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$[(^{\text{Cl}}\text{Im}^{\text{Dipp}})\text{P}=\text{P}(\text{Dipp})][\text{GaCl}_4]$: a polarized, cationic diphosphene[†]

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The reaction of the neutral diphosphanide $[(^{\text{Cl}}\text{Im}^{\text{Dipp}})\text{P}-\text{P}(\text{Cl})(\text{Dipp})]$ (**6**) ($^{\text{Cl}}\text{Im}^{\text{Dipp}} = 4,5$ -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 $[(^{\text{Cl}}\text{Im}^{\text{Dipp}})(\text{Me})\text{P}-\text{P}(\text{Cl})(\text{Dipp})]^+$ (**8**⁺) in a stereoselective methylation. In contrast, reacting **6** with the Lewis acid GaCl₃ yields cationic diphosphene $[(^{\text{Cl}}\text{Im}^{\text{Dipp}})\text{P}=\text{P}(\text{Dipp})]^+$ (**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 PMe₃ gives cation $[(^{\text{Cl}}\text{Im}^{\text{Dipp}})\text{P}-\text{P}(\text{PMe}_3)(\text{Dipp})]^+$ (**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-*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

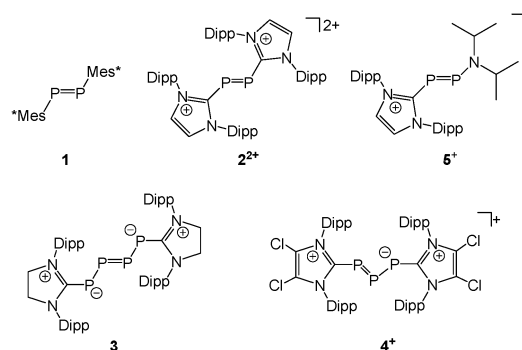


Fig. 1 First reported diphosphene **1** and selected imidazoliumyl functionalized polyphosphorus compounds (**2**²⁺–**5**⁺) (only one representative Lewis structure is presented).

isolated the dicationic P₂ species **2**²⁺,⁶ illustrating that imidazoliumyl-substituents can be used for the stabilization of cations (Fig. 1). The activation of white phosphorus (P₄) by carbenes was investigated thoroughly and gave access to extended frameworks of low-coordinate P atoms,^{4,7} such as the neutral *catena* P₄-species **3**.^{7a,b} We reported on the stepwise transformation of P₄ by using an electrophilic phosphonium cation and a nucleophilic carbene ^{Cl}NHC^{Dipp} which yielded the linear P₃ cation **4**⁺ featuring two terminal imidazoliumyl-substituents.^{8,9} In a very recent contribution, Grützmacher isolated the cationic diphosphene **5**⁺, *via* the reaction of (Im^{Dipp})PH with PCl₂(Ni-Pr₂) in the presence of DABCO (1,4-diazabicyclo[2.2.2]octane) and subsequent chloride abstraction with GaCl₃.¹⁰

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 **2**²⁺–**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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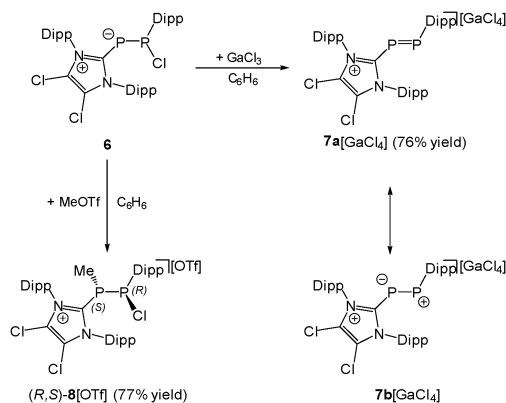
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and an imidazoliumyl-substituent has a polarized P=P double bond and serves well for an interesting reactivity.

Aiming at the synthesis of such a diphosphene, we reacted neutral diphosphanide **6** with distinct electrophiles (GaCl₃, MeOTf). This gave rise to cationic diphosphene salt **7**[GaCl₄] *via* halide abstraction or cationic diphosphene salt **8**[OTf] *via* stereoselective methylation. Reactions of **7**⁺ with nucleophiles (PMe₃, Cl⁻) demonstrate its remarkable acceptor properties. The reaction of diphosphanide **6** with GaCl₃ in a 1:1 stoichiometry in C₆H₆ 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 ³¹P{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 (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=PMe* 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 ³¹P NMR spectroscopy for π-donor substituted diphosphenes (e.g. Mes*-P₁=P₂-(Ni-Pr₂): δ(P₁) = 276 ppm, δ(P₂) = 447 ppm,¹³ 5⁺: (Im^{Dipp})-P₁=P₂-(Ni-Pr₂)⁺: δ(P₂) = 158 ppm, δ(P₁) = 492 ppm).¹⁰ Cation **7**⁺ is bright, red-colored and the UV/vis spectrum of **7**[GaCl₄] reveals two absorptions at 490 nm (ε = 429 cm² mol⁻¹) and 349 nm (ε = 4995 cm² 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**[GaCl₄] 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**[GaCl₄] and **8**[OTf] (comprised of a pair of enantiomers, only the (*R,S*) enantiomer is shown) and resonance structures **7a**⁺ and **7b**⁺.

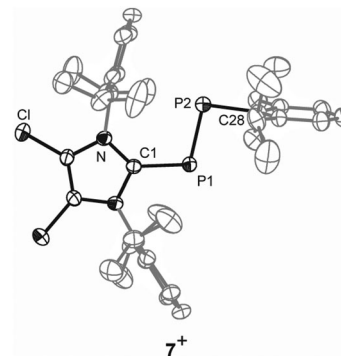


Fig. 2 Molecular structure of cation **7**⁺ in **7**[GaCl₄]-C₆H₅F (anions, hydrogen atoms and solvate molecules are omitted for clarity and thermal ellipsoids are displayed at 50% probability); selected experimental bond lengths [Å] and angles [°]: C1-P1 1.834(2), P1-P2 2.038(1), P2-C28 1.854(4), C1-P1-P2 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 ³¹P{¹H} 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_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 CF₃ 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_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 **8**⁺. Most likely, a *trans*-conformation of the sterically demanding imidazoliumyl- and Dipp-substituent represents the most stable rotamer of **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



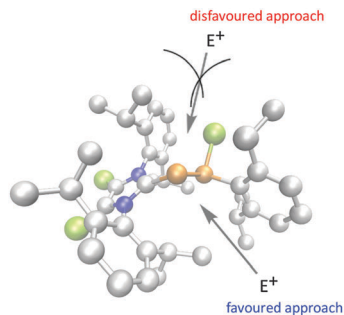


Fig. 3 Molecular structure of **6** (M06-2X/def2svp) showing the favoured and disfavoured approach of electrophiles. Hydrogen atoms are omitted for clarity.

the di-coordinate P atom exhibits the most nucleophilic properties. Therefore, it is reasonable to assume that the halide abstraction from **6** by GaCl₃, which yields 7[GaCl₄], proceeds *via* coordination of the electrophile to the di-coordinate P atom, followed by 1,2-elimination of GaCl₄⁻. 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 +0.44e 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[GaCl₄] with suitable nucleophiles – a Cl⁻ source and PMe₃ (Scheme 2). The addition of [n-Bu₄N][Cl] to a solution of 7[GaCl₄] in *o*-C₆H₄F₂ results in the immediate color change from red to yellow, associated with diphosphanide **6**. ³¹P 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

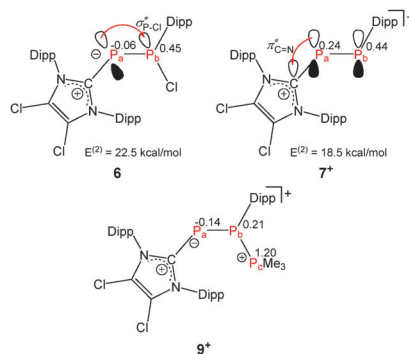


Fig. 5 Natural charges and selected secondary interactions of NBO analysis on DFT optimized structures of **6**, **7**⁺ and **9**⁺.

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^{Me})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 Ph₂P–Cl (*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 Ph₂P–Cl (Fig. S4.1, ESI[†]). This result further proves the weaker P–Cl bond in **6** compared to regular chlorophosphanes.

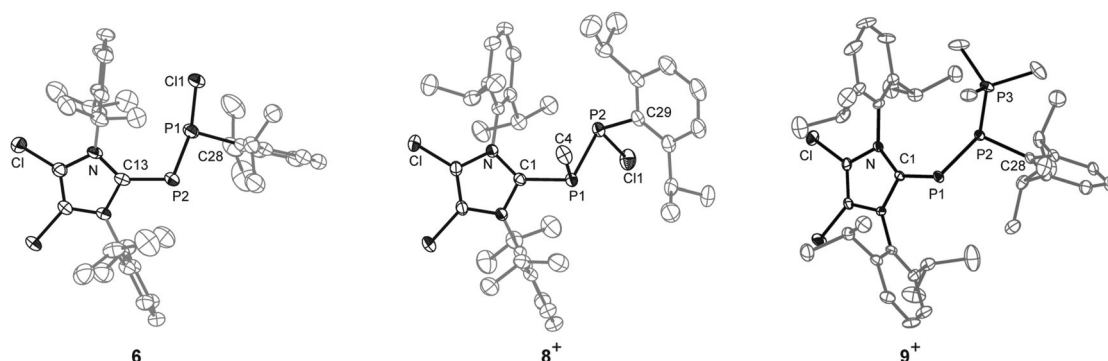
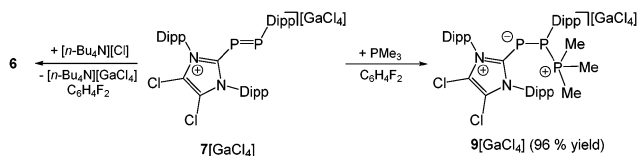


Fig. 4 Molecular structure of **6**·(Et₂O)·(*n*-hexane), **8**⁺ in **8**[OTf]·2(1,2-C₆H₄F₂), **9**⁺ in **9**[GaCl₄] (hydrogen atoms and solvent molecules are omitted for clarity and thermal ellipsoids are displayed at 50% probability); selected experimental bond lengths in Å and angles in °: **6**: C1–P1 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[GaCl₄].

The addition of PMe₃ to a red solution of 7[GaCl₄] in *o*-C₆H₄F₂ again leads to an immediate color change to yellow. The phosphane adduct 9[GaCl₄] was isolated in high yields from the reaction mixture (96%, Scheme 2). Its ³¹P{¹H} NMR spectrum shows an AMX spin system. The A part of the spin system ($\delta(\text{P}_A) = -108.1$ ppm) is assigned to the di-coordinate P atom and the pronounced high field shift indicates an inverse polarized phosphalkene (or a phosphanide) moiety.²⁰ The resonance at lowest field ($\delta(\text{P}_X) = 11.2$ ppm) is assigned to the tetra-coordinate P atom (compare [Ph₂P-PMe₃]⁺: $\delta(\text{P}_{\text{Me}}) = 15$ ppm)²¹ while the M part ($\delta(\text{P}_M) = -62.1$ 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 (Fig. 4). Its P-C bond length involving the imidazoliumyl-moiety is in the typical range of inverse polarized phosphalkenes (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 ($\sum r_{\text{vdw}}(\text{P}, \text{P}) = 3.80$ 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 rare²⁴ 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 diphosphane 6 with selected electrophiles (GaCl₃, MeOTf). They proceed either *via* stereoselective methylation yielding cationic diphosphane 8⁺ or halide abstraction giving the remarkable cationic diphosphane 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 PMe₃ 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 diphosphane chemistry, which is subject of ongoing studies in our laboratories.

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