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[(${}^{Cl}Im^{Dipp}$)P═P(Dipp)][$GaCl_4$]: a polarized, cationic diphosphene†

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The reaction of the neutral diphosphanide [(${}^{Cl}Im^{Dipp}$)P–P(Cl)(Dipp)] (6) (${}^{Cl}Im^{Dipp}$ = 4,5-dichloro-1,3-bis(Dipp)-imidazol-2-yl; Dipp = 2,6-di-iso-propylphenyl) with methyl triflate (MeOTf) leads to the formation of cationic diphosphane [(${}^{Cl}Im^{Dipp}$)(Me)P–P(Cl)(Dipp)]$^+$ (8^+) in a stereoselective methylation. In contrast, reacting 6 with the Lewis acid $GaCl_3$ yields cationic diphosphene [(${}^{Cl}Im^{Dipp}$)P═P(Dipp)]$^+$ (7^+), which is explained by a low P–Cl bond dissociation energy. The significantly polarized P═P double bond in 7^+ allows for its utilization as an acceptor for nucleophiles – the reaction with Cl^- regenerates diphosphanide 6 and the reaction with PMe_3 gives cation [(${}^{Cl}Im^{Dipp}$)P–P(PMe_3)(Dipp)] (9^+). In depth DFT investigation provides detailed insights into the bonding situation of the reported compounds.

A few decades ago, the concept of kinetic stabilization by sterically demanding substituents provided a breakthrough in the field of multiple bonded compounds based on heavier main group elements.[1] In 1981 Yoshifuji succeeded in the preparation of the first diphosphene Mes*P═PMes* **1** by introducing the very bulky Mes* substituent (Mes* = 2,4,6-tri-*tert*-butylphenyl, "super-mesityl", Fig. 1).[2] Only recently, N-heterocyclic carbenes (NHCs) have gathered comparable attention in phosphorus chemistry for their ability to stabilize low-coordinate bonding environments in poly-phosphorus compounds, which can also be explained by thermodynamic stabilization (conjugated π-system, charge delocalization).[3] This was shown by Robinson who prepared the neutral (Im^{Dipp})P–P(Im^{Dipp}) (Im^{Dipp} = 1,3-bis(Dipp)-imidazol-2-yl)[4] and explored its further reactivity.[5] Later, Bertrand reported on the stepwise oxidation of (Im^{Dipp})P–P(Im^{Dipp}) and isolated the dicationic P_2 species $\mathbf{2}^{2+}$,[6] illustrating that imidazoliumyl-substituents can be used for the stabilization of cations (Fig. 1). The activation of white phosphorus (P_4) by carbenes was investigated thoroughly and gave access to extended frameworks of low-coordinate P atoms,[4,7] such as the neutral *catena* P_4-species **3**.[7a,b] We reported on the stepwise transformation of P_4 by using an electrophilic phosphenium cation and a nucleophilic carbene ${}^{Cl}NHC^{Dipp}$ which yielded the linear P_3 cation $\mathbf{4}^+$ featuring two terminal imidazoliumyl-substituents.[8,9] In a very recent contribution, Grützmacher isolated the cationic disphosphene $\mathbf{5}^+$, *via* the reaction of (Im^{Dipp})PH with PCl_2(Ni-Pr_2) in the presence of DABCO (1,4-diazabicyclo[2.2.2]octane) and subsequent chloride abstraction with $GaCl_3$.[10]

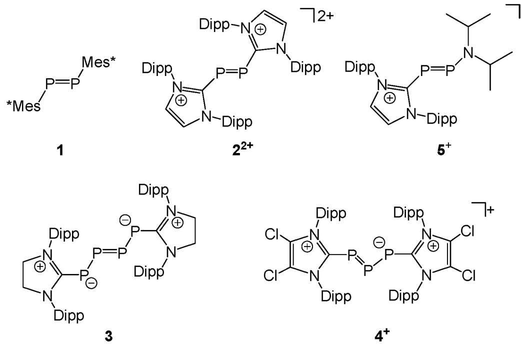

Fig. 1 First reported diphosphene **1** and selected imidazoliumyl functionalized polyphosphorus compounds ($\mathbf{2}^{2+}$–$\mathbf{5}^+$) (only one representative Lewis structure is presented).

The aforementioned compounds have illustrated the ability of imidazoliumyl-substituents to accept π-electron density from adjacent two-coordinate P atoms which is important for their stability since it significantly lowers the nucleophilicity of the phosphorus moiety. The termination of the P_n (n = 2, 3, 4) chains in $\mathbf{2}^{2+}$–$\mathbf{4}^+$ by two imidazoliumyl-groups, however, leads to symmetrical distribution of electron density within the multiple bonded polyphosphorus fragments. We envisioned that a diphosphene, bearing a sterically demanding aryl group

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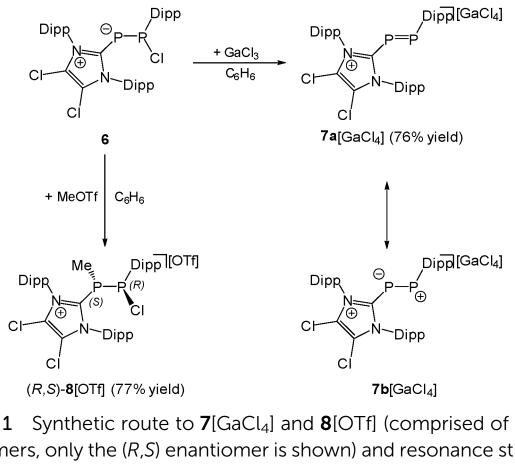
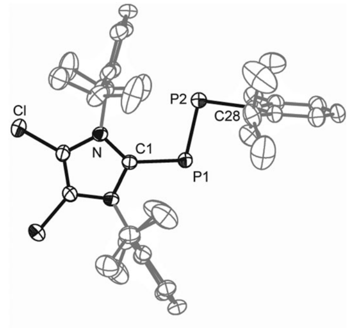
and an imidazoliumyl-substituent has a polarized P═P double bond and serves well for an interesting reactivity.

Aiming at the synthesis of such a diphosphene, we reacted neutral diphosphanide **6** with distinct electrophiles ($GaCl_3$, MeOTf). This gave rise to cationic diphosphene salt **7**[$GaCl_4$] *via* halide abstraction or cationic diphosphane salt **8**[OTf] *via* stereoselective methylation. Reactions of $\mathbf{7}^+$ with nucleophiles (PMe_3, Cl^-) demonstrate its remarkable acceptor properties. The reaction of diphosphanide **6** with $GaCl_3$ in a 1 : 1 stoichiometry in C_6H_6 solution resulted in the immediate formation of a red precipitate of **7**[$GaCl_4$] (Scheme 1, 76% yield). This compound constitutes a rare example of an unsymmetrically substituted, cationic diphosphene.[10,11] Its $^{31}P\{^1H\}$ NMR spectrum shows an AX spin system. The observed large $^1J(PP)$ coupling constant ($^1J(P_AP_X) = -577.9$ Hz) is characteristic for a P═P double bond.[12] The A part, assigned to the imidazoliumyl-substituted P atom, is shifted to higher field ($\delta(P_A) = 398.1$ ppm). On the other hand, the X part, assigned to the Dipp-substituted P atom, is at remarkable low field ($\delta(P_X) = 605.8$ ppm) compared to (*E*)-configured diphosphenes (*e.g.* Mes*P═PMes* $\delta(P) = 492$ ppm).[12] This implies a significant polarization of the P═P double bond, which can be indicated by resonance structure $\mathbf{7b}^+$ (Scheme 1). An inverse polarization was observed previously by ^{31}P NMR spectroscopy for π-donor substituted diphosphenes (*e.g.* Mes*–P_1═P_2–(Ni-Pr_2): $\delta(P_1) = 276$ ppm, $\delta(P_2) = 447$ ppm,[13] $\mathbf{5}^+$: (Im^{Dipp})–P_1═P_2–(Ni-Pr_2)$^+$: $\delta(P_2) = 158$ ppm, $\delta(P_1) = 492$ ppm).[10] Cation $\mathbf{7}^+$ is bright, red-colored and the UV/vis spectrum of **7**[$GaCl_4$] reveals two absorptions at 490 nm ($\varepsilon = 429$ cm^2 mol^{-1}) and 349 nm ($\varepsilon = 4995$ cm^2 mol^{-1}). The first absorption is assigned to a symmetry forbidden n(P) → π*(P═P) transition and the second to the symmetry allowed π(P–P) → π*(P═P) transition.[12] The molecular structure of **7**[$GaCl_4$] is depicted in Fig. 2 and confirms the (*E*)-configuration (C28–P2–P1–C1: 179.9(2)°). The P═P bond length (P1–P2: 2.038(1) Å) is typical for diphosphenes.[10,12] The C–P–P angle involving the imidazoliumyl-substituent (C1–P1–P2: 105.0(1)°) is larger than that involving the Dipp-substituent (C28–P2–P1 95.1(1)°). This might be a result of a higher degree of π-bonding interactions involving the more electron withdrawing imidazoliumyl-group, or the large steric demand of the imidazoliumyl-substituent.[14]



Scheme 1 Synthetic route to **7**[$GaCl_4$] and **8**[OTf] (comprised of a pair of enantiomers, only the (*R*,*S*) enantiomer is shown) and resonance structures $\mathbf{7a}^+$ and $\mathbf{7b}^+$.



$\mathbf{7}^+$

Fig. 2 Molecular structure of cation $\mathbf{7}^+$ in **7**[$GaCl_4$]·C_6H_5F (anions, hydrogen atoms and solvate molecules are omitted for clarity and thermal ellipsoids are displayed at 50% probability); selected experimental bond lengths [Å] and angles [°]: C1–P1 1.834(2), P1–P2 2.038(1), P2–C28 1.854(4), C1–P1–P2 105.0(1), C28–P2–P1 95.1(1).

Interestingly, the reaction of **6** with MeOTf does not yield MeCl and **7**[OTf]. Instead, addition of MeOTf to a solution of **6** in benzene gave a yellowish reaction mixture from which **8**[OTf] was conveniently obtained in good yields *via* addition of *n*-hexane and isolation of the formed precipitate (77% yield). The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture shows the prominent resonances of an AX spin system. These are assigned to diastereomeric $\mathbf{8}^+$ ($\delta(P_A) = -15.1$ ppm, $\delta(P_X) = 75.1$ ppm, $^1J(P_AP_X) = -218.2$ Hz) which mainly comprises a pair of enantiomers with (*R*,*S*)- and (*S*,*R*)-configuration. Thus, the relatively small absolute value of the $^1J(PP)$ coupling constants in (*R*,*S*)- and (*S*,*R*)-configuration is attributed to an anti-periplanar arrangement of the lone pairs of electrons.[15] In contrast, the relatively large absolute value observed for the (*S*,*S*)- and (*R*,*R*)-configuration is attributed to the gauche arrangement.[15] Similar observations were reported for *meso*- and *rac*-1,2-bis(trifluoromethyl)-diphosphane where the *trans* dispositions of electronegative CF_3 groups determines the favoured rotamers.[16] The A part is assigned to the Me-substituted P atom on the basis of the observed $^2J(PH)$ coupling constant (8.7 Hz). A second AX spin system of low intensity (<5%) is assigned to the second diastereomer of $\mathbf{8}^+$ ($\delta(P_A) = -10.5$ ppm, $\delta(P_X) = 86.4$ ppm, $^1J(P_AP_X) = -354.8$ Hz) comprised of a pair of enantiomers with (*R*,*R*)- and (*S*,*S*)-configuration. The significantly different values of $^1J(PP)$ coupling constants observed for the (*R*,*S*)/(*S*,*R*) and (*R*,*R*)/(*S*,*S*) pairs of enantiomers are explained by the relative arrangement of the lone pairs of electrons in $\mathbf{8}^+$. Most likely, a *trans*-conformation of the sterically demanding imidazoliumyl- and Dipp-substituent represents the most stable rotamer of $\mathbf{8}^+$.[15] The high stereoselectivity of the methylation of **6** might be a consequence of significant differences in the steric demand of the substituents at both, the di-coordinate P atom and the adjacent chiral P atom. Thus, the favoured approach of the electrophile (E^+) to the di-coordinate P atom occurs from the less crowded side as illustrated in Fig. 3. The molecular structure of **8**[OTf] confirms the (*R*,*S*)- and (*S*,*R*)-configuration of the major isomer (Fig. 4). The anti-periplanar conformation of the imidazoliumyl- and Dipp-substituents as observed in solution is also present in the solid state (C1–P1–P2–C29: 152.8(1)°). The formation of **8**[OTf] in the reaction of **6** with MeOTf indicates that

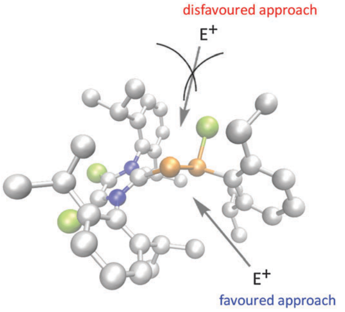


Fig. 3 Molecular structure of **6** (M06-2X/def2svp) showing the favoured and disfavoured approach of electrophiles. Hydrogen atoms are omitted for clarity.

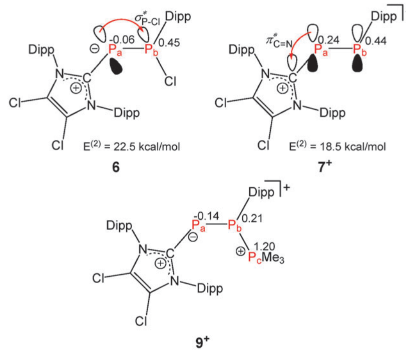
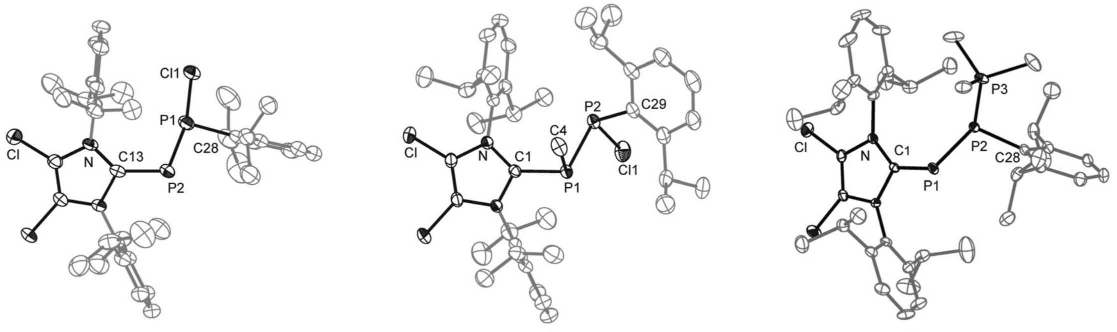


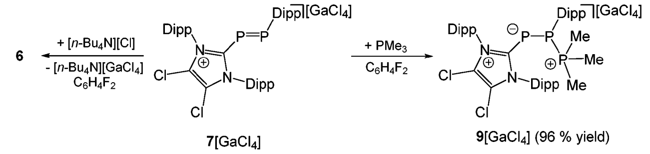
Fig. 5 Natural charges and selected secondary interactions of NBO analysis on DFT optimized structures of **6**, **7$^+$** and **9$^+$**.

the di-coordinate P atom exhibits the most nucleophilic properties. Therefore, it is reasonable to assume that the halide abstraction from **6** by $GaCl_3$, which yields **7**[$GaCl_4$], proceeds *via* coordination of the electrophile to the di-coordinate P atom, followed by 1,2-elimination of $GaCl_4^-$. Additionally, resonance structure **7b$^+$** indicates that this compound is a suitable acceptor for nucleophiles due to the polarization of the diphosphene moiety by the adjacent imidazoliumyl-substituent. The acceptor properties of **7$^+$** were further investigated by DFT calculations (Fig. 5). The polarization of the P═P double bond is expressed by a higher contribution of P_a (57.4% *vs.* 42.6% for P_b) to the π-type orbital and a donor acceptor interaction with the adjacent π* C═N orbital of 18.5 kcal mol^{-1}, indicating a stabilization of the positive charge by delocalization. Analysis of the natural charges of **7$^+$** showed that P_b carries the highest charge in the molecule of +0.44*e* compared to +0.24*e* on P_a, making P_b the preferred reaction site for nucleophiles. This reactivity was elucidated by the reaction of **7**[$GaCl_4$] with suitable nucleophiles – a Cl^- source and PMe_3 (Scheme 2). The addition of [n-Bu_4N][Cl] to a solution of **7**[$GaCl_4$] in o-$C_6H_4F_2$ results in the immediate color change from red to yellow, associated with diphosphanide **6**. ^{31}P NMR investigation of the reaction mixture revealed quantitative regeneration to **6** *via* adduct formation of the cationic diphosphene with the chloride anion. The previously unknown molecular structure of **6**[8] was determined by means of X-ray single crystal structure determination in the course of this study (Fig. 4). The P–C bond length of compound **6** involving the imidazoliumyl-substituent (P2–C13: 1.803(2) Å) is longer than related bond distances in (Im^{Mes})PPh (P–C: 1.763(6) Å)[17] or **2** (P–C: 1.750(2) Å).[4] In addition, the P–P bond length (P1–P2: 2.1327(9) Å) is shorter than the typical P–P single bond distance observed for diphosphanes (2.22 Å)[18] but significantly longer than a typical P═P double bond length observed for diphosphenes (2.00 Å).[12] This can be explained by the donation of electron density from the p-type lone pairs of electrons on P2 into the lobe of the σ*-orbital of the adjacent P–Cl bond (*vide infra*). This is supported by a longer P–Cl bond length (P1–Cl1: 2.1586(8) Å) than those typically observed for chloro-substituted diphosphanes (2.10 Å).[19] Collectively, the structural data indicates that the interaction of chloride in **6** is significantly weaker than a covalent P–Cl bond in a chlorophosphane. This is supported by computations which show a significant donor acceptor interaction of 22.5 kcal mol^{-1} of the p-type lone pair of P_a and the antibonding σ* P_b–Cl orbital (Fig. 5). A comparison of the energy profiles of the P–Cl bond dissociation of **6$_{me}$** (all iso-propyl moieties are substituted by methyl groups, r_0 = 2.131 Å) and Ph_2PCl (r_0 = 2.104 Å) yielded a dissociation energy of 34.1 kcal mol^{-1} and a force constant of 154.4 N m^{-1} for **6$_{me}$** *versus* 88.2 kcal mol^{-1} and 218 N m^{-1} for Ph_2PCl (Fig. S4.1, ESI†). This result further proves the weaker P–Cl bond in **6** compared to regular chlorophosphanes.



6 **8$^+$** **9$^+$**

Fig. 4 Molecular structure of **6**·(Et_2O)·(n-hexane), **8$^+$** in **8**[OTf]·2(1,2-$C_6H_4F_2$), **9$^+$** in **9**[$GaCl_4$] (hydrogen atoms and solvent molecules are omitted for clarity and thermal ellipsoids are displayed at 50% probability); selected experimental bond lengths in Å and angles in °; **6**: C1–P1 1.865(3), P1–P2 2.1327(9), P1–Cl1 2.1586(8), C1–P1–P2 95.83(8), C13–P2–P1 102.2(1). **8$^+$**: C1–P1 1.842(2), P1–P2 2.2250(9), P2–C29 1.841(2), P2–Cl1 2.0673(9); **9$^+$**: C1–P1 1.799(3), P1–P2 2.151(1), P2–P3 2.208(1), P1···P3 3.478(1), C1–P1–P2 100.5(1), P1–P2–P3 105.8(1).



Scheme 2 Synthetic route to **6** and **9**[GaCl$_4$].

The addition of PMe$_3$ to a red solution of **7**[GaCl$_4$] in *o*-C$_6$H$_4$F$_2$ again leads to an immediate color change to yellow. The phosphane adduct **9**[GaCl$_4$] was isolated in high yields from the reaction mixture (96%, Scheme 2). Its ^{31}P{^{1}H} NMR spectrum shows an AMX spin system. The A part of the spin system (δ(P$_A$) = −108.1 ppm) is assigned to the di-coordinate P atom and the pronounced high field shift indicates an inverse polarized phosphaalkene (or a phosphanide) moiety.[20] The resonance at lowest field (δ(P$_X$) = 11.2 ppm) is assigned to the tetra-coordinate P atom (compare [Ph$_2$P–PMe$_3$]$^+$: δ(P$_{Me}$) = 15 ppm)[21] while the M part (δ(P$_M$) = −62.1 ppm) corresponds to the tri-coordinate P atom.[22] As the ^1J(PP) couplings are of expected magnitude (^1J(P$_A$P$_M$) = −322.1 Hz, ^1J(P$_M$P$_X$) = −343.3 Hz) a comparatively large ^2J(PP) coupling (^2J(P$_A$P$_X$) = 72.8 Hz) might indicate a through space interaction between the di- and tetra-coordinate P centers. The connectivity of **9**$^+$ was confirmed by X-ray single crystal structure determination (Fig. 4). Its P–C bond length involving the imidazoliumyl-moiety is in the typical range of inverse polarized phosphaalkenes (C1–P1: 1.799(3) Å) and is comparable to **6**. Two distinct P–P bond lengths are observed in **9**$^+$ (P1–P2: 2.151(1) Å, P2–P3: 2.208(1) Å) and that one involving the di-coordinate P atom is significantly shorter than a typically P–P single bond (P–P: 2.22 Å).[18] The distance between both terminal P atoms (P1···P3: 3.478(1) Å) is well within the sum of the van der Waals radii of the respective atoms ($\sum r_{vdW}$(P,P) = 3.80 Å),[23] which might explain the observed large ^2J(PP) coupling between both atoms. It is important to note that polyphosphorus compounds featuring di-, tri- and tetra-coordinate P atoms in one molecule are very rare[24] and, to the best of our knowledge, **9**$^+$ is the first example of a phosphane environment that bridges a phosphanide and a phosphonium moiety.

In summary, we have studied reactions of neutral diphospanide **6** with selected electrophiles (GaCl$_3$, MeOTf). They proceed either *via* stereoselective methylation yielding cationic diphosphane **8**$^+$ or halide abstraction giving the remarkable cationic diphosphene **7**$^+$. The latter features a sterically demanding aryl group and a cationic, π-electron accepting imidazoliumyl-substituent. The substitution pattern in **7**$^+$ causes a significant polarization of the P═P double bond. This allows for its utilization as an acceptor towards chloride or PMe$_3$ as nucleophiles and the corresponding adducts **6** and **9**$^+$ were obtained. The utilization of polarized P═P double bonded cations as Lewis acids is expected to provide new avenues in diphosphene chemistry, which is subject of ongoing studies in our laboratories.

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