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Formation of an imidazoliumyl-substituted $[(L_C)_4P_4]^{4+}$ tetracation and transition metal mediated fragmentation and insertion reaction ($L_C = NHC$)[†]

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Tetracationic cyclo-tetraphosphane $[(L_C)_4P_4]^{4+}$ as triflate salt (**3**[OTf]₄) ($L_C = 4,5$ -dimethyl-1,3-diisopropyl-imidazol-2-yl) is obtained in high yield from the reduction of $[L_C PCl_2]^+$ (**4**[OTf]) with 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (**6**) and represents the first salt of the cationic cyclo-phosphane series with the general formula $[L_n P_n]^{n+}$. Theoretical calculations reveal the electrophilic nature of the P atoms within the P_4 -ring due to the influence of the imidazoliumyl-substituents. Further reduction of **3**[OTf]₄ with **6** affords the unexpected formation of the nortricyclane P_7 -type cation $[(L_C)_3 P_7]^{3+}$ (**9**[OTf]₃). Selective transition metal mediated $[2 + 2]$ -fragmentation of **3**⁴⁺ is achieved when **3**[OTf]₄ is reacted with $Fe_2(CO)_9$, $Pd(PPh_3)_4$ and $Pt(PPh_3)_4$ leading to the formation of the dicationic diphosphene complexes $[(\eta^2-L_C P=PL_C)Fe(CO)_4]^{2+}$ (**12**[OTf]₂) and $[(\eta^2-L_C P=PL_C)M(PPh_3)_2]^{2+}$ (**13**[OTf]₂ for $M = Pd$; **14**[OTf]₂ for $M = Pt$). In contrast, the reaction of **3**[OTf]₄ with an excess of $AuCl(tht)$ gives rise to the formation of the five-membered ring complex $[(L_C)_4 P_4]AuCl_2]^{3+}$ (**15**[OTf]₃), where the Au(I) atom reductively inserts into a P–P bond of **3**⁴⁺.

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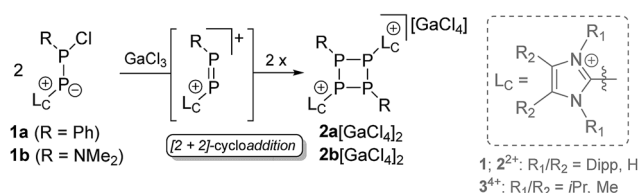
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Introduction

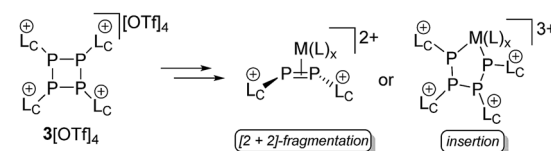
The fact that phosphorus tends to assemble into homo-nuclear cyclic and cage-like structural motifs is not only illustrated by the variety of phosphorus allotropes,¹ but also by the multitude of known polyphosphanes.² Particularly, neutral monocyclic polyphosphanes with the general formula $P_n R_n$ ($R = \text{alkyl, aryl, } n = 3-5$) are already known for decades and their chemistry is well established.³⁻⁵ There are several synthetic protocols for this group of compounds, of which the reduction of a dichlorophosphane $RPCL_2$ ($R = \text{alkyl, aryl}$) with various reducing agents represents the most common approach.⁶ The steric demand of the substituents at the P atom determines the favored ring-size.^{6,7} Thus, the reduction of $CyPCL_2$ with Mg yields the thermodynamically favored cyclo- $Cy_4 P_4$,⁸ whereas the reduction of $PhPCL_2$ gives mainly cyclo- $Ph_5 P_5$.⁹ A mixture of compounds with several ring sizes is often observed in the initial reaction, however, a scrambling to the thermodynamically favored ring-size typically occurs over time.⁶⁻⁹ When the

steric demand of the substituent is too large, the formation of cyclo-phosphanes does not proceed, as illustrated by the reduction of Mes^*PCL_2 ($Mes^* = 2,4,6$ -tri(*tert*-butyl)phenyl) to diphosphene $Mes^*-P=P-Mes^*$.¹⁰ Generally, mixed-substituted or cationic cyclo-phosphanes are very scarce and the only examples of dicationic cyclo-phosphanes of type $[R_2(L_C)_2 P_4]^{2+}$ (**2a**, **2b**²⁺) ($L_C = 1,3$ -bis(2,6-diisopropylphenyl)-imidazol-2-yl, **1a**: $R = Ph$, **1b**: $R = NMe_2$; Scheme 1) were recently introduced by Grützmacher and co-workers as a result of a $GaCl_3$ -induced

Grützmacher 2016



this work



Scheme 1 Cationic cyclo-phosphanes of type $[R_2(L_C)_2 P_4]^{2+}$ (**2a**, **2b**²⁺) and $[(L_C)_4 P_4]^{4+}$ (**3**⁴⁺) and subsequent transition metal mediated fragmentation and insertion reactions.

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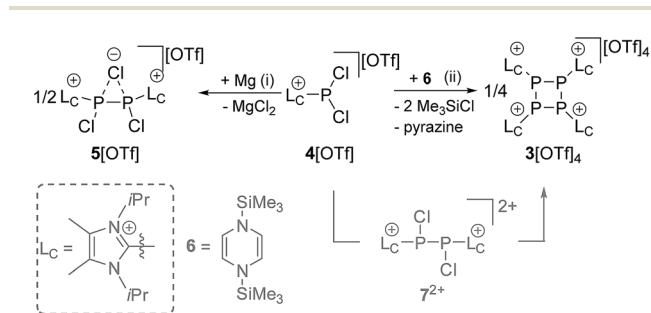
dimerization reaction of **1a,b**.¹¹ Mechanistically, it has been shown that cyclo-phosphanes **2a,b**²⁺ are formed *via* a [2 + 2]-cycloaddition of the generated diphosphene intermediates. We targeted the replacement of all substituents R in cyclo-P_nR_n by an imidazoliumyl-substituent L_C, resulting in the new group of cationic cyclo-phosphanes of type [(L_C)_nP_n]ⁿ⁺ (Scheme 1). These cationic substituents L_C are frequently employed in phosphorus chemistry as they are known to have a significant influence on the reactivity of the directly bonded P atom.^{12–15} In this contribution we present the formation of a tetracationic cyclo-tetraphosphane [(L_C)₄P₄]⁴⁺ as triflate salt (3[OTf]₄) *via* the reduction of [L_CPCl₂]⁺ (4[OTf])¹² and elucidate the mechanism for its formation. Furthermore, the reductive build-up reaction to a larger cationic phosphorus framework and selective transition metal mediated [2 + 2]-fragmentation and ring opening reactions were investigated.

Results and discussion

We first reduced compound 4[OTf] with Mg in THF and observed the formation of a yellow-colored reaction mixture (Scheme 2). After removing MgCl₂ by filtration, the ³¹P NMR spectrum of the obtained clear solution reveals a singlet resonance at δ(P) = −24.0 ppm. This resonance can be attributed to the chloride bridged P₂-compound 5[OTf] which was confirmed by X-ray analysis (see Fig. S2†).¹⁶ As compound 5[OTf] is similar to our previous findings, in which we employed a sterically more demanding imidazoliumyl-substituent (L_C = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-yl), we abstain from a detailed discussion here.^{17,18} It is noteworthy to mention, however, that reduction of 4[OTf] with Na gives the same result. The reduction proceeds completely different when 4[OTf] is reacted with 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (**6**) in fluorobenzene as solvent. Within 12 h the formation of a colorless precipitate is observed which after filtration and removal of all volatiles *in vacuo* gives the analytically pure triflate salt of the tetracationic cyclo-tetraphosphane **3**⁴⁺ in very good yield (86%, Scheme 2). Although compound 3[OTf]₄ is well soluble in CH₃CN it slightly decomposes in solution in the course of several days. The ³¹P NMR spectrum of 3[OTf]₄ dissolved in CD₃CN, shows a singlet resonance at δ(P) = −55.7 ppm, which is comparable to ^tBu₄P₄

(δ(P) = −58.1 ppm).¹⁹ Single crystals suitable for X-ray analysis are obtained by slow diffusion of Et₂O into a saturated CH₃CN solution of 3[OTf]₄ at −35 °C. Fig. 1 shows the molecular structure of tetracation 3⁴⁺ and reveals the typical butterfly-shaped P₄ motif with an averaged P–P–P angle of 81.59°. All imidazoliumyl-substituents at the P₄ ring system are arranged in equatorial and all-*trans* position. The P–P bond lengths in 3⁴⁺ (av. 2.235 Å) are in the range for P–P single bonds (2.22 Å)²⁰ and the P–C bond lengths (av. 1.822 Å) are similar to comparable imidazoliumyl-substituted phosphorus compounds.¹⁵ In order to elucidate whether the formation of tetracation 3⁴⁺ proceeds through a diphosphene intermediate, we monitored the aforementioned reaction by means of ³¹P NMR spectroscopy (see Fig. S3†). Notably, Tamm and co-workers recently reported on the isolation of a diphosphene derivative obtained by the reduction of related dichlorophosphane with compound **6**.²¹ The ³¹P NMR spectrum of the reaction mixture shows only one major prominent intermediate with a singlet resonance at δ(P) = −29.1 ppm, which is in the range for diphosphanes.²² We assign this intermediate to dication 7²⁺ which is similar to findings of Goicoechea and co-workers who isolated a related dibromo-diphosphane compound featuring imidazoliumyl-substituents.¹⁸ To further proof our assumption we calculated the chemical shift of intermediate 7²⁺ and found a theoretical ³¹P NMR shift of δ(P) = −33.4 ppm being in a reasonable range compared to the experimentally found shift.^{16,23} We confirmed the existence of dication 7²⁺ by the addition of a chloride source, namely *n*Bu₄N[Cl] and observed the formation of chloride-bridged cation 5⁺ from 7²⁺.¹⁶

Mechanistically, we propose that 2 equivalents of 4⁺ react with one equivalent of **6** to give intermediate 7²⁺ which subsequently reacts with another equivalent of **6** ultimately leading to tetracation 3⁴⁺. The first reduction step might also lead to the formation of an [L_CP]⁺-synthon which is supported by the formation of [(L_C)₃P₃]³⁺ (**8**³⁺) in this reaction (Scheme 3). A few



Scheme 2 Reduction of 4[OTf] with Mg (left) and **6** (right) yields either 5[OTf] or 3[OTf]₄, respectively. Proposed reaction pathway with intermediate 7²⁺ to 3[OTf]₄ (grey); (i): +ex. Mg, 12 h, −2MgCl₂, 99% (determined by ³¹P NMR spectroscopy); (ii): +**6**, C₆H₅F, 12 h, −pyrazine, −2Me₃SiCl, 86%.

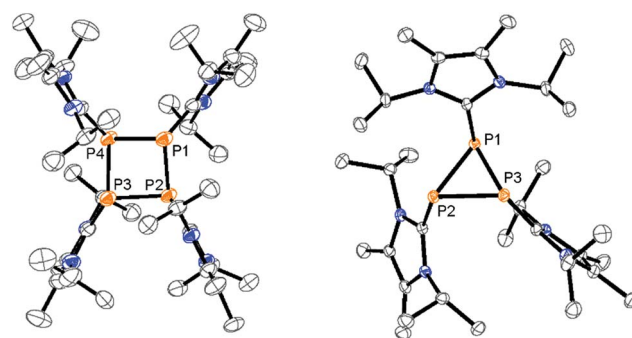
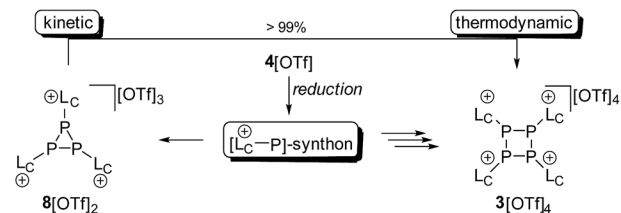


Fig. 1 Molecular structures of tetracation 3⁴⁺ in 3[OTf]₄·2CH₃CN (left) and trication 8³⁺ in 8[OTf]₃ (right; hydrogen atoms, solvate molecules and anions are omitted for clarity and thermal ellipsoids are displayed at 50% probability); selected bond lengths (Å) and angles (°) for 3⁴⁺: P1–P2 2.2382(8), P2–P3 2.2356(8), P3–P4 2.2400(8), P4–P1 2.2298(8), P1–C1 1.8222(2), P2–C12 1.824(2), P3–C23 1.823(2), P4–C34 1.822(2); P4–P1–P2 81.69(3), P1–P2–P3 81.54(3), P2–P3–P4 81.53(3), P3–P4–P1 81.62(3); 8³⁺: P1–P2 2.2459(6), P2–P3 2.2293(6), P1–P3 2.2139(6), P1–C1 1.8429(17), P2–C12 1.8373(17), P3–C23 1.8303(17); P1–P2–P3 59.300(18); P2–P3–P1 60.72(2), P3–P1–P2 59.975(18).





Scheme 3 Formation of $3[\text{OTf}]_4$ and $8[\text{OTf}]_3$ from the proposed $[\text{Lc-P}]^+$ -synthon by reduction of $4[\text{OTf}]$. Compound $8[\text{OTf}]_3$ readily rearranges in a CH_3CN solution at room temperature within 24 h to $3[\text{OTf}]_4$.

crystals of $8[\text{OTf}]_3$ could be isolated by overlaying the filtrate of the aforementioned reaction with *n*-hexane at -35°C . The molecular structure is depicted in Fig. 1. The bonding parameters of trication 8^{3+} are well in the expected range. Accordingly, one imidazoliumyl-substituent at the planar P_3 ring is *trans*-arranged to the other two imidazoliumyl-substituents which results in the characteristic pattern in the ^{31}P NMR spectrum.^{3,6} The ^{31}P NMR spectrum of 8^{3+} shows the AB_2 spin system ($\delta(\text{P}_\text{A}) = -142.5$ ppm, $\delta(\text{P}_\text{B}) = -130.8$ ppm; $^1J(\text{PP}) = -162$ Hz) in the typical region for cyclo-triphosphanes.¹⁹ To our surprise, time dependent ^{31}P NMR spectra reveal the rearrangement of 8^{3+} into cyclo-tetraphosphane 3^{4+} in a CD_3CN solution in the course of 24 h (Fig. 2), suggesting that 8^{3+} is the kinetic product of this reaction, while 3^{4+} is thermodynamically favorable. Although such ring expansions are known for neutral cyclo-phosphanes, it seems, due to electrostatic repulsive effects, thermodynamically contradicting that a trication (8^{3+}) transforms into the corresponding tetracation (3^{4+}),²⁴ rather than its fragmentation into charge separated species.^{24,25} We calculated the HOMO and the LUMO and optimized the structure by DFT methods using the PBE0/def2-TZVP level of theory (Fig. 3).¹⁶ The HOMO of cation 3^{4+} is basically located at the imidazoliumyl-substituents, whereas the LUMO is mostly located at the P_4 ring, suggesting

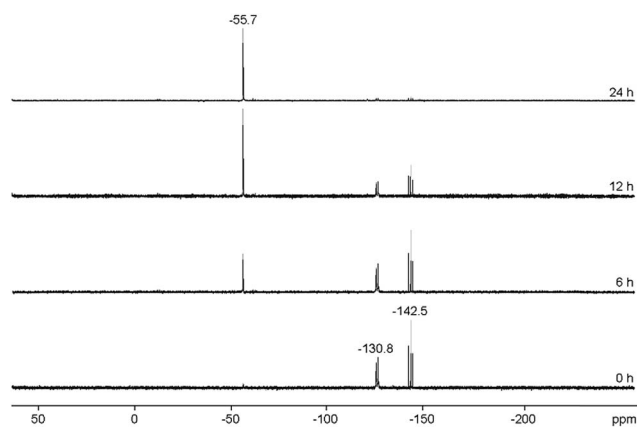


Fig. 2 Time dependent ^{31}P NMR spectra of 8^{3+} , revealing a slow conversion of triphosphirane 8^{3+} into cyclo-tetraphosphane 3^{4+} over the course of 24 h (300 K, CD_3CN). The resonances can be assigned as follows: $\delta(\text{P}) = -55.7$ ppm to 3^{4+} ; and AB_2 spin system $\delta(\text{P}_\text{A}) = -142.5$ ppm, $\delta(\text{P}_\text{B}) = -130.8$ ppm to 8^{3+} .

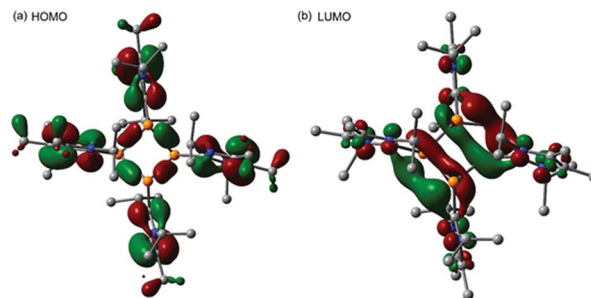
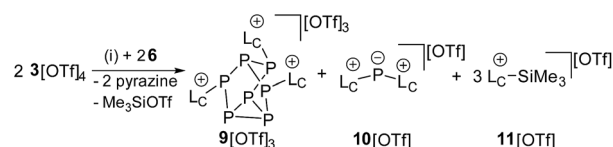


Fig. 3 HOMO (a) and LUMO (b) from the DFT optimized structure of 3^{4+} using the PBE0/def2-TZVP functional.

an electrophilic nature of the P atoms within the P_4 ring. The small degree of delocalization of the LUMO onto the imidazoliumyl-substituents also contributes to the stability of the tetracation 3^{4+} . We further reduced cyclo-tetraphosphane $3[\text{OTf}]_4$ again using the metal free reducing agent **6** (Scheme 4). Upon reaction of $3[\text{OTf}]_4$ with **6** in CH_3CN , the reaction mixture turned from colorless to orange. The ^{31}P NMR spectrum of this mixture showed after 8 hours a broad singlet resonance at $\delta(\text{P}) = -124.6$ ppm and a dynamic $\text{AA}'\text{A}''\text{BXX}'\text{X}''$ spin system with resonances at $\delta(\text{P}_\text{A}) = -178.5$ ppm, $\delta(\text{P}_\text{B}) = -164.9$ ppm and $\delta(\text{P}_\text{X}) = 13.2$ ppm (see Fig. S5†).¹⁶ The singlet resonance is assigned to cation 10^+ which was first reported by Macdonald and co-workers²⁶ whereas the spin system of higher order is attributed to the P_7 trication $[(\text{Lc})_3\text{P}_7]^{3+}$ (9^{3+}). Imidazolium cation 11^+ has been identified by its characteristic chemical shift in the ^{29}Si NMR spectrum.¹² $9[\text{OTf}]_3$ can be isolated by washing the obtained crude oil with THF and CH_2Cl_2 . After removal of all volatiles *in vacuo*, salt $9[\text{OTf}]_3$ is obtained as colorless solid in an overall yield of 61%. Fig. 3 shows the $^{31}\text{P}\{\text{H}\}$ NMR spectrum of 9^{3+} at 260 K which is iteratively fitted to an $\text{AA}'\text{A}''\text{BXX}'\text{X}''$ spin system and indicates the formation of a C_3 -symmetric stereoisomer (Fig. 4).²⁷ The A part at $\delta(\text{P}_\text{A}) = -178.5$ ppm is assigned to the P atoms of the basal P_3 -ring, the B part at $\delta(\text{P}_\text{B}) = -164.9$ ppm to the apical P atom and the X part at $\delta(\text{P}_\text{X}) = 13.2$ ppm to the bridging P atoms carrying the imidazoliumyl-substituents. Details on coupling constants are included in the ESI in Table S1.† Single crystals suitable for X-ray analysis are obtained by slow diffusion of CH_2Cl_2 into a saturated CH_3CN solution of $9[\text{OTf}]_3$ at -35°C . The molecular structure confirms the C_3 -symmetric, heptaphosphanor-tricycane cage with three imidazoliumyl-substituents at the bridging phosphorus atoms P2, P3 and P4 (Fig. 4). The P-C bond lengths (av. 1.834 Å) are comparable to those of tetracation 3^{4+} (av. 1.822 Å) and other imidazoliumyl-substituted

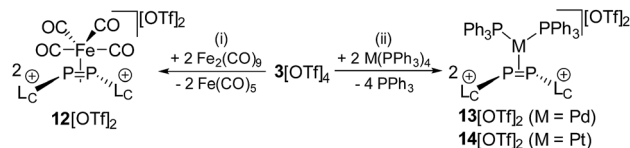


Scheme 4 Reaction of $3[\text{OTf}]_4$ with **6** to $9[\text{OTf}]_3$, $10[\text{OTf}]$ and $11[\text{OTf}]$; (i) +2 **6**, CH_3CN , 8 h, -2 pyrazine, $-\text{Me}_3\text{SiOTf}$, 61%.



phosphorus derivatives.¹⁵ The bonding parameters within the P₇-cage are comparable to those of our previously reported triarsonium-substituted P₇ cage compound,^{27a} *i.e.* the P–P bond lengths of the basal P atoms and the bridging P atoms (P2–P5, P3–P6 and P4–P7: av. 2.2238 Å) are slightly longer compared to those in the basal P₃-ring (av. 2.2166 Å) and to those between the apical and the bridging P atoms (P1–P2, P1–P3 and P1–P4: av. 2.1882 Å).

As the DFT calculations suggest rather electrophilic P atoms in **3**⁴⁺, we investigated its reactivity towards a series of low valent transition metal compounds in order to evaluate the ligand properties of **3**⁴⁺. **3**[OTf]₄ readily reacts with two equivalents of Fe₂(CO)₉ in a 1 : 1 mixture of THF/CH₃CN under the immediate formation of a brown-colored reaction mixture. The addition of Et₂O gives a yellow-colored precipitate in a 98% yield which was identified as complex **12**[OTf]₂.¹⁶ In this complex, a Fe(CO)₄ moiety is η²-coordinated by the diphosphene ligand [L_CP=PL_C]²⁺, which is formed *via* the metal induced [2 + 2]-fragmentation (Scheme 5). Single crystals suitable for X-ray analysis are obtained by slow diffusion of *n*-hexane into a saturated CH₂Cl₂ solution of **12**[OTf]₂. The complex reveals a trigonal core including the P atoms of the [L_CP=PL_C]²⁺ ligand and the Fe atom of the Fe(CO)₄ moiety. The imidazoliumyl-substituents of the [L_CP=PL_C]²⁺ ligand are arranged in an *E*-configuration (C1–P1–P2–C12 149.205(1)°) and the P1–Fe–P2 angle is relatively acute with a value of 54.490(19)°. The shortest distance between the diphosphene unit and the Fe atom is 2.105 Å as a result of the rather long Fe–P contacts (Fe–P1 2.3774(6) Å and Fe–P2 2.3590(6) Å). In contrast, typically Fe–P distances in η¹-coordination complexes are usually in the region of 2.2 Å.²⁸ The P–P bond length with a value of 2.1684(7) Å is significantly longer compared to those in a typical diphosphene such as Mes*–P=P–Mes* (2.034(2) Å),¹⁰ but slightly shorter compared to a typical P–P single bond (compare **3**⁴⁺: av. 2.235 Å). This also supports the η²-coordination of the P₂ ligand. The IR stretching frequencies of



Scheme 5 Transition metal induced [2 + 2]-fragmentation of **3**[OTf]₄ to give diphosphene complexes **12**[OTf]₂, **13**[OTf]₂ and **14**[OTf]₂; (i) + 2 Fe₂(CO)₉, CH₃CN/THF, 12 h, –2 Fe(CO)₅, 98%; (ii) + 2 M(PPh₃)₄ (M = Pd, Pt), CH₃CN/THF, 12 h, –4 PPh₃, 93% for **13**[OTf]₂ and 88% for **14**[OTf]₂.

the CO ligands are found at 2048 cm^{−1}, 2074 cm^{−1} and 2116 cm^{−1} and are significantly shifted to higher wave numbers compared to related reported phosphorus Fe(CO)₄ complexes (*e.g.* [(L₂–P–L₂)Fe(CO)₄][BPh₄]: 2029 cm^{−1}, 1947 cm^{−1}, 1907 cm^{−1}).²⁹ According to Tolman analysis,³⁰ this suggests that the [L_CP=PL_C]²⁺ ligand is a very strong π-acceptor which even surpasses PF₃ ([PF₃)Fe(CO)₄]: 2101 cm^{−1}, 2022 cm^{−1}, 2018 cm^{−1}, 1999 cm^{−1})³¹ due to the electron withdrawing effect of the imidazoliumyl-substituents.^{16,32} We therefore computed the π-accepting properties of the [L_CP=PL_C]²⁺ ligand which is related to the LUMO energy and shape of the ligand (see Fig. S12†).¹⁶ Our calculations show that the LUMO is the π*(P=P) bond which is perfectly pre-organized to interact with the d-orbitals of the Fe atom. Furthermore, the calculations indicated that, due to the dicationic charge, the LUMO is very low in energy (−9.313 eV; compare [L_CP=P–Dipp]⁺: −5.900 eV;^{16,33} L_C = 4,5-dichloro-1,3-bis(Dipp)-imidazol-2-yl; Dipp = 2,6-diisopropylphenyl; see Fig. S12†) which is beneficial for π-bonding with the corresponding transition metal. In addition, the second order perturbation analysis of **12**⁺ reveals a strong back-bonding from the d-orbitals of the Fe atom into the σ*(P–C)-orbital (*E*⁽²⁾ = 35.77 kcal mol^{−1}) indicating the stability of this complex.¹⁶ Similar findings have been recently reported by Macdonald and

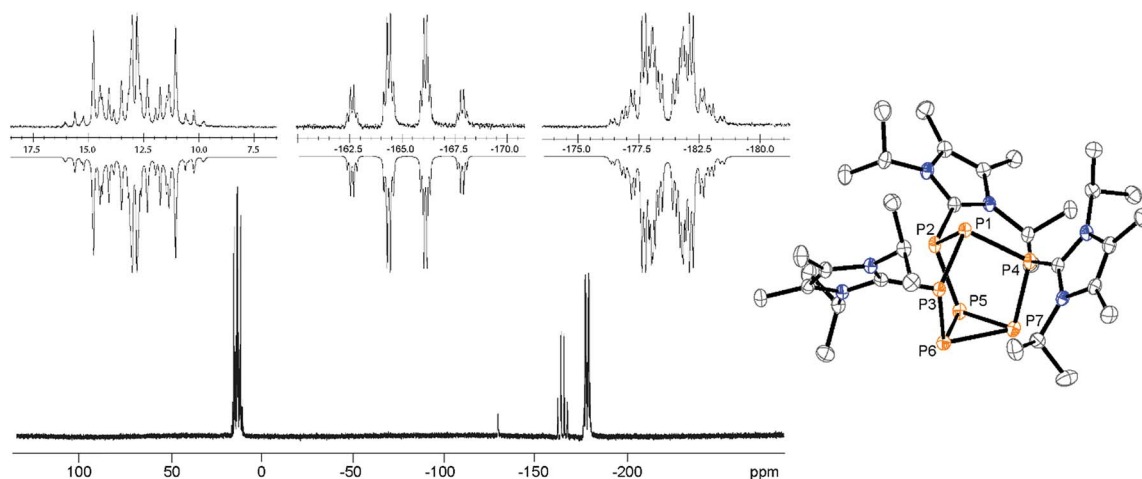


Fig. 4 ³¹P{H} NMR spectrum of **9**³⁺ (CD₃CN, 260 K). Insets show the extension of the experimental (upwards) and the iteratively fitted (downwards) AA'BB'XX' spin system (left); molecular structure of trication **9**³⁺ in **9**[OTf]₃·0.8CH₃CN·1.7CH₂Cl₂ (right); hydrogen atoms, solvate molecules and anions are omitted for clarity and thermal ellipsoids are displayed at 50% probability; selected bond lengths (Å) and angles (°) for: P1–P2 2.1810(6), P1–P3 2.1816(6), P1–P4 2.2022(6), P2–P5 2.2189(7), P3–P6 2.2282(7), P4–P7 2.2243(7), P5–P6 2.2250(7), P5–P7 2.2021(7), P6–P7 2.2227(7), P2–C1 1.8339(19), P3–C12 1.8291(19), P4–C23 1.8418(19).



co-workers for a related diphosphene nickel complex featuring two phosphoniumyl-substituents.³⁴

Similar [2 + 2]-fragmentation reactions are observed when $3[\text{OTf}]_4$ is reacted with 2 equivalents of $\text{M}(\text{PPh}_3)_4$ ($\text{M} = \text{Pd}, \text{Pt}$) in a 1 : 1 mixture of THF/ CH_3CN which leads to the formation of diphosphene complexes $13[\text{OTf}]_2$ ($\text{Pd}(\text{PPh}_3)_4$) and $14[\text{OTf}]_2$ ($\text{Pt}(\text{PPh}_3)_4$), respectively, under concomitant release of 4 equivalents PPh_3 (Scheme 5). After workup, complexes $13[\text{OTf}]_2$ and $14[\text{OTf}]_2$ are obtained as analytically pure red-colored ($13[\text{OTf}]_2$, 93%) or yellow-colored ($14[\text{OTf}]_2$, 88%) crystalline powders. The ^{31}P NMR spectrum of $13[\text{OTf}]_2$ at 300 K shows a broad singlet resonance at $\delta(\text{P}) = 10.2$ ppm for the phosphorus atoms of the diphosphene moiety which upon cooling to 270 K appears as *pseudo* triplet with a $^2J(\text{PP})$ coupling constant of 31 Hz. The two PPh_3 ligands give rise to a *pseudo*-triplet resonance at $\delta(\text{P}) = 23.4$ ppm ($^2J(\text{PP}) = 31$ Hz). The chemical shift is comparable to the related diphosphene complex $[(\eta^2\text{-F}_3\text{C-P=P-CF}_3)\text{Pd}(\text{PPh}_3)_2]$.³⁵ In contrast to the *trans*- $^2J(\text{PP})$ coupling, the magnitude of the *cis*- $^2J(\text{PP})$ coupling is not resolved, resulting in the observed *pseudo*-triplet splitting of this resonance. The ^{31}P NMR spectrum of $14[\text{OTf}]_2$ shows dynamic behavior at 300 K which upon cooling resolves to an AA'BB'X spin system. The high field shifted A part at $\delta(\text{P}_\text{A}) = -42.9$ ppm is assigned to the diphosphene moiety and shows a $^2J(\text{PP})$ coupling constant of 29 Hz similar to that of $13[\text{OTf}]_2$. The $^1J(\text{PPt})$ coupling with a value of 235 Hz is significantly smaller compared to typical $^1J(\text{PPt})$ coupling constants,³⁵ indicating the η^2 -coordination of the diphosphene ligand and the Pt atom.^{35,36} The B part at $\delta(\text{P}_\text{B}) = 25.1$ ppm ($^2J(\text{PP}) = 29$ Hz) is assigned to the PPh_3 ligands and reveals a typical $^1J(\text{PPt})$ coupling constant of 3279 Hz. The ^{195}Pt NMR spectrum shows a triplet of triplet resonance at $\delta(\text{Pt}) = -5015.7$ ppm ($^1J(\text{PtP}) = 3279$ Hz; $^1J(\text{PtP}) = 235$ Hz; see Fig. S8†). For both complexes a set of resonances with low intensities indicates the presence of rotational isomers in the NMR spectra which, however, only appears at temperatures below 270 K (see Fig. S6 and S7†). Single crystals suitable for X-ray analysis are

obtained for both complexes by slow diffusion of Et_2O into a saturated CH_3CN solutions (Fig. 5). Similar to complex 12 $[\text{OTf}]_2$, the η^2 -coordination of the corresponding metal by the diphosphene ligand is observed with the metal atoms being in a distorted square planar bonding environment. The averaged distance between the diphosphene unit and metals are in the same range (13^{2+} : $\text{Pd}\cdots\text{P-P}$ 2.124 Å, Pd-P1 2.3543(6) Å, Pd-P2 2.4003(8) Å; 14^{2+} : $\text{Pt}\cdots\text{P-P}$ 2.114 Å, Pt-P1 2.3530(7) Å, Pt-P2 2.3930(6) Å). The P-P bond lengths are only marginally shorter (13^{2+} 2.1340(12) Å and 14^{2+} 2.1562(9) Å) compared to that of complex 12^{2+} (2.1684(7) Å). Similar to the Fe complex the $[\text{L}_\text{C}\text{P}=\text{PL}_\text{C}]^{2+}$ ligand is in both cases also in the *E*-configuration (13^{2+} : C1-P1-P2-C12 148.393°; 14^{2+} : C1-P1-P2-C12 147.088°).

Notably, the known diphosphene complexes $[(\eta^2\text{-F}_3\text{C-P=P-CF}_3)\text{M}(\text{PPh}_3)_2]$ ($\text{M} = \text{Pd}, \text{Pt}$)^{35,37} are also synthesized from the reaction of the tetraphosphetane $(\text{CF}_3)_4\text{P}_4$ and the corresponding transition metal precursor $\text{M}(\text{PPh}_3)_4$ ($\text{M} = \text{Pd}, \text{Pt}$) suggesting the necessity of electron withdrawing substituents at the P atoms for the observed [2 + 2]-fragmentation. However, the formation of the dicationic diphosphene complexes (12^{2+} , 13^{2+} and 14^{2+}), featuring imidazoliumyl-substituents at the P atom, illustrate the potential use of cyclo-tetraphosphane 3^{4+} to synthesize a variety of novel cationic transition metal complexes. When $3[\text{OTf}]_4$ is reacted with one equivalent $\text{AuCl}(\text{tht})$ in THF/ CH_3CN (1 : 1) the formation of a small set of two coupled broad resonances at $\delta(\text{P}) = -49.9$ ppm and $\delta(\text{P}) = -24.7$ ppm along with a singlet resonance for $1[\text{OTf}]$ ($\delta(\text{P}) = 107.8$ ppm) can be observed in the ^{31}P NMR spectrum of the reaction mixture (see Fig. S9†). A complete consumption of 3 $[\text{OTf}]_4$ is achieved with 4 equivalents of $\text{AuCl}(\text{tht})$ (see Fig. S10†). Filtration of the reaction mixture after 12 h and recrystallization from THF, complex $15[\text{OTf}]_3$ can be isolated as a yellow powder. The yield can be increased by further recrystallization steps up to 57%. The ^{31}P NMR spectrum of $15[\text{OTf}]_3$ dissolved in CD_2Cl_2 shows at 300 K two broad resonances which resolve to an AA'BB' spin system at 260 K (Fig. 6). The A part at $\delta(\text{P}) = -49.9$ ppm can

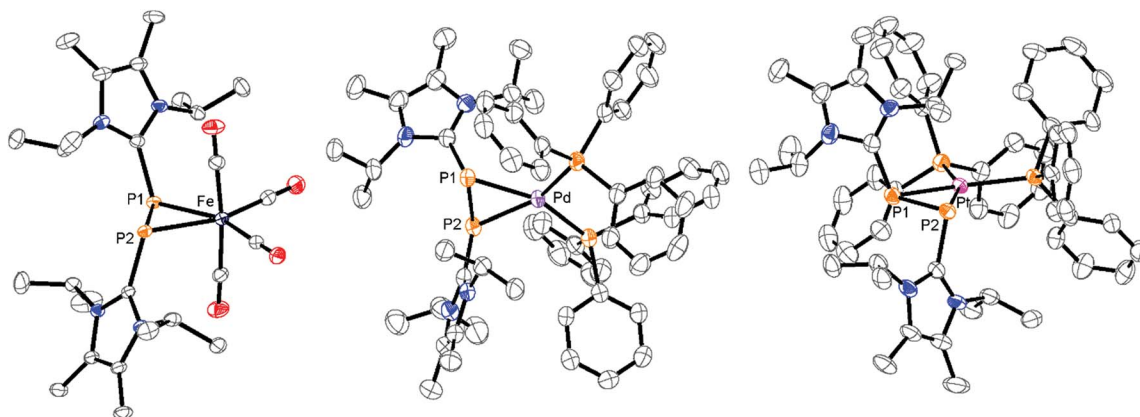


Fig. 5 Molecular structures of diphosphene complexes 12^{2+} in $12[\text{OTf}]_2$, 13^{2+} in $13[\text{OTf}]_2 \cdot 3\text{C}_6\text{H}_5\text{F}$ and 14^{2+} in $14[\text{OTf}]_2 \cdot 3\text{C}_6\text{H}_5\text{F}$; hydrogen atoms, solvate molecules and anions are omitted for clarity and thermal ellipsoids are displayed at 50% probability; selected bond lengths (Å) and angles (°) for $12^{2+}(\text{Fe})$: P1-P2 2.1684(7), $\text{Fe}\cdots\text{P-P}$ 2.105, Fe-P1 2.3774(6), Fe-P2 2.3590(6); C1-P1-P2-C12 149.205(1), P1-Fe-P2 54.490(19); $13^{2+}(\text{Pd})$: P1-P2 2.1340(12), $\text{Pd}\cdots\text{P-P}$ 2.124, Pd-P1 2.3543(6), Pd-P2 2.4003(8); C1-P1-P2-C12 148.393; $14^{2+}(\text{Pt})$: 2.1562(9), $\text{Pt}\cdots\text{P-P}$ 2.114, Pt-P1 2.3530(7), Pt-P2 2.3930(6); C1-P1-P2-C12 147.088.



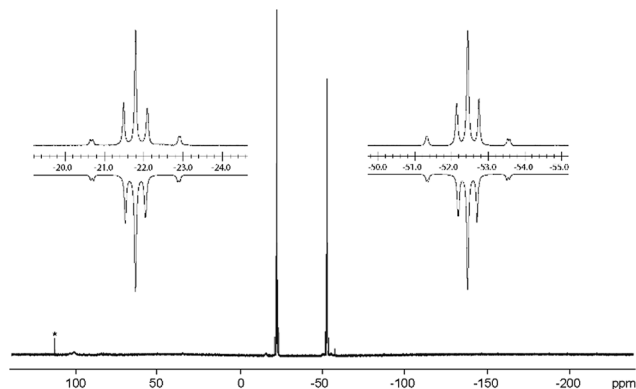


Fig. 6 $^{31}\text{P}(\text{H})$ NMR spectrum of 15^{3+} (CD_2Cl_2 , 260 K). Insets show the extension of the experimental (upwards) and the iteratively fitted (downwards) AA'XX' spin system; trace amounts of unidentified side product is marked with an asterisk.

be assigned to the backbone P atoms and the B part at $\delta(\text{P}) = -24.7$ ppm to the Au-coordinating P atoms. Details on coupling constants are included in the ESI in Table S2.† Single crystals suitable for X-ray analysis are obtained by overlaying a saturated CH_2Cl_2 solution of $15[\text{OTf}]_3$ with pentane at -35°C (Fig. 7). The Au atom is coordinated by two P atoms resulting in a five-membered P_4Au -core structure which reveals an envelope conformation. Hey-Hawkins and co-workers reported on a similar structural motif where a *catena*-tetraphosphane-1,4-diide coordinates $\text{Ni}(0)$ and $\text{Pd}(0)$, respectively.³⁸ The gold atom in 15^{3+} reveals a square-planar geometry where the P_4 -chain chelates the gold atom *via* P1 and P4. The phosphorus gold bond lengths (P1–Au 2.3053(11) Å and P4–Au 2.3103(10) Å) are well in the range for related P–Au^{III} bonds (av. 2.314).³⁹ The four P atoms exhibit a pyramidal bonding environment with P–P bond lengths (av. 2.237 Å) being in the range of typical P–P single bonds (2.22 Å).²⁰ As expected, the bond angles around the phosphorus atoms P1 and P4 (Au–P1–P2 107.79(5)° and P3–P4–Au 107.90(5)°) are wider compared to the other angles within

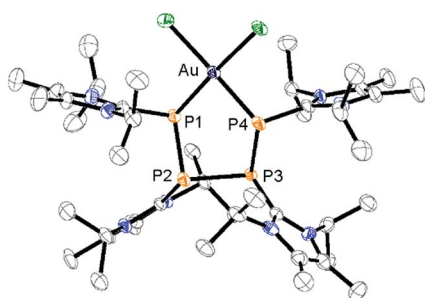
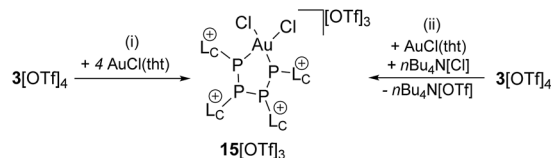


Fig. 7 Molecular structure of gold complex 15^{3+} in $15[\text{OTf}]_3 \cdot 3\text{CH}_2\text{Cl}_2$; hydrogen atoms, solvate molecules and anions are omitted for clarity and thermal ellipsoids are displayed at 50% probability; selected bond lengths (Å) and angles (°): P1–P2 2.2364(14), P2–P3 2.2304(13), P3–P4 2.2467(15), P1–Au 2.3053(11), P4–Au 2.3103(10); P1–Au–P4 92.63(4), Au–P1–P2 107.79(5), P1–P2–P3 93.22(5), P2–P3–P4 90.66(5), P3–P4–Au 107.90(5).



Scheme 6 Formation of the 5-membered P_4Au -complex $15[\text{OTf}]_3$; (i) +4 $\text{AuCl}(\text{tht})$, $\text{THF}/\text{CH}_3\text{CN}$, 8 h 57%; (ii) + $\text{AuCl}(\text{tht})$, + $n\text{Bu}_4\text{N}[\text{Cl}]$, $\text{THF}/\text{CH}_3\text{CN}$, $-n\text{Bu}_4\text{N}[\text{OTf}]$, 76% determined by ^{31}P NMR spectroscopy.

the P_4Au -core structure (P1–Au–P4 92.63(4)°, P1–P2–P3 93.22(5)°, P2–P3–P4 90.66(5)°). Different from the above mentioned reactions, the reaction of $3[\text{OTf}]_4$ with an excess of AuCl leads to a reductive insertion of the gold atom into the P_4 -ring of $3[\text{OTf}]_4$ leading to the formation of a five-membered P_4Au -core structure (Scheme 6).

In this reaction, the Au(I) atom reductively inserts into a P–P bond of 3^{4+} and is oxidized to Au(III). The free coordination site at the Au atom is saturated by a further chloride anion, leading to the square planar coordination environment at the Au(III) atom. Thus, it appears that the excess of the $\text{AuCl}(\text{tht})$ merely serves as chloride source in this reaction. We found that the reaction can be carried out with one equivalent $\text{AuCl}(\text{tht})$ and one equivalent $n\text{Bu}_4\text{N}[\text{Cl}]$ as chloride source which leads to the consumption of $3[\text{OTf}]_4$ up to 90% and to the formation of the P_4Au -complex $15[\text{OTf}]_3$ in 70% yield as judged by ^{31}P NMR spectroscopy (see Fig. S11†).

Conclusions

In summary, we successfully synthesized the first example of a cationic cyclo-phosphane with the general formula $[(\text{L}_\text{C})_n\text{P}_n]^{n+}$ ($3[\text{OTf}]_4$) *via* the reduction of $4[\text{OTf}]$ using 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (6). Due to the electrophilic nature of the P atoms within the P_4 ring, which was shown by theoretical calculations, we further reduced compound $3[\text{OTf}]_4$ to give the nortricyclane P_7 compound $9[\text{OTf}]_3$. The reaction of $3[\text{OTf}]_4$ with low oxidation state transition metal complexes $\text{Fe}_2(\text{CO})_9$, $\text{Pd}(\text{PPh}_3)_4$ and $\text{Pt}(\text{PPh}_3)_4$ leads to the formation of dicationic diphosphene complexes $12[\text{OTf}]_2$, $13[\text{OTf}]_2$ and $14[\text{OTf}]_2$, respectively. The transition metal mediated [2 + 2]-fragmentation reaction of 3^{4+} is attributed to the cationic imidazoliumyl-substituents causing the electrophilic nature of the P atoms in 3^{4+} . Due to the dicationic charge, the P_2 ligand in the aforementioned complexes is a very good π -acceptor with an exceptionally low lying LUMO ($\pi^*-\text{P}=\text{P}$ bond) rendering this ligand optimal for the complexation of a π -basic metal center. In contrast, the reaction of $3[\text{OTf}]_4$ with an excess of $\text{AuCl}(\text{tht})$ gives rise to the formation of complex $15[\text{OTf}]_3$ featuring a five-membered P_4Au -core structure. In this reaction, the Au(I) atom reductively inserts into a P–P bond of 3^{4+} and is oxidized to Au(III). As the DFT calculations of the optimized structure of 3^{4+} reveal rather Lewis acidic P atoms, the reactivity towards nucleophiles promises a variety of novel phosphorus compounds featuring interesting bonding motifs and properties.



Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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