[(ClImDipp)P=P(Dipp)][GaCl4]: A Polarized, Cationic Diphosphene

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COMMUNICATION

$[(^{Cl}Im^{Dipp})P{=}P(Dipp)][GaCl_4]$: A Polarized, Cationic Diphosphene

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The reaction of the neutral diphosphanide $[(^{Cl}Im^{Dipp})P\text{-}P(Cl)(Dipp)]$ (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 $[(^{Cl}Im^{Dipp})(Me)P\text{-}P(Cl)(Dipp)]^+$ (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 acceptor for nucleophiles – the reaction with Cl^- regenerates diphospanide 6 and the reaction with PMe_3 gives cation $[(^{Cl}Im^{Dipp})P\text{-}P(PMe_3)(Dipp)]$ (9^+). In depth DFT investigation provides detailed insights into the bonding situation of the reported compounds.

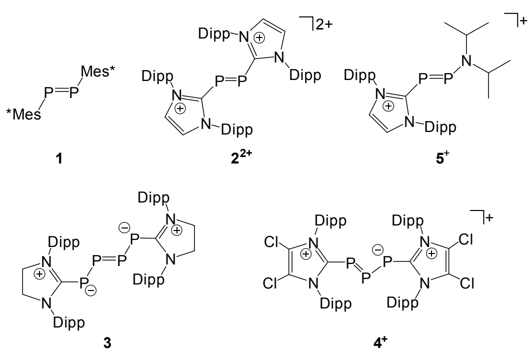

Figure 1. First reported diphosphene **1** and selected imidazoliumyl functionalized polyphosphorus compounds ($\mathbf{2}^{2+}$ - $\mathbf{5}^{+}$) (only one representative *Lewis* structure is presented).

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”, Figure 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 $(Im^{Dipp})P\text{–}P(Im^{Dipp})$ (Im^{Dipp} = 1,3-*bis*(Dipp)-imidazol-2-ylidene)[4] and explored its further reactivity.[5] Later, Bertrand reported on the stepwise oxidation of $(Im^{Dipp})P\text{–}P(Im^{Dipp})$ and isolated the P_2 dicationic species $\mathbf{2}^{2+}$,[6] illustrating that imidazoliumyl-substituents can be used for the stabilization of cations (Figure 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 $^{Cl}Im^{Dipp}$ 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 $PCl_2(N\textit{i}\text{-}Pr_2)$ in the presence of DABCO (1,4-diazabicyclo[2.2.2]octane) and subsequent chloride abstraction with $GaCl_3$.[10]

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

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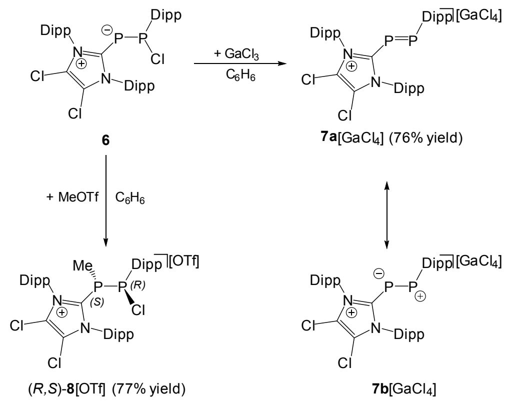


Scheme 1. Synthetic route to **7**[GaCl$_4$] and **8**[OTf] (comprised of a pair of enantiomers, only the (*R*,*S*) enantiomer is shown) and resonance structures **7a**$^+$ and **7b**$^+$.

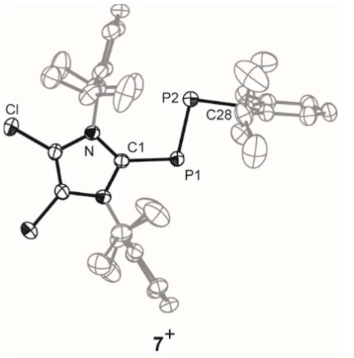


Figure 2. Molecular structure of cation **7**$^+$ in **7**[GaCl$_4$]•C$_6$H$_5$F (anions, hydrogen atoms and solvate molecules are omitted for clarity and thermal ellipsoids are displayed at 50% probability); selected experimental bond lengths [Å] and angles [°]: C1–P1 1.834(2), P1–P2 2.038(1), P2–C28 1.854(4), C1–P1–P2 105.0(1), C28–P2–P1 95.1(1).

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 **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$_6$H$_6$ solution resulted in the immediate formation of a red precipitate of **7**[GaCl4] (Scheme 1, 76% yield). This compound constitutes a rare example of an unsymmetrically substituted, cationic diphosphene.[10,11] Its ^{31}P{^{1}H} NMR spectrum shows an AX spin system. The observed large ^1J(PP) coupling constant (^1J(P$_A$P$_X$) = –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 (δ(P$_A$) = 398.1 ppm). On the other hand, the X part, assigned to the Dipp-substituted P atom, is at remarkable low field (δ(P$_X$) = 605.8 ppm) compared to (*E*)-configured diphosphenes (e.g. Mes*P=PMes* δ(P) = 492 ppm).[12] This implies a significant polarization of the P=P double bond, which can be indicated by resonance structure **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$_2$–(N*i*-Pr$_2$: δ(P$_1$) = 276 ppm, δ(P$_2$) = 447 ppm,[13] **5**$^{+:}$ (Im$^{\mathrm{Dipp}}$)–P$_1$=P$_2$–(N*i*-Pr$_2$)$^{+:}$ δ(P$_2$) = 158 ppm, δ(P$_1$) = 492 ppm).[10] Cation **7**$^+$ is bright, red-colored and the UV/vis spectrum of **7**[GaCl$_4$] reveals two absorptions at 490 nm (*ε* = 429 cm^2/mol) and 349 nm (*ε* = 4995 cm^2/mol). 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 Figure 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] 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{^{1}H} NMR spectrum of the reaction mixture shows the prominent resonances of an AX spin system. These are assigned to diastereomeric **8**$^+$ (δ(P$_A$) = –15.1 ppm, δ(P$_X$) = 75.1 ppm, ^1J(P$_A$P$_X$) = –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 **8**$^+$ (δ(P$_A$) = –10.5 ppm, δ(P$_X$) = 86.4 ppm, ^1J(P$_A$P$_X$) = –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 **8**$^+$. Most likely, a

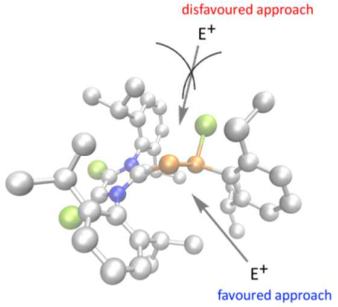


Figure 3. Molecular structure of **6** (M06-2X/def2svp) showing the favoured and disfavoured approach of electrophiles. Hydrogen atoms are omitted for clarity.

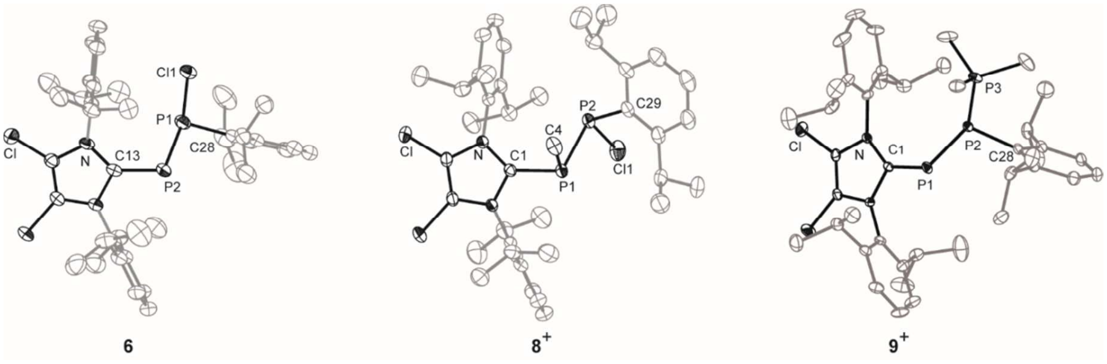
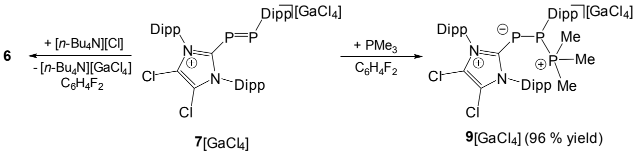


Figure 4. Molecular structure of **6**•(Et_2O)•(*n*-hexane), $\mathbf{8}^+$ in **8**[OTf]•2(1,2-$C_6H_4F_2$), $\mathbf{9}^+$ in **9**[$GaCl_4$] (hydrogen atoms and solvent molecules are omitted for clarity and thermal ellipsoids are displayed at 50% probability); selected experimental bond lengths in 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). $\mathbf{8}^+$: C1–P1 1.842(2), P1–P2 2.2250(9), P2–C29 1.841(2), P2–Cl1 2.0673(9); $\mathbf{9}^+$: 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).

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 Figure 3. The molecular structure of **8**[OTf] confirms the (*R,S*)- and (*S,R*)-configuration of the major isomer (Figure 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 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 $\mathbf{7b}^+$ indicates that this compound is a suitable acceptor for nucleophiles due to the polarization of the diphosphene mojety by the adjacent imidazoliumyl-substituent. The acceptor properties of $\mathbf{7}^+$ were further investigated by DFT calculations (Figure 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 orbital and a donor acceptor interaction with the adjacent π* C=N orbital of 18.5 kcal/mol, indicating a stabilization of the positive charge by delocalization. Analysis of the natural charges of $\mathbf{7}^+$ showed that P_b carries the highest charge in the molecule of +0.44e compared to +0.24e 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 X-ray single crystal structure determination in the course of this study (Figure 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)[18] 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)[19] but significantly longer than the 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).[20] 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 of the p-type lone pair of P_a and the antibonding σ* P_b-Cl orbital (Figure 5). A comparison of the energy profiles of the P−Cl bond dissociation of $\mathbf{6_{me}}$ (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 and a force constant of 154.4 N/m for $\mathbf{6_{me}}$ versus 88.2 kcal/mol and 218 N/m for Ph_2PCl (Figure S4.1). This result further proves the weaker P−Cl bond in **6** compared to regular chlorophosphanes.



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*-$C_6H_4F_2$ 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 $^{31}P\{^1H\}$ NMR spectrum shows an AMX spin system. The A part of the spin system ($\delta(P_A) = -108.1$ ppm) is assigned to the di-coordinate P atom

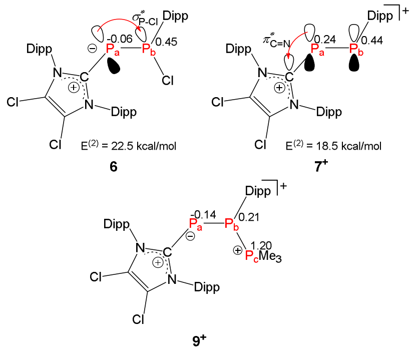


Figure 5: Natural charges and selected secondary interactions of NBO analysis on DFT optimized structures of **6**, **7**$^+$ and **9**$^+$.

and the pronounced high field shift indicates an inverse polarized phosphaalkene (or a phosphanide) moiety.[20] The resonance at lowest field ($\delta(P_X)$ = 11.2 ppm) is assigned to the tetra-coordinate P atom (compare $[Ph_2P{-}PMe_3]^+$: $\delta(P_{Me})$ = 15 ppm)[21] while the M part ($\delta(P_M)$ = -62.1 ppm) corresponds to the tri-coordinate P atom.[22] As the $^1J(PP)$ couplings are of expected magnitude ($^1J(P_AP_M)$ = –322.1 Hz, $^1J(P_MP_X)$ = –343.3 Hz) a comparatively large $^2J(PP)$ coupling ($^2J(P_AP_X)$ = 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 (Figure 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).[19] 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 ($\Sigma r_{vdW}(P,P)$ = 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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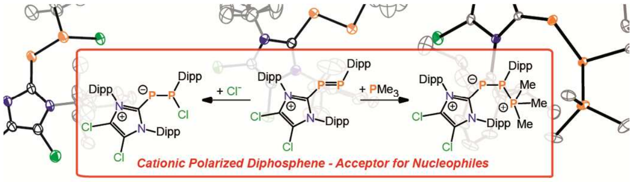

The reaction of neutral diphosphanide $[(^{Cl}Im^{Dipp})P\text{-}P(Cl)(Dipp)]$ with the *Lewis* acid $GaCl_3$ yields cationic diphosphene $[(^{Cl}Im^{Dipp})P{=}P(Dipp)]^+$, which is explained by a low P–Cl bond dissociation energy. The polarized P=P double bond in $[(^{Cl}Im^{Dipp})P{=}P(Dipp)]^+$, allows for its utilization as acceptor for nucleophiles, such as Cl^- or PMe_3.