



Cite this: *Chem. Commun.*, 2016, 52, 1409

Received 3rd October 2015,
Accepted 23rd November 2015

DOI: 10.1039/c5cc08248j

www.rsc.org/chemcomm

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

Kai Schwedtmann,^a Michael H. Holthausen,^a Chris H. Sala,^a Felix Hennersdorf,^a Roland Fröhlich^b and Jan J. Weigand^{*a}

The reaction of the neutral diphosphanide $[(\text{ClIm}^{\text{Dipp}})\text{P}-\text{P}(\text{Cl})(\text{Dipp})]$ (**6**) ($\text{ClIm}^{\text{Dipp}} = 4,5\text{-dichloro-1,3-bis}(\text{Dipp})\text{-imidazol-2-yl}$; $\text{Dipp} = 2,6\text{-di-iso-propylphenyl}$) with methyl triflate (MeOTf) leads to the formation of cationic diphosphene $[(\text{ClIm}^{\text{Dipp}})(\text{Me})\text{P}-\text{P}(\text{Cl})(\text{Dipp})]^+$ (**8**⁺) in a stereoselective methylation. In contrast, reacting **6** with the Lewis acid GaCl_3 yields cationic diphosphene $[(\text{ClIm}^{\text{Dipp}})\text{P}=\text{P}(\text{Dipp})]^+$ (**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 PMe_3 gives cation $[(\text{ClIm}^{\text{Dipp}})\text{P}-\text{P}(\text{PMe}_3)(\text{Dipp})]$ (**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 $\text{Mes}^*\text{P}=\text{PMes}^*$ **1** by introducing the very bulky Mes^* substituent ($\text{Mes}^* = 2,4,6\text{-tri-}t\text{-butylphenyl}$, “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 $(\text{Im}^{\text{Dipp}})\text{P}-\text{P}(\text{Im}^{\text{Dipp}})$ ($\text{Im}^{\text{Dipp}} = 1,3\text{-bis}(\text{Dipp})\text{-imidazol-2-yl}$)⁴ and explored its further reactivity.⁵ Later, Bertrand reported on the stepwise oxidation of $(\text{Im}^{\text{Dipp}})\text{P}-\text{P}(\text{Im}^{\text{Dipp}})$ and

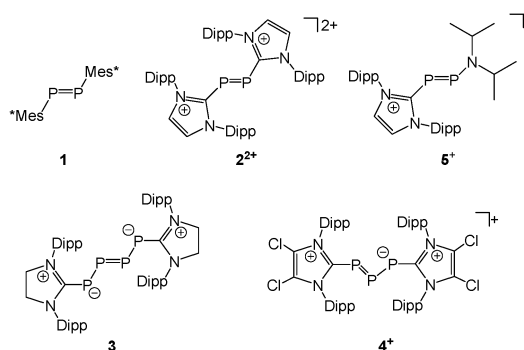


Fig. 1 First reported diphosphene **1** and selected imidazoliumyl functionalized polyphosphorus compounds (**2**²⁺–**5**⁺) (only one representative Lewis structure is presented).

isolated the dicationic P_2 species **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 phosphonium cation and a nucleophilic carbene $\text{ClNHC}^{\text{Dipp}}$ which yielded the linear P_3 cation **4**⁺ featuring two terminal imidazoliumyl-substituents.^{8,9} In a very recent contribution, Grützmacher isolated the cationic diphosphene **5**⁺, *via* the reaction of $(\text{Im}^{\text{Dipp}})\text{PH}$ with $\text{P}(\text{Cl})_2(\text{Ni-Pr}_2)$ 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 **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

^a Chair of Inorganic Molecular Chemistry, University of Technology Dresden, 01062 Dresden, Germany. E-mail: jan.weigand@tu-dresden.de

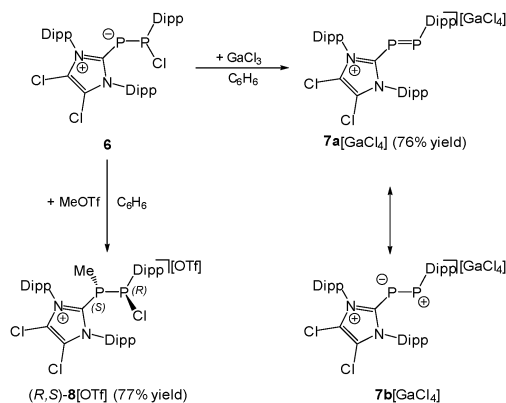
^b Institute of Organic Chemistry, Westfälische Wilhelms-Universität Münster, 48149 Münster, Germany

[†] Electronic supplementary information (ESI) available: For detailed experimental procedures and characterization details of new compounds, NMR spectra, crystallographic details and computational data. CCDC 1429021–1429024. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc08248j



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 diphosphane 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**⁺.

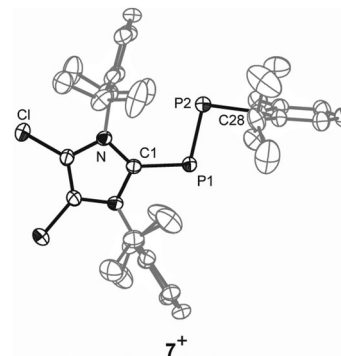


Fig. 2 Molecular structure of cation **7**⁺ in **7**[GaCl₄]-C₆H₅F (anions, hydrogen atoms and solvate molecules are omitted for clarity and thermal ellipsoids are displayed at 50% probability); selected experimental bond lengths [Å] and angles [°]: C1-P1 1.834(2), P1-P2 2.038(1), P2-C28 1.854(4), C1-P1-P2 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



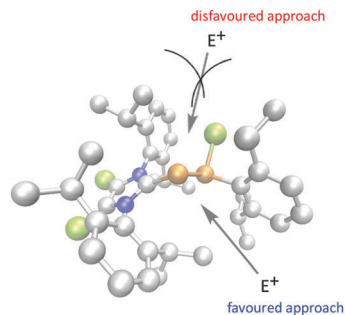


Fig. 3 Molecular structure of **6** (M06-2X/def2svp) showing the favoured and disfavoured approach of electrophiles. Hydrogen atoms are omitted for clarity.

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

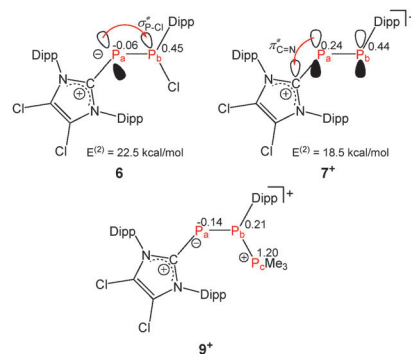


Fig. 5 Natural charges and selected secondary interactions of NBO analysis on DFT optimized structures of **6**, **7**⁺ and **9**⁺.

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 Ph₂PCL (*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 Ph₂PCL (Fig. S4.1, ESI[†]). This result further proves the weaker P–Cl bond in **6** compared to regular chlorophosphanes.

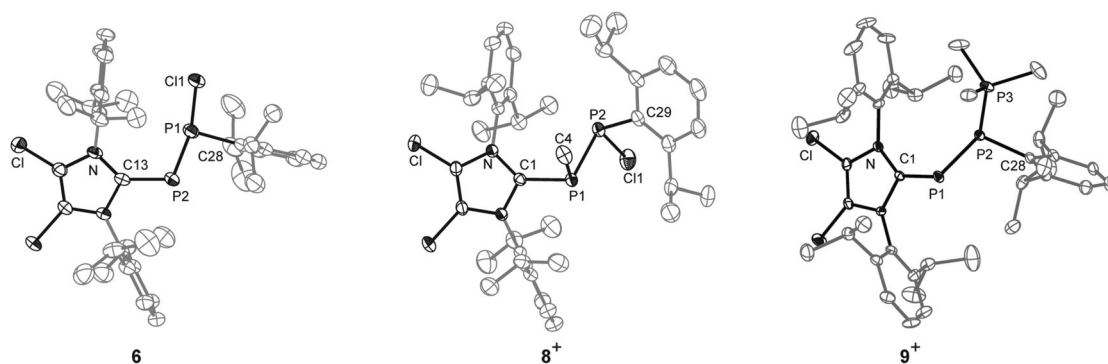
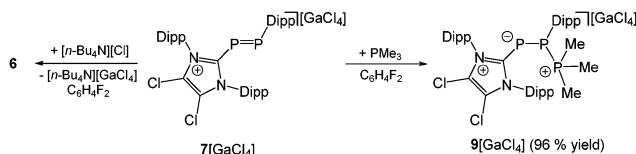


Fig. 4 Molecular structure of **6**·(Et₂O)·(*n*-hexane), **8**⁺ in **8**[OTf]·2(1,2-C₆H₄F₂), **9**⁺ in **9**[GaCl₄] (hydrogen atoms and solvent molecules are omitted for clarity and thermal ellipsoids are displayed at 50% probability); selected experimental bond lengths in Å and angles in °: **6**: C1–P1 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 PMe_3 to a red solution of $7[\text{GaCl}_4]$ in $o\text{-C}_6\text{H}_4\text{F}_2$ again leads to an immediate color change to yellow. The phosphane adduct $9[\text{GaCl}_4]$ was isolated in high yields from the reaction mixture (96%, Scheme 2). Its $^{31}\text{P}\{^1\text{H}\}$ 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 $[\text{Ph}_2\text{P-PMe}_3]^+$: $\delta(\text{P}_{\text{Me}}) = 15$ ppm)²¹ while the M part ($\delta(\text{P}_M) = -62.1$ ppm) corresponds to the tri-coordinate P atom.²² As the $^1J(\text{PP})$ couplings are of expected magnitude ($^1J(\text{P}_A\text{P}_M) = -322.1$ Hz, $^1J(\text{P}_M\text{P}_X) = -343.3$ Hz) a comparatively large $^2J(\text{PP})$ coupling ($^2J(\text{P}_A\text{P}_X) = 72.8$ 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 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 $^2J(\text{PP})$ 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 (GaCl_3 , 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 $\text{P}=\text{P}$ 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 $\text{P}=\text{P}$ double bonded cations as Lewis acids is expected to provide new avenues in diphosphane chemistry, which is subject of ongoing studies in our laboratories.

This work was supported by the Fonds der Chemischen Industrie (FCI, scholarships for M. H. H. and F. H.), the German Science Foundation (DFG, WE 4621/2-1) and the ERC (SynPhos 307616). We thank the Center for Information Services and High Performance Computing (ZIH) for the generous allocation of computation time.

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