Figure 5. Schematic representation of (a) the isolated "metallaallenes" (Ref. 45) and (b) a carbodicarbene.

Figure 6. Schematic representation of the isolated silylones and germylones (Refs. 48, 49).

Figure 7. Top: Schematic view of the orbital interactions in CL_2 and $(BH)L_2$. Experimental and calculated excitation energies for C and BH. Bottom: Interaction energies ΔE_{int} between the fragments in the frozen geometries and electronic reference states and bond dissociation energies D_e. All values in kcal/mol. Ref. 51.

Figure 8. Geometries of the borylene complex $(BH)(cAAC)_2$, the radical cation $[(BH)(CAAC)_2]^{+\bullet}$ and the protonated $(BH_2)^+(cAAC)_2$. Experimental bond lengths and angles with calculated data [in brackets]. The values are taken from ref. 53.

Figure 9. Schematic view of the borylene complexes L→(BR)←L which were recently synthesized and structurally characterized. (a) Complex with two oxazol-2-ylidene ligands that was isolated by Kinjo[54] and (b) dicarbonyl complex synthesized by Braunschweig.[55]

Figure 10. Schematic view of the groups-14 complexes $E_2(NHC)_2$ with E = Si, Ge, Sn that have been isolated[58-60]

Figure 11. Schematic view of the most important valence orbitals of group-14 diatomic moleculs E_2 (E = Si – Sn) and the orbital occupation in (a) the $X^3\Sigma_g^-$ ground state and (b) $^1\Delta_g$ excited state. Schematic view of (c) out-of-phase (+/-) donation of the ligand σ orbitals into the vacant $1\pi_u'$ orbital of E_2 and (d) in-phase (+/+) donation of the ligand σ orbitals into the vacant $1\pi_g'$ orbital of E_2.

Figure 12. (a) Calculated geometry of $C_2(NHC)_2$.[65] (b) Experimental geometry of cAAC-CC-cAAC; (c) Experimental geometry of $[cAAC\text{-}CC\text{-}cAAC]^+$; (d) Experimental geometry of $[cAAC\text{-}CC\text{-}cAAC]^{2+}$.[64]

Figure 13. Graphical display of the attempted deprotonation of $[C_2H_2(NHC^R)_2]^{2+}$ which turned into a reduction yielding the neutral species $C_2H_2(NHC^R)_2$ instead of $C_2(NHC^R)_2$.[65]

Figure 14. Schematic representation of some electronic states of C_2. (a) $X^1\Sigma_g^+$ ground state. (b) Excited $(1)^1\Delta_g$ state. (c) Excited $(2)^1\Delta_g$ state.

Figure 15. Calculated geometries and most important bond lengths [Å] and bond angles [°] of the compounds $E_2(NHC)_2$ (E = B – In).[67]

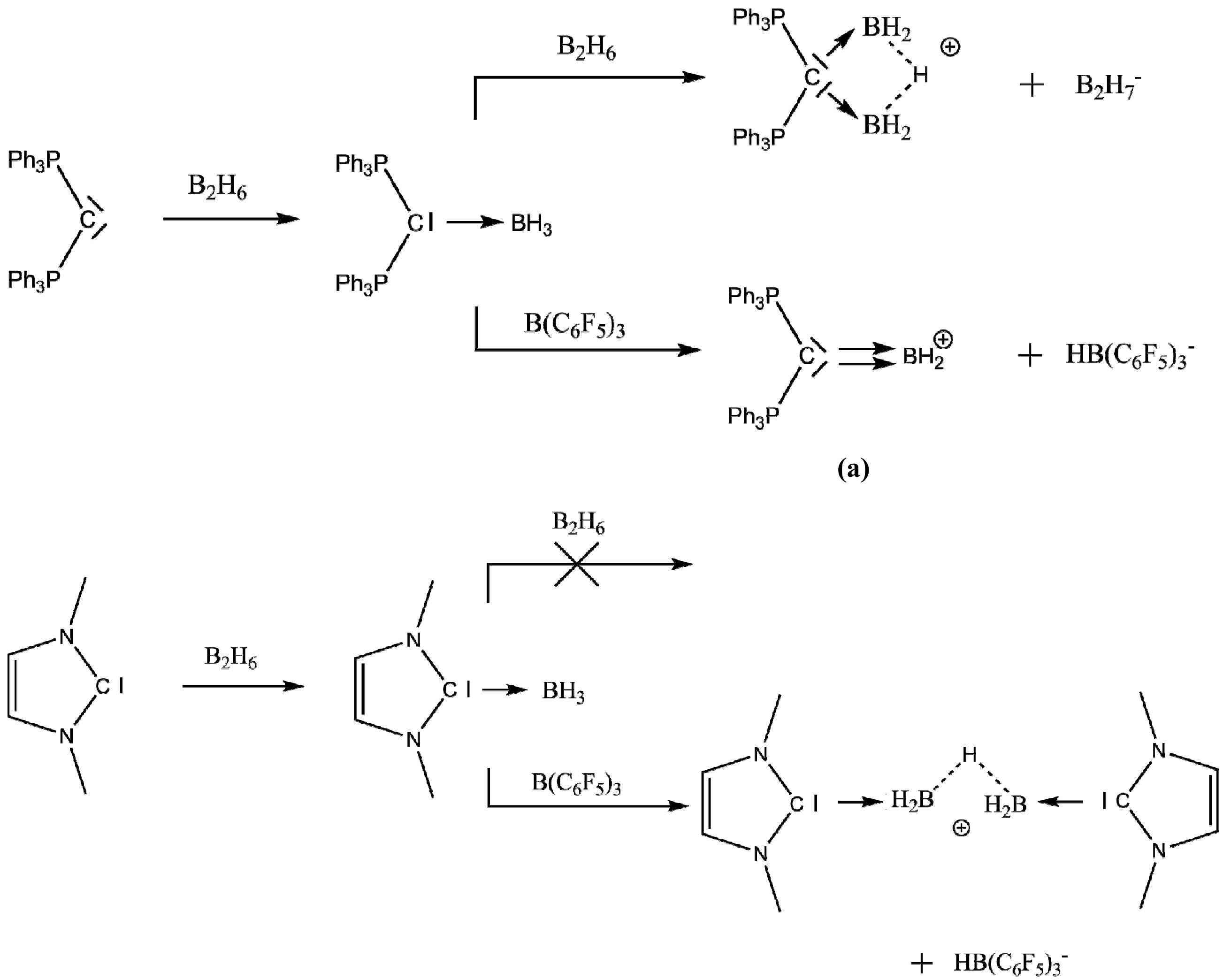
Figure 16. Schematic view of the most important valence orbitals of B_2 and the orbital occupation in (a) the $X^3\Sigma_g^-$ ground state and (b) $(3)^1\Sigma_g^+$ excited state. Schematic view of (c) out-of-phase (+/-) donation of the ligand σ orbitals into the vacant $1\pi_u'$ orbital of E_2 and (d) in-phase (+/+) donation of the ligand σ orbitals into the vacant $1\pi_g'$ orbital of E_2.

Figure 17. Schematic view of the isolated complexes L→B≡B←L with different ligands L and measured bond lengths L-B and B-B (in Å). (a) L = NHC. (b) L = NHC^{sat}. (b) L = cAAC. [72,73]

Figure 18. (a) Calculated equilibrium geometries of the complexes $[B_3(NN)_3]^+$ and $[B_3(CO)_3]^+$ at CCSD(T)/cc-pVTZ. Bond lengths are given in Å. Calculated bond dissociation energies D_e and D_o at CCSD(T)/cc-pVTZ.[78] (b) Plot of the HOMO of $[B_3(NN)_3]^+$ and HOMO and LUMO of B_3^+.

Figure 19. Experimental geometry and most important bond lengths [Å] and angle [°] of the complex $Si_3(CAAC)_3$. Calculated values at BP86/def2-SVP are given in parentheses. The values are taken from ref. 79.

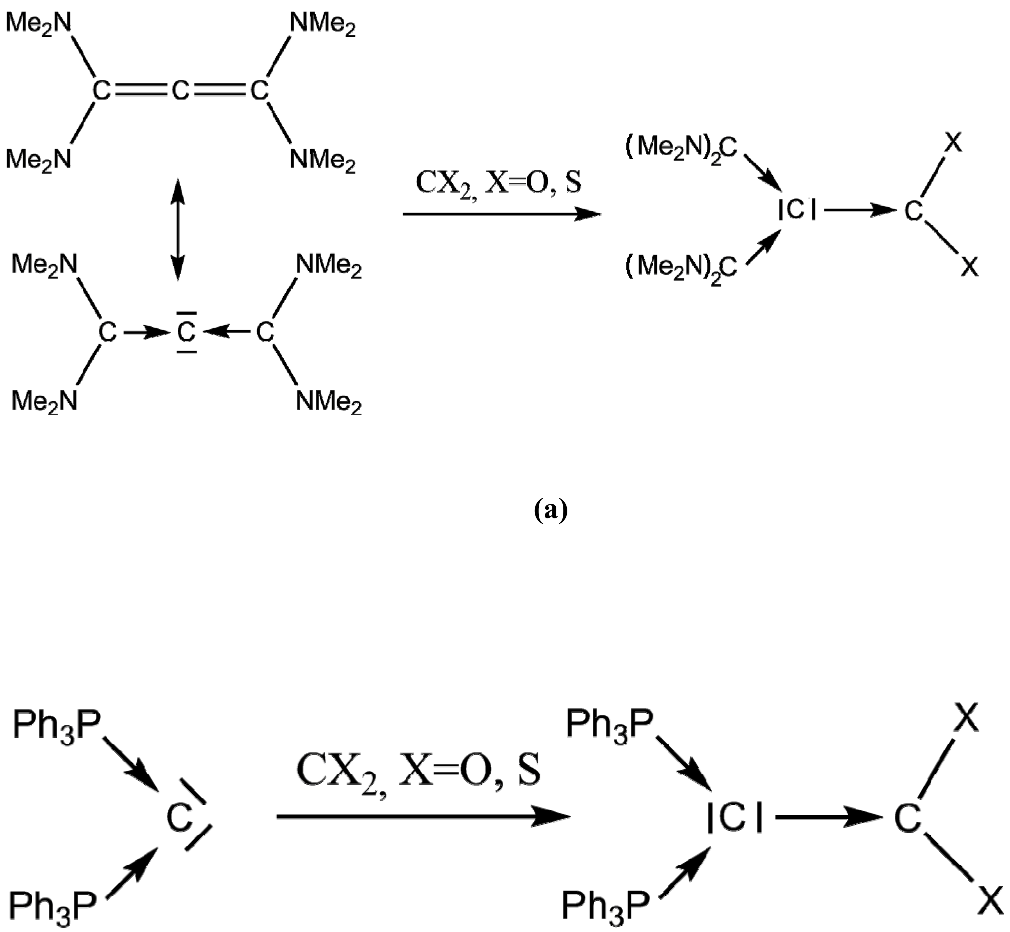
Figure 20. Schematic representation of one-, two- and three-centre complexes of (a) boron and (b) silicon which have been experimentally observed.


Ph3P
Ph3P
C
B2H6
Ph3P
Ph3P
C
BH3
B2H6
Ph3P
Ph3P
C
BH2
H
BH2
⊕
+ B2H7-
B(C6F5)3
Ph3P
Ph3P
C
BH2 ⊕
+ HB(C6F5)3-
N
N
C
B2H6
N
N
C
BH3
B2H6
B(C6F5)3
N
N
C
H2B
H
H2B
⊕
C
N
N
+ HB(C6F5)3-

(a)

(b)

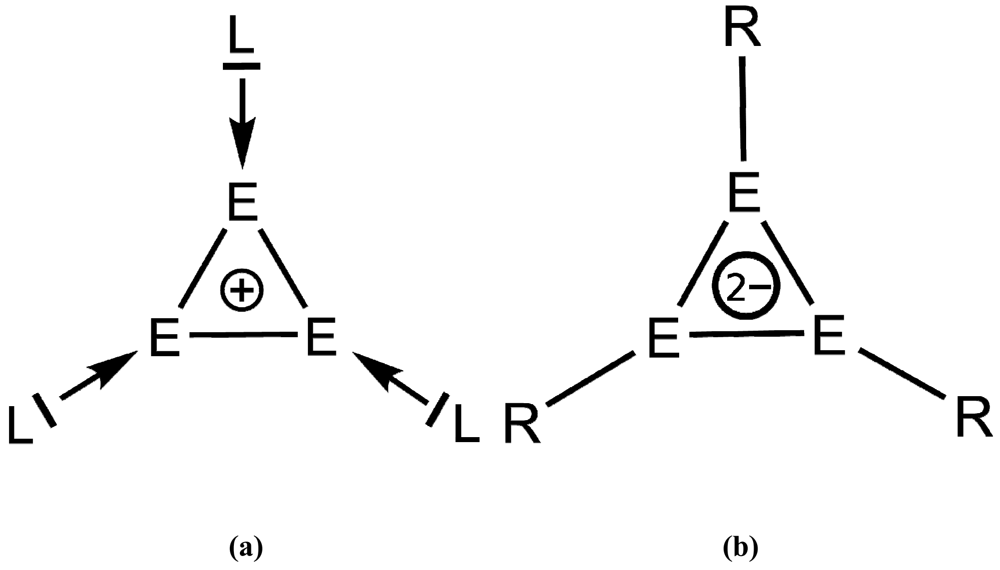
Scheme 1


Me2N
NMe2
Me2N
NMe2
CX2, X=O, S
(Me2N)2C
(Me2N)2C
C
X
X
Ph3P
Ph3P
CX2, X=O, S
Ph3P
Ph3P
C
X
X

(a)

(b)

Scheme 2



Scheme 3

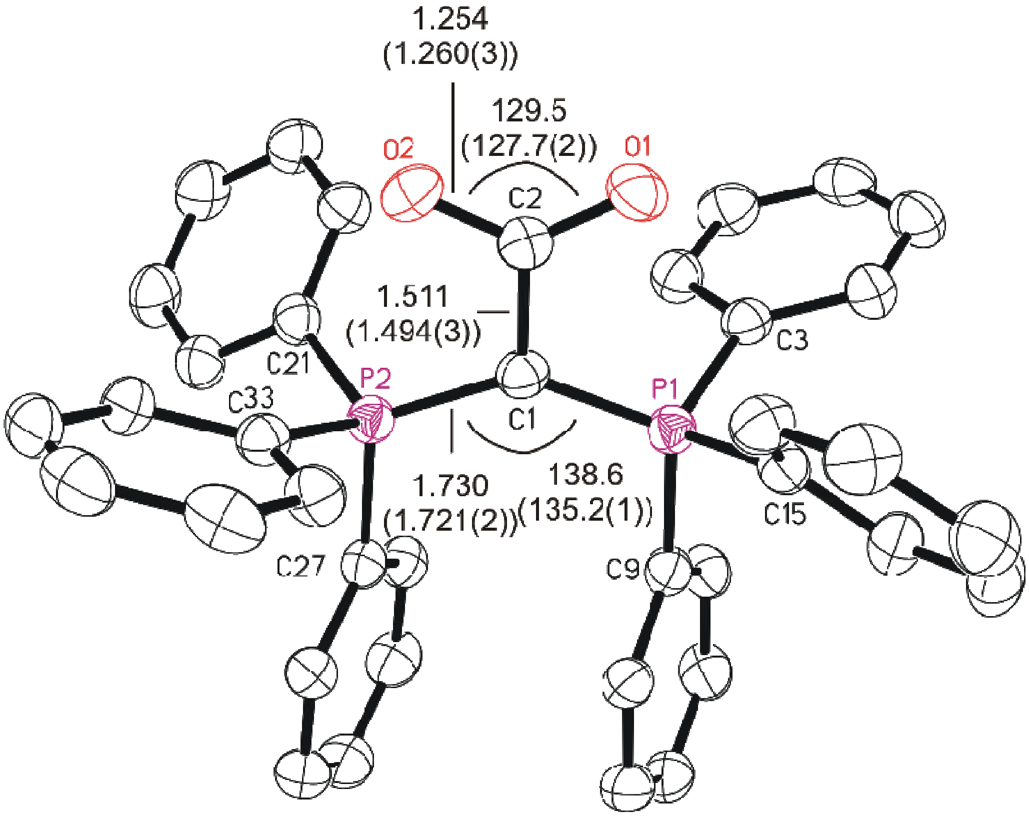

1.254
(1.260(3))
129.5
(127.7(2))
O2
O1
C2
1.511
(1.494(3))
C21
P2
C33
C1
P1
C3
1.730
(1.721(2))
138.6
(135.2(1))
C15
C27
C9

Figure 1

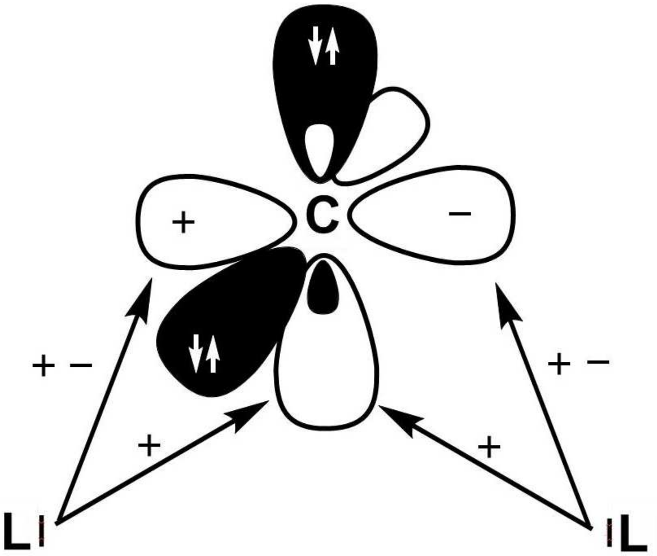


Figure 2

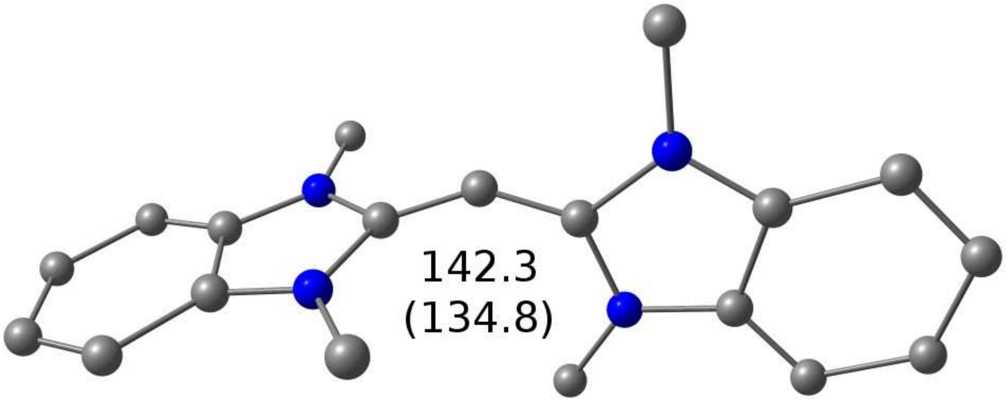
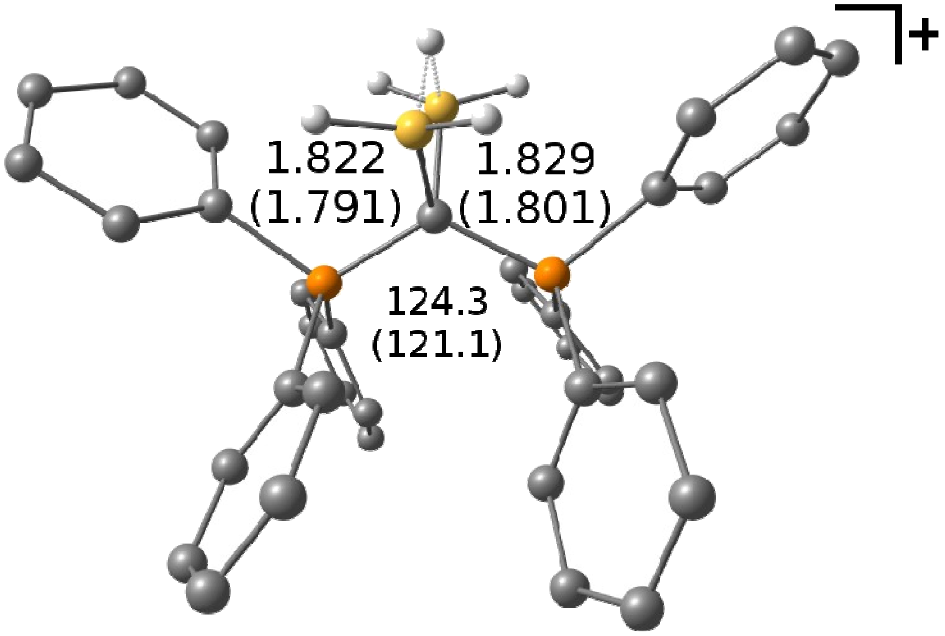
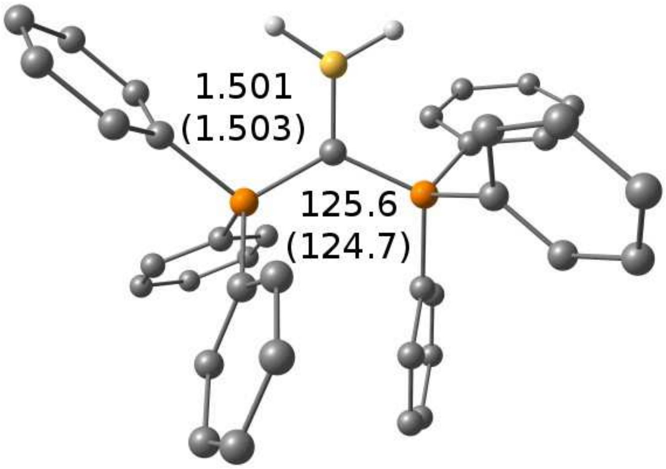


Figure 3

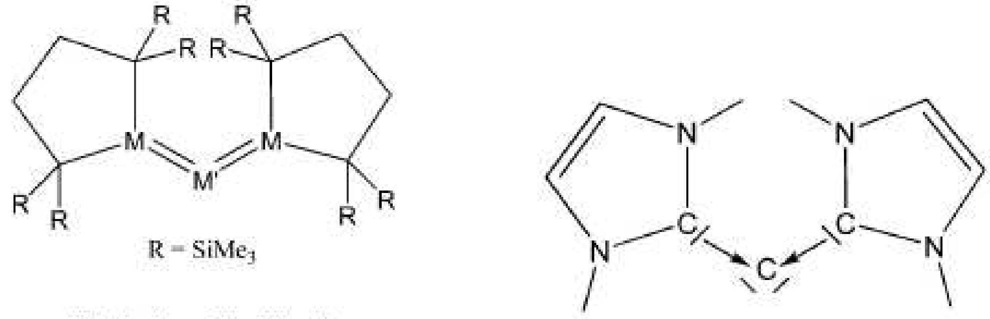


(a)



(b)

Figure 4



Trisilaallene M = M' = Si
Trigermaallene M = M' = Ge
1,3-Digermasilaallene M = Ge, M' = Si

(a)

Carbodicarbene

(b)

Figure 5

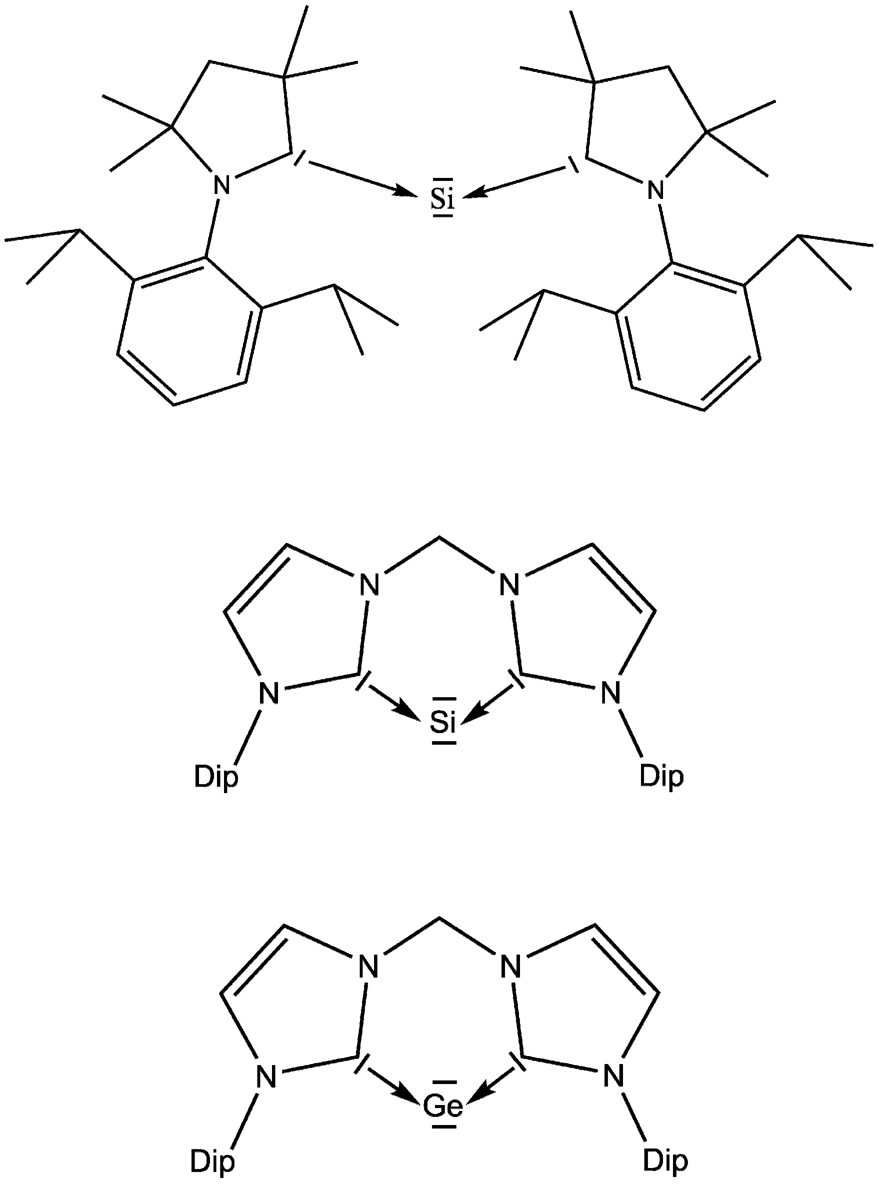
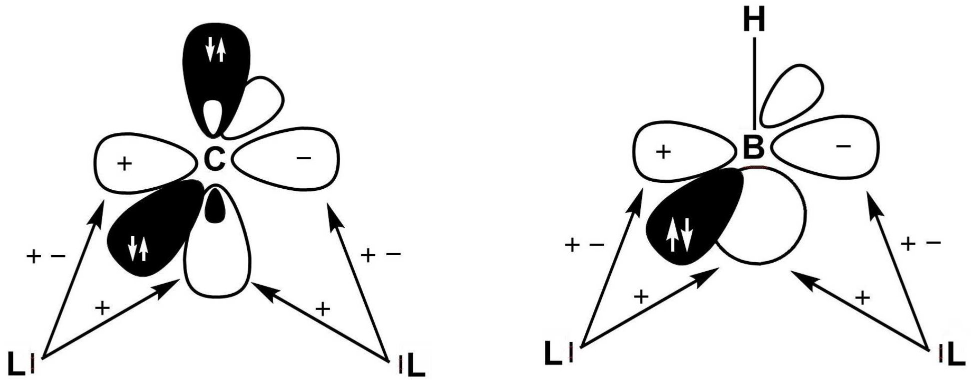


Figure 6



(a) (b)

C: $X\,^3P \rightarrow {}^1D$ 29.1 kcal/mol (calc.: 43.5 kcal/mol)

BH: $X\,^1\Sigma^+ \rightarrow {}^1\Delta$ 131.5 kcal/mol (calc.: 128.4 kcal/mol)

L	CL_2		$(BH)L_2$	
	ΔE_{int}	D_e	ΔE_{int}	D_e
PPh_3	189.3	158.5	226.0	81.6
CO	233.8	206.9	262.2	120.6
NHC	260.8	210.0	314.9	150.8

Figure 7

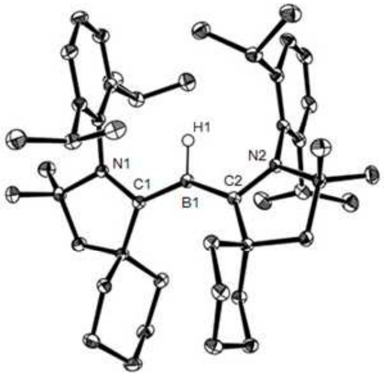
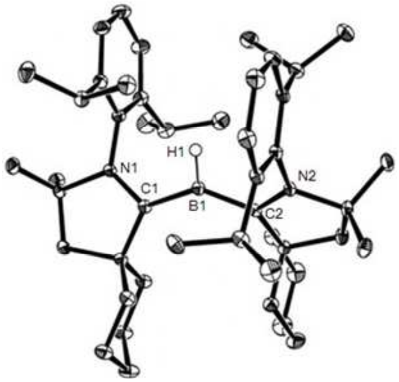
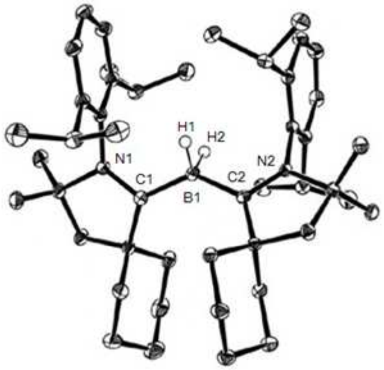
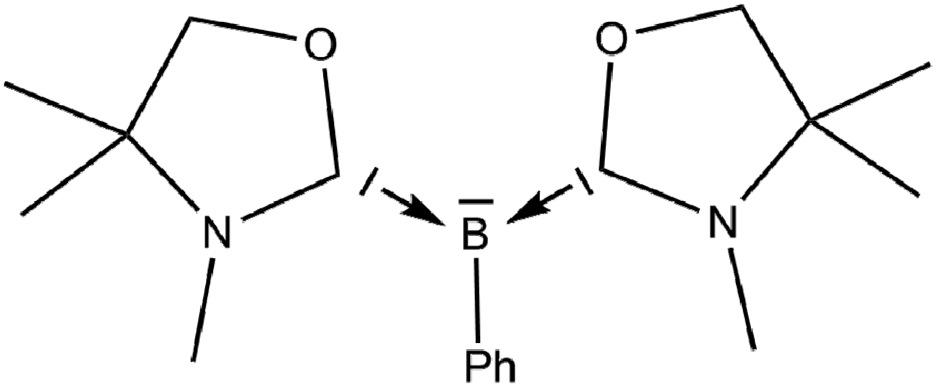
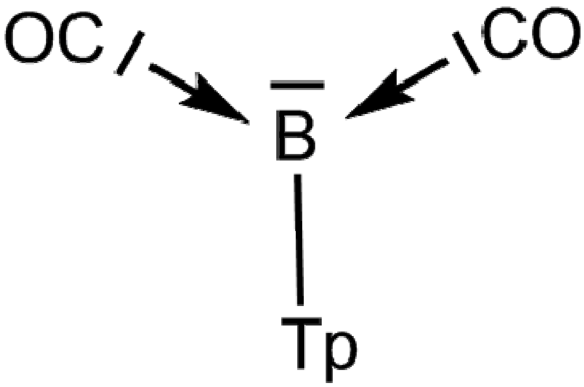
	$[(BH)(CAAC)_2]$	$[(BH)(CAAC)_2]^{+\bullet}$	$[(BH_2)^+(CAAC)_2]$
			
B-C (Å)	1.5175(15) [1.535] 1.5165(15) [1.532]	1.583(2) [1.575] 1.582(2) [1.575]	1.610(3) [1.617] 1.607(3) [1.617]
C-N (Å)	1.3772(13) [1.394] 1.3905(13) [1.402]	1.3573(18) [1.357] 1.3534(17) [1.354]	1.308(3) [1.334] 1.308(3) [1.334]
C-B-C (°)	138.85(10) [140.1]	137.75(10) [139.6]	133.7(2) [136.4]
ε(HOMO)	-3.34 eV		
Proton Affinity	264.8 kcal/mol [PA(BH) = 204.6 kcal/mol]		

Figure 8



(a)



(b)

Figure 9

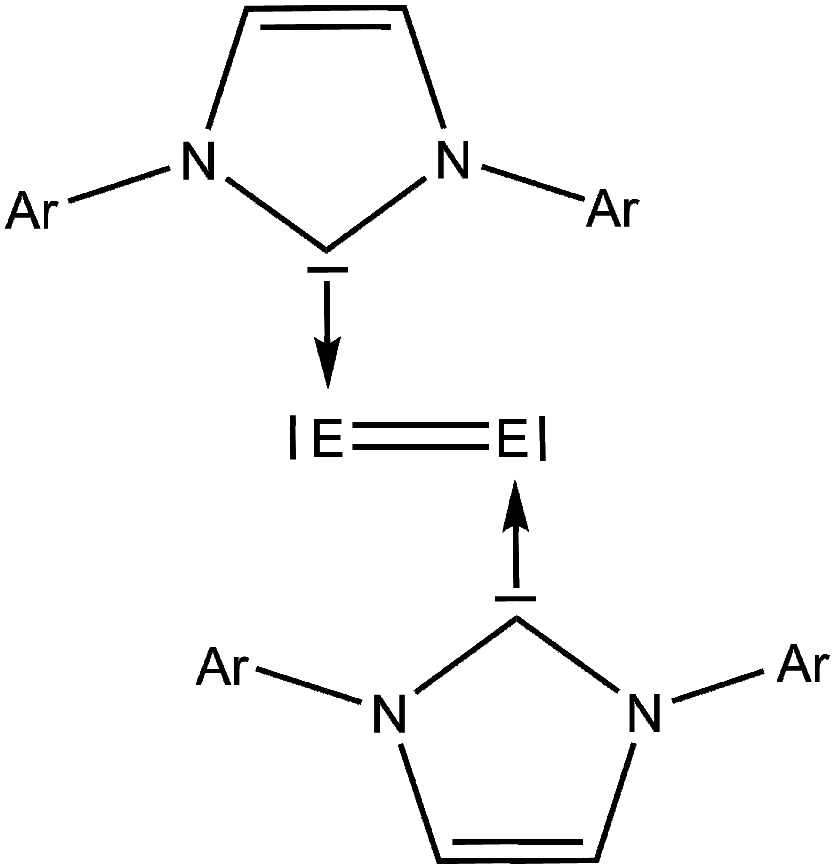
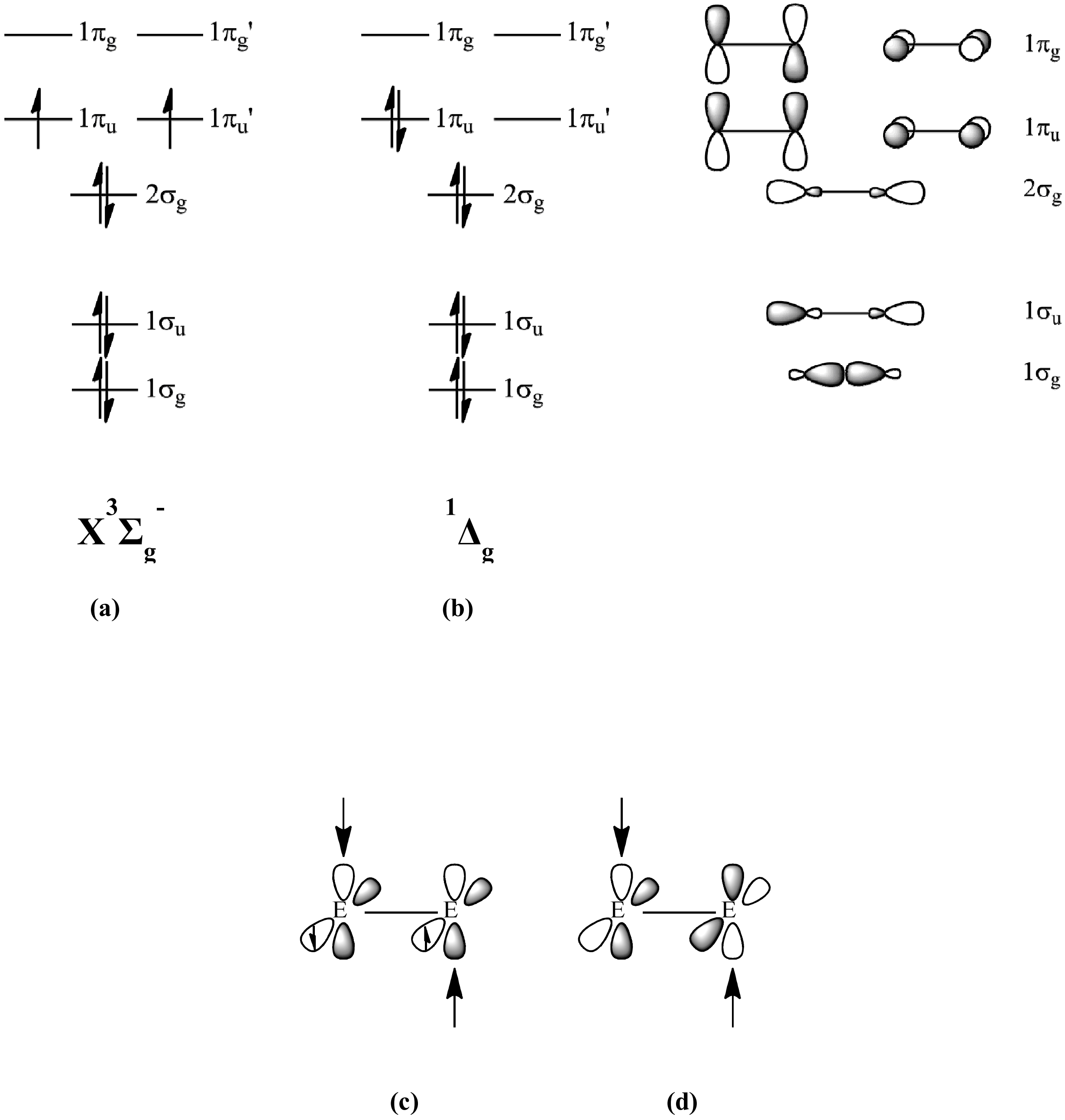


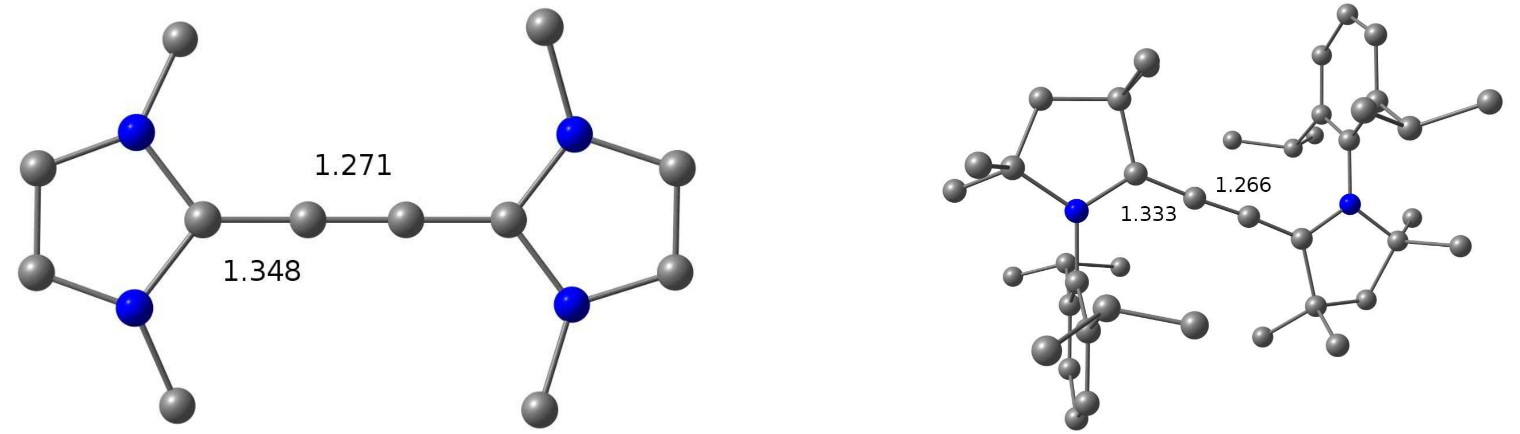
Figure 10



(a) (b)

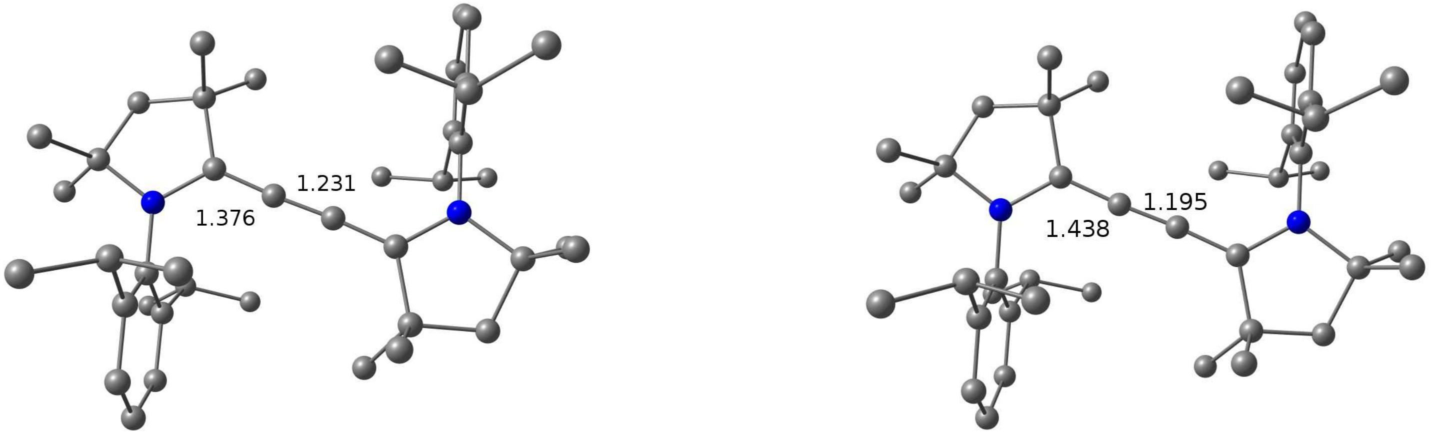
(c) (d)

Figure 11



(a) NHC-CC-NHC (Calc.)

(b) cAAC-CC-cAAC (Exper.)



(c) $[\text{cAAC-CC-cAAC}]^{+}$ (Exper.)

(d) $[\text{cAAC-CC-cAAC}]^{2+}$ (Exper.)

Figure 12

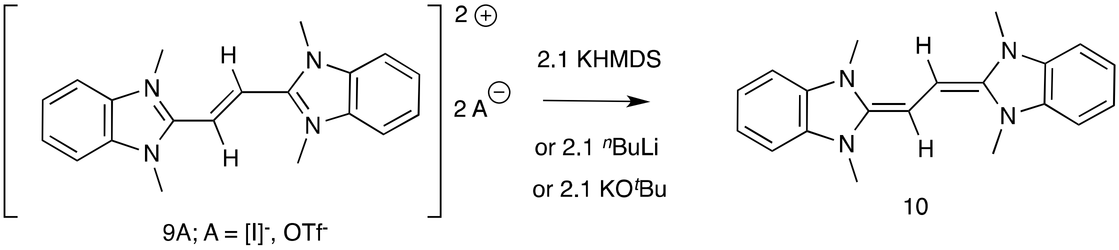


Figure 13

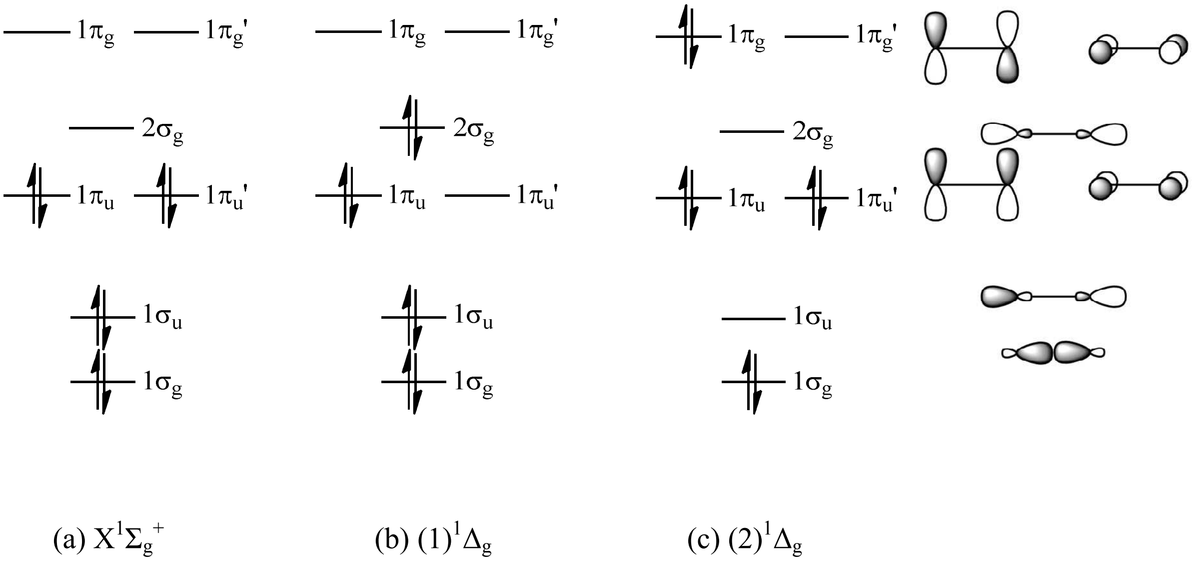

$1\pi_g$
$1\pi_g'$
$2\sigma_g$
$1\pi_u$
$1\pi_u'$
$1\sigma_u$
$1\sigma_g$
(a) $X^1\Sigma_g^+$
(b) $(1)^1\Delta_g$
(c) $(2)^1\Delta_g$

Figure 14

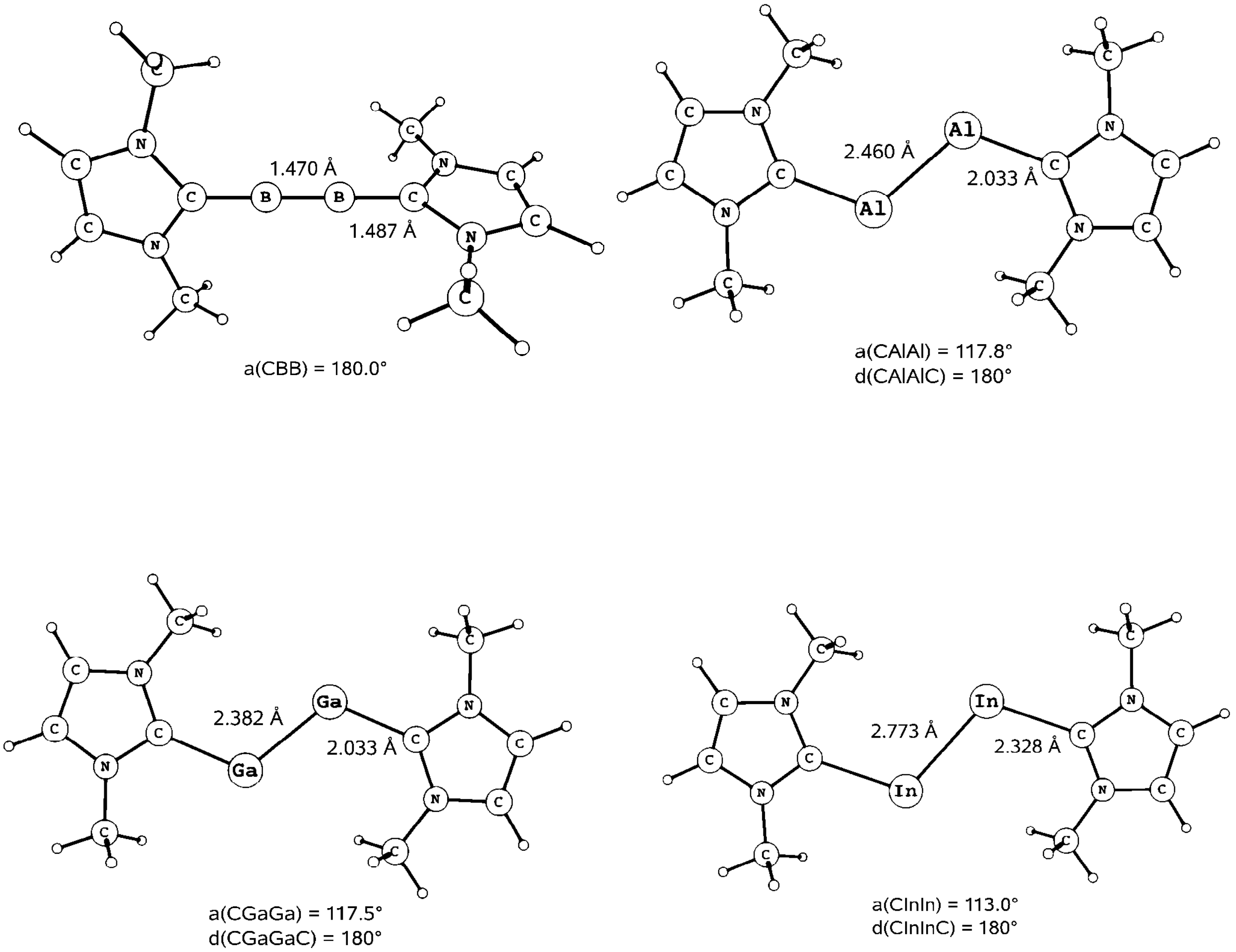
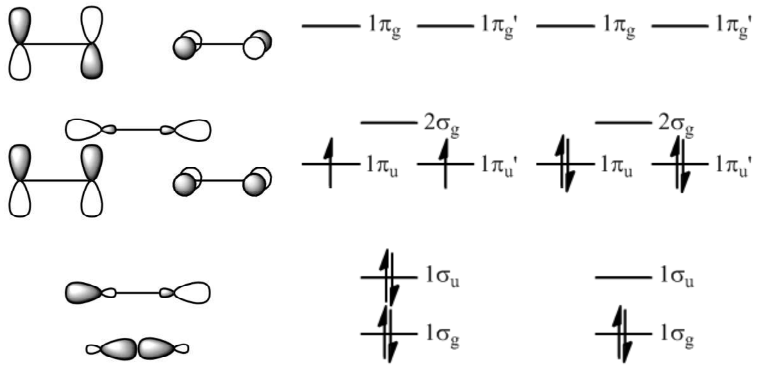
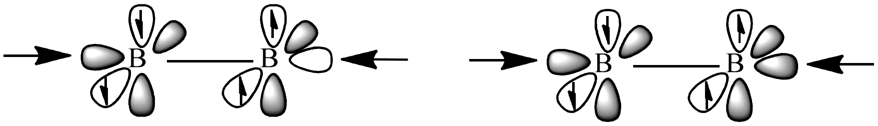

1.470 Å
1.487 Å
a(CBB) = 180.0°
2.460 Å
2.033 Å
a(CAlAl) = 117.8°
d(CAlAlC) = 180°
2.382 Å
2.033 Å
a(CGaGa) = 117.5°
d(CGaGaC) = 180°
2.773 Å
2.328 Å
a(CInIn) = 113.0°
d(CInInC) = 180°

Figure 15



(a) X $^3\Sigma_g^-$ **(b)** (3) $^1\Sigma_g^+$



(c) **(d)**

$B_2[X^3\Sigma_g^-] \longrightarrow B_2[(3)^1\Sigma_g^+]$ D_e = 106.4 kcal/mol

$B_2(NHC^{Me})_2 \longrightarrow B_2[X^3\Sigma_g^-] + 2\ NHC^{Me}$ D_e = 187.9 kcal/mol

(e)

Figure 16

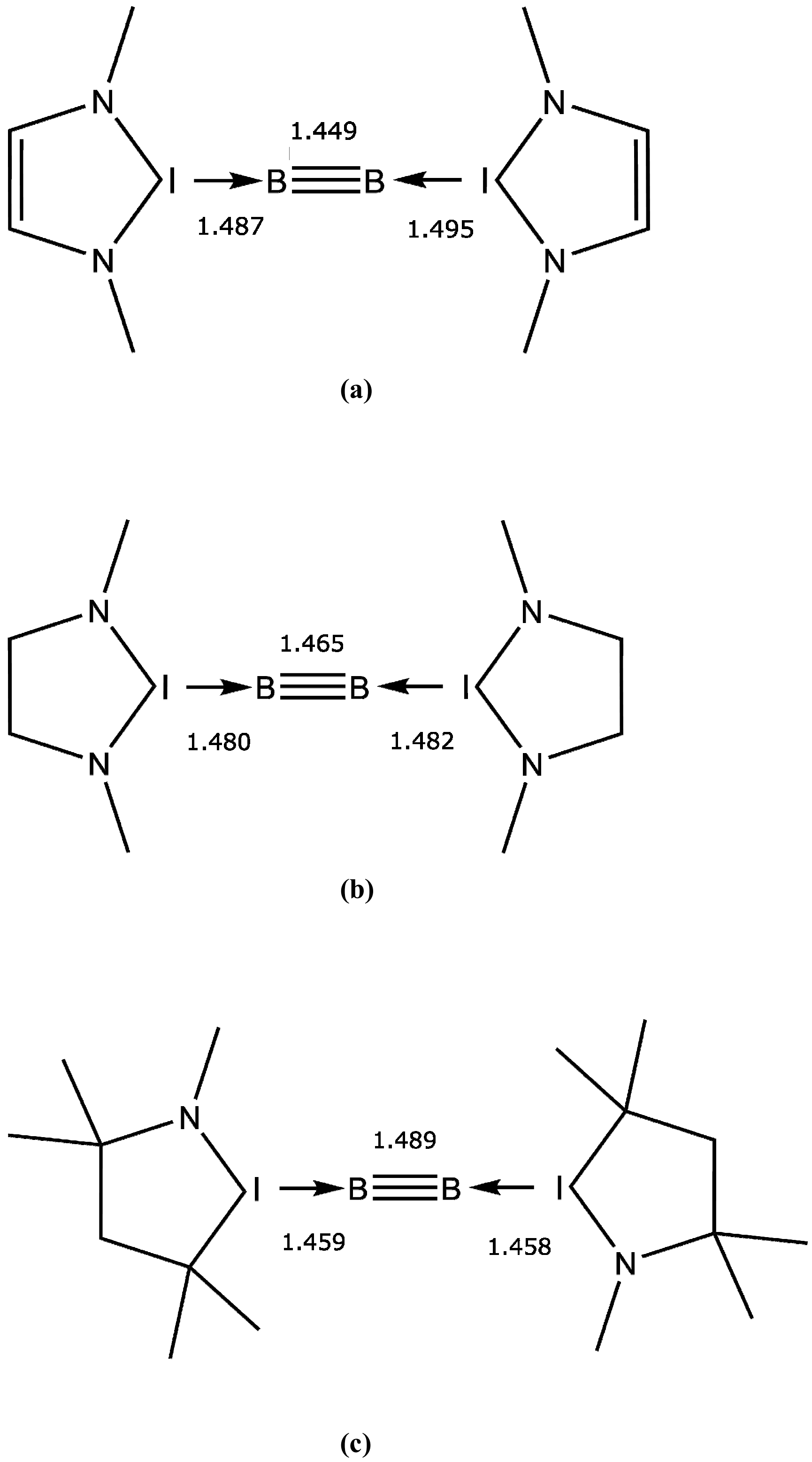
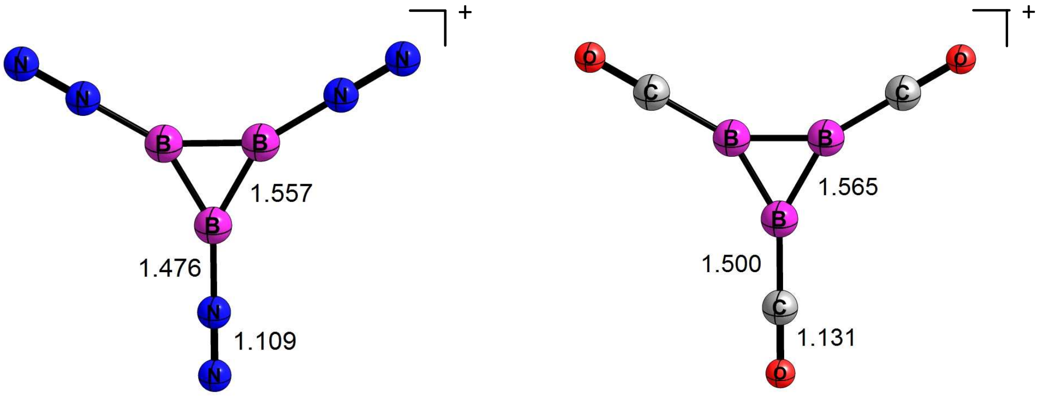


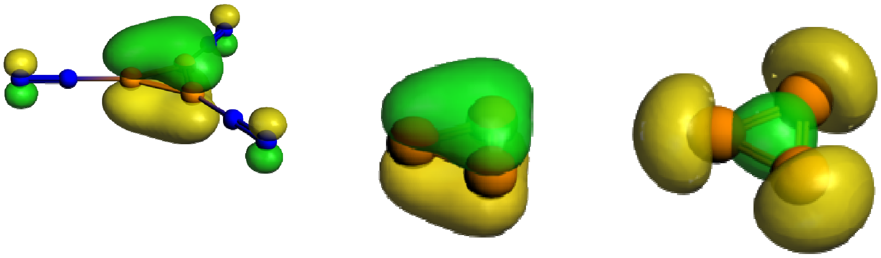
Figure 17



(a)

$[B_3(NN)_3]^+ \rightarrow (X^1A_1')\ B_3^+ + 3\ N_2$ $D_e = 123.5$ kcal/mol ($D_0 = 115.0$ kcal/mol)

$[B_3(CO)_3]^+ \rightarrow (X^1A_1')\ B_3^+ + 3\ CO$ $D_e = 193.2$ kcal/mol ($D_0 = 183.6$ kcal/mol)



HOMO $[B_3(NN)_3]^+$ HOMO B_3^+ LUMO B_3^+

(b)

Figure 18

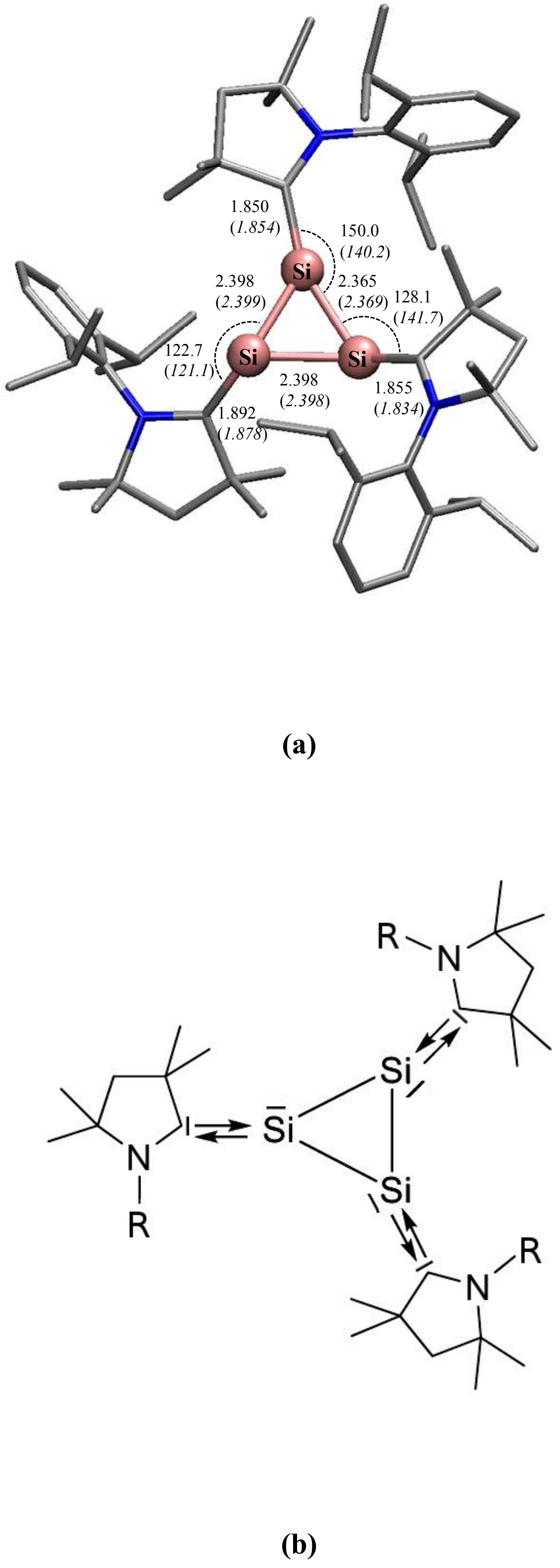

1.850
(1.854)
150.0
(140.2)
Si
2.398
(2.399)
2.365
(2.369)
128.1
(141.7)
122.7
(121.1)
Si
Si
2.398
(2.398)
1.855
(1.834)
1.892
(1.878)
(a)
R
N
Si
Si
N
R
Si
N
R
(b)

Figure 19

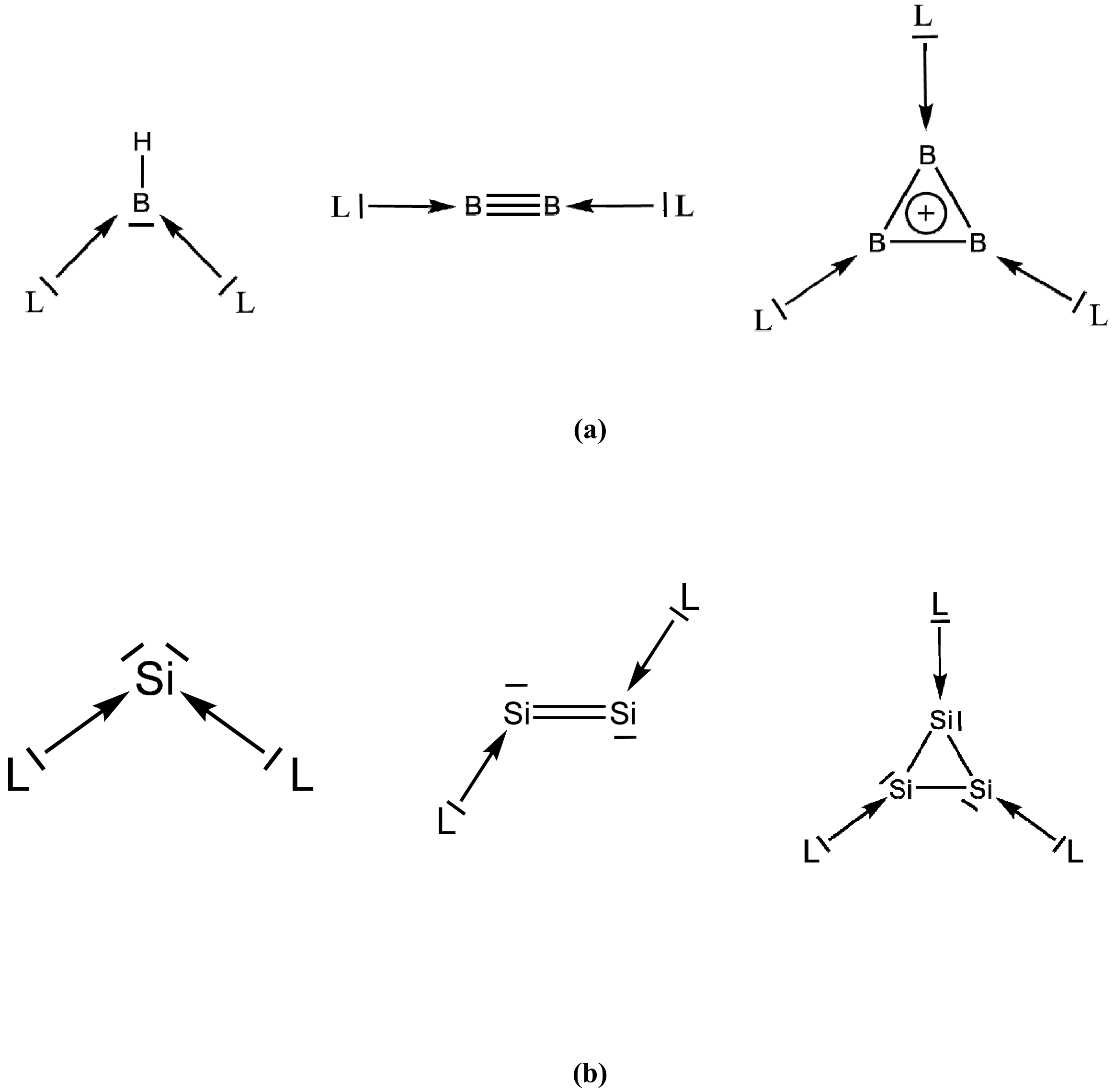


Figure 20

Table 1. Top: Energy decomposition analysis of $[B_3L_3]^+$ at the BP86/TZ2P+ level using CCSD(T)/cc-pVTZ optimized geometries. Energy values are given in kcal/mol. Values are taken from ref. **Error! Bookmark not defined.**. Bottom: Plot of the deformation densities Δρ of the pairwise orbital interactions between $[B_3(NN)_2]^+$ and N_2 in $[B_3(NN)_3]^+$ and associated stabilization energies ΔE in kcal/mol. The color code of the charge flow is red→blue. Shape of the most important interacting orbitals of $[B_3(NN)_2]^+$ and N_2.

Fragments	$[B_3(NN)_2]^+$ + N_2	$[B_3(CO)_2]^+$ + CO
ΔE_{int}	-50.7	-76.9
ΔE_{Pauli}	171.6	202.4
$\Delta E_{elstat}{}^{a}$	-79.3 (35.6%)	-100.2 (35.9%)
$\Delta E_{orb}{}^{a}$	-143.0 (64.3%)	-179.1 (64.1 %)
ΔE_{orb} $(1)^{b}$ L→$[B_3(NN)_2]^+$ σ-donation	-83.6 (58.5%)	-112.3 (62.7%)
ΔE_{orb} $(2)^{b}$ L←$[B_3(NN)_2]^+$ $\pi_{\parallel}$-backdonation	-20.3 (14.2%)	-26.7 (14.9%)
ΔE_{orb} $(3)^{b}$ L←$[B_3(NN)_2]^+$ $\pi_{\perp}$-backdonation	-18.5 (12.9%)	-19.6 (10.9%)
$\Delta E_{orb}(rest)^{b}$ polarization	-20.6 (14.4%)	-20.5 (12.2%)

[a] The value in parentheses gives the percentage contribution to the total attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$.

[b] The value in parentheses gives the percentage contribution to the total orbital interactions ΔE_{orb}