P−P Condensation and P−N/P−P Bond Metathesis: Facile Synthesis of Cationic Tri- and Tetraphosphanes

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Dedicated to Professor F. Ekkehardt Hahn on the occasion of his 65th birthday

Abstract: *$[L_C^R P((PhP)_2C_2H_4)][OTf]$ (**4a,b**[OTf]) and $[L_C^{iPr}P(PPh_2)_2][OTf]$ (**5b**[OTf]) were prepared from the reaction of imidazoliumyl-substituted dipyrazolylphosphane triflate salts $[L_C^R P(pyr)_2][OTf]$ (**3a,b**[OTf]; **a**: R = Me, **b** = iPr; L_C^R = 1,3-dialkyl-4,5-dimethylimidazol-2-yl; pyr = 3,5-dimethylpyrazol-1-yl) with the secondary phosphanes PhP-(H)C_2H_4P(H)Ph and Ph_2PH. A stepwise double P−N/P−P bond metathesis to catena-tetraphosphane-2,3-diium triflate salt $[(Ph_2P)_2(L_C^{Me}P)_2][OTf]_2$ (**7a**[OTf]$_2$) is observed when reacting **3a**[OTf] with diphosphane P_2Ph_4. The coordination ability of **5b**[OTf] was probed with selected coinage metal salts $[Cu(CH_3CN)_4]OTf$, AgOTf and AuCl(tht) (tht = tetrahydrothiophene). For AuCl(tht), the helical complex $[\{(Ph_2PPL_C^{iPr})Au\}_4][OTf]_4$ (**9**[OTf]$_4$) was unexpectedly formed as a result of a chloride-induced P−P bond cleavage. The weakly coordinating triflate anion enables the formation of the expected copper(I) and silver(I) complexes $[(5b)M-(CH_3CN)_3][OTf]_2$ (M = Cu, Ag) (**10**[OTf]$_2$, **11**[OTf]$_2$).*

Introduction

Next to carbon, phosphorus has the strongest tendency to form homoatomic frameworks.[1] As shown by the pioneering work of Baudler,[2] von Schnering,[3] Krossing,[4] and numerous other groups, this has resulted in a large variety of neutral, anionic, and cationic polyphosphanes.[5] Synthetic methods for the preparation of polyphosphanes from P_1 sources are typically based on salt metathesis of a halophosphane with a metal phosphide,[2,6] the reaction of chlorophosphanes with silyl- or stannylphosphanes,[7] or the reduction of a halophosphane with alkali metals.[8] Nevertheless, the established routes towards neutral polyphosphanes are often plagued by poor selectivity and low yields.[9] Alkyl chain analogous *catena*-phosphanes consisting of tricoordinated phosphorus atoms are mostly restricted to neutral triphosphanes[10] and tetraphosphanes.[11] Phosphanyl phosphonium ions are related cationic derivatives, but comprise tetracoordinate phosphorus atoms,[12] while onio-substituted polyphosphanes are still elusive. In this regard, we developed a selective, high-yielding synthetic strategy based on pyrazolyl-substituted phosphanes such as **1** as readily accessible P_1 units (Scheme 1).[13] Pyrazolyl substituents are excellent leaving groups, which enable clean condensation reactions with primary and secondary phosphanes for the construction of

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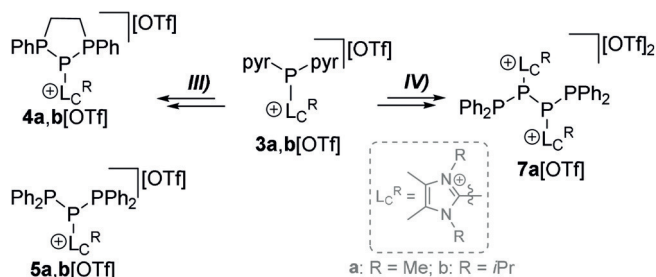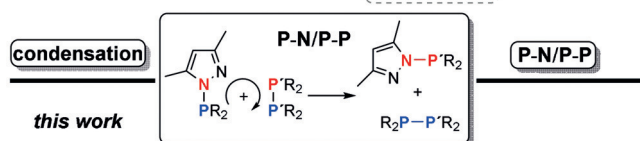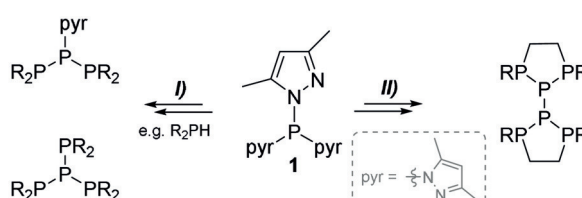   Institute of Inorganic Chemistry, Universität Regensburg
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Scheme 1. Condensation and P−N/P−P metathesis reactions for P−P bond formation reactions to access neutral (previous work; I-II) and cationic (this work; III-IV) polyphosphanes from pyrazolyl-substituted P_1 units such as **1** and **3a,b**[OTf] (L_C = 1,3-dialkyl-4,5-dimethylimidazol-2-yl; a: R = Me; b: R = iPr; pyr = 3,5-dimethylpyrazol-1-yl).

P–P bonds.[14] Previous examples gave rise to diverse structural motifs such as triphosphanes and *iso*-tetraphosphanes (Scheme 1, **I**).[15] Larger frameworks, such as hexaphosphanes, are accessible through the concept of P–N/P–P bond metathesis (Scheme 1, **II**).[16] This concept allows for a cross exchange of bonding partners similar to olefin metathesis[17] in the reaction of a pyrazolyl-substituted phosphane featuring a P–N bond with a diphosphane featuring a P–P bond. In such a reaction, the total number of P–N and P–P bonds remains constant (Scheme 1, black box).[16]

Polyphosphorus cations stabilized by imidazoliumyl substituents are very scarce, and we envisioned the use of our recently developed P–N/P–P bond metathesis strategy for their formation. The exchange of one pyrazolyl substituent (pyr = 3,5-dimethylpyrazol-1-yl) in tripyrazolylphosphane Ppyr$_3$ (**1**) with the imidazoliumyl substituent L_C^R (L_C^R = 1,3-dialkyl-4,5-dimethyl-imidazol-2-yl; **a**: R = Me; **b**: R = *i*Pr) gives triflate salts $[L_C^R Ppyr_2][OTf]$ (**3a,b**[OTf]). Since imidazoliumyl substituents such as L_C^R are known to stabilize unusual bonding motifs at the directly bonded P atom,[18] we were keen to explore the synthetic potential of these readily accessible P$_1$ building blocks. Herein, we describe the facile synthesis of cationic triphosphorus (**4a,b**[OTf], **5b**[OTf]) and tetraphosphorus (**7a**[OTf]$_2$) compounds via the condensation of dipyrazolylphosphanes **3a,b**[OTf] with secondary phosphanes and via a stepwise P–N/P–P bond metathesis in the reaction of **3a**[OTf] with P$_2$Ph$_4$. A detailed NMR spectroscopic investigation provides mechanistic insight into the unusual P–N/P–P bond metathesis reaction. By investigating the coordination properties of **5b**[OTf] in the reaction with AuCl(tht) (tht = tetrahydrothiophene), we discovered a tetranuclear gold complex (**9**[OTf]$_4$) that is formed as a result of a chloride induced P–P bond cleavage of **5b**[OTf]. The critical mechanistic role of nucleophilic chloride ions is underlined by the synthesis of copper(I) and silver(I) complexes **10**[OTf]$_2$ and **11**[OTf]$_2$, which contain intact triphosphane units **5b**$^+$.

Results and Discussion

The synthesis of dipyrazolylphosphane salts **3a,b**[OTf] follows our established procedure for the synthesis of **1**,[19] which is conveniently adapted to the condensation of the dichlorophosphane salts **2a,b**[OTf][20] with two equiv of 3,5-dimethyl-1-(trimethylsilyl)-1*H*-pyrazole (pyrSiMe$_3$) under release of two equiv Me$_3$SiCl (Scheme 2). The addition of *n*-hexane to the reaction mixture leads to the precipitation of
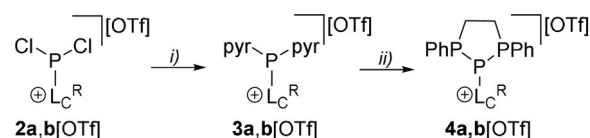
Scheme 2. Synthesis of **3a,b**[OTf] and **4a,b**[OTf]; i) +2 pyrSiMe$_3$; −2 Me$_3$SiCl, C$_6$H$_5$F for **3a**[OTf] and CH$_2$Cl$_2$ for **3b**[OTf], r.t., 16 h, **3a**[OTf]: 96%, **3b**[OTf]: 88%; ii) + PhP(H)C$_2$H$_4$P(H)Ph, −2 pyrH, C$_6$H$_5$F, r.t., 16 h; **4a**[OTf]: 72%, **4b**[OTf]: 85%.

analytically pure, colorless salts **3a**[OTf] (96% yield) and **3b**[OTf] (88% yield).[21] The ^{31}P{^{1}H} NMR resonances of **3a,b**[OTf] in CD$_2$Cl$_2$ (**3a**[OTf]: δ(P) = 36.9 ppm; **3b**[OTf]: δ(P) = 41.5 ppm) are significantly high-field shifted compared to **2a,b**[OTf] (**2a**[OTf]: δ(P) = 107.8 ppm; **2b**[OTf]: δ(P) = 109.1 ppm).[20b,21] The molecular structures of the cations are confirmed by X-ray diffraction analyses (**3a**[OTf]: Figure S1, **3b**[OTf]: Figure 1),[21] which show the expected pyramidal bonding environment at the P atom and typical P–N bond lengths ranging from 1.7055(13) to 1.7334(11) Å (cf. **1**: 1.714(4) Å).[22]

The P–P condensation reaction of **3a,b**[OTf] (Scheme 2) proceeds cleanly with racemic 1,2-bis(phenylphosphanyl)-ethane (PhP(H)C$_2$H$_4$P(H)Ph, one equiv.) to give 1,2,3-triphospholanium salts **4a,b**[OTf] under release of 3,5-dimethyl-1*H*-pyrazole (pyrH). After work-up, both compounds can be isolated in 72% and 85% yield, respectively. Suitable crystals for X-ray diffraction analyses were obtained by slow diffusion of *n*-hexane into a saturated CH$_2$Cl$_2$ solution of **4a**[OTf] and
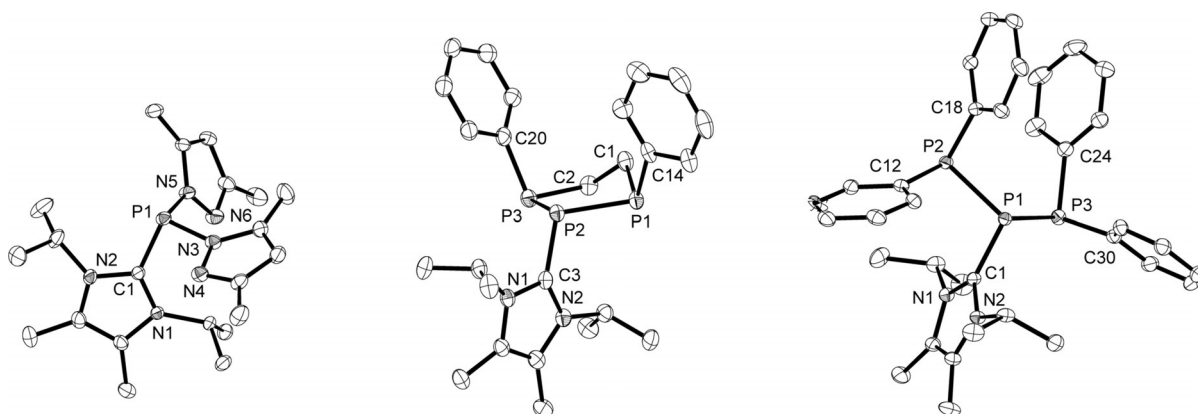
Figure 1. Molecular structure of cations **3b**$^+$, **4b**$^+$, and **5b**$^+$ of the respective triflate salts;[33] hydrogen atoms, solvate molecules, and anions are omitted for clarity and ellipsoids are set at 50% probability; selected bond lengths [Å] and angles [°]: **3b**$^+$: P1–N1 1.7334(11), P1–N2 1.7007(11), N5-P1-N3 102.51(5); **4b**$^+$: P1–P2 2.2248(11), P2–P3 2.2181(11), P1-P2-P3 98.37(4) **5b**$^+$: P1–P2 2.2222(5), P1–P3 2.2311(5), P2-P1-P3 106.539(19).

by diffusion of Et_2O into a CH_3CN solution of **4b**[OTf] at −30°C.[21] The molecular structures are shown in the Supporting Information, Figure S2 for **4a**[OTf] and in Figure 1 for **4b**[OTf]. Similar to related 1,2,3-triphospholane derivatives,[16,23] both cations show an envelope conformation of the five-membered ring in the solid state in which the phenyl and the imidazoliumyl substituents adopt an all-*trans* configuration. The P−P bond lengths range from 2.2156(4) to 2.2291-(4) Å and are comparable to other structurally related 1,2,3-triphospholanes.[24] The P1-P2-P3 angles with a value of 98.261(16)° for **4a**[OTf] and 101.83(4) for **4b**[OTf] are more acute compared to acyclic derivatives. The ^{31}P NMR spectrum of **4a**[OTf] reveals at room temperature two sharp resonances of an AX_2 spin system (**4a**[OTf]: $\delta(P_A) = -47.4$ ppm, $\delta(P_X) = 5.5$ ppm; $^1J(P_AP_X) = -219$ Hz), while the resonances are broadened in case of **4b**[OTf] owing to dynamic behavior attributed to the presence of two conformational isomers which are in exchange.[25,26] A detailed discussion is given in the Supporting Information.[21]

The related reaction of **3a,b**[OTf] with diphenylphosphane to form triphosphanes **5a,b**[OTf] is less selective (Scheme 3, **I**). The ^{31}P NMR spectrum of a 1:2 reaction mixture of **3a**[OTf] and Ph_2PH (Figure S6)[21] reveals the formation of several compounds, where **5a**[OTf] is only the minor product ($\delta(P_A) = -57.1$ ppm, $\delta(P_X) = -22.4$ ppm; $^1J(P_AP_X) = -157$ Hz). The ^{31}P NMR spectrum of the crude reaction mixture additionally shows the presence of cation $L_C^{Me}P(H)PPh_2$ (**6a**$^+$: $\delta(P_A) = -52.4$ ppm, $\delta(P_X) = -17.8$ ppm, $^1J(P_AP_X) = -158$ Hz, $^1J_{PH} = -230$ Hz), $pyrPPh_2$ ($\delta(P) = 39.3$ ppm), pyrH, P_2Ph_4 ($\delta(P) = -15.3$ ppm) and *catena*-tetraphosphane **7a**[OTf]$_2$ (see below). Cations **5a**$^+$ and **6a**$^+$ are the result of a stepwise condensation of **3a**[OTf] and Ph_2PH (Scheme 3, **I**) accompanied by the formation of 1,3-(dimethylpyrazolyl)diphenylphosphane ($pyrPPh_2$) and 3,5-dimethyl-1*H*-pyrazole (pyrH). Diphosphane P_2Ph_4 is the condensation product of Ph_2PH and $pyrPPh_2$ (Scheme 3, **II**). *Catena*-tetraphosphane-2,3-diium triflate **7a**[OTf]$_2$ can be isolated in 29% yield by filtration of the reaction mixture and washing with C_6H_5F.

The formation of P_2Ph_4 in the aforementioned reaction prompted us to investigate its reaction with **3a**[OTf] in a 2:3 ratio as we envisioned a P−N/P−P bond metathesis for the formation of **7a**$^{2+}$. Indeed, **7a**[OTf]$_2$ is formed selectively in this reaction in C_6H_5F, where the triflate salt of **7a**$^{2+}$ precipitates as analytically pure, colorless material in a much higher yield (77%) over the course of three days. Mechanistically, this reaction involves a twofold P−N/P−P bond metathesis. In the first step, **3a**$^+$ reacts with P_2Ph_4 to give **8a**$^+$ and **5a**$^+$ under concomitant formation of $pyrPPh_2$ (Scheme 3, **III**), which is confirmed by ^{31}P NMR investigations of the reaction mixture showing **8a**$^+$ (AX spin system, $\delta(P_A) = -23.6$ ppm, $\delta(P_X) = 34.1$ ppm, $^1J(P_AP_X) = -221$ Hz) and **5a**$^+$ as intermediates (Supporting Information, Figure S4).[21] In the second step, **8a**$^+$ and **5a**$^+$ undergo a further P−N/P−P bond metathesis reaction, which ultimately gives **7a**$^{2+}$ via the release of another equivalent of $pyrPPh_2$ (Scheme 3, **III**). Dication **7a**$^{2+}$ gives rise to an AA′XX′ spin system in the ^{31}P NMR spectrum with resonances at $\delta(P_A) = -66.5$ ppm and $\delta(P_X) = -22.6$ ppm ($^1J(P_AP_{A'}) = -132$ Hz, $^1J(P_AP_X) = -138$ Hz, $^2J(P_AP_{X'}) = 80$ Hz and $^3J(P_XP_{X'}) = -7$ Hz; Supporting Information, Figure S5; detailed ^{31}P NMR parameters are included in Table S1).[21]

The molecular structure of **7a**$^{2+}$ reveals a *catena*-P_4 structural motif with two imidazoliumyl substituents L_C^{Me} bound to the inner P atoms (Figure 2). In the solid state, **7a**$^{2+}$ adopts a *meso*-configuration. The *rac*-isomer is likely energetically unfavorable due to the steric bulk of the imidazoliumyl substituents. The three P−P bond lengths are nearly equal (2.2364(5) Å, 2.2345(6) Å and 2.2397(5) Å) and compare well to the similar P−P bonds in comparable acyclic compounds.[12,27]

When the analogous condensation reaction is performed with compound **3b**[OTf] and Ph_2PH, the related dication **7b**$^{2+}$ is not formed and an equilibrium mixture of cations **5b**$^+$, **6b**$^+$, and **8b**$^+$ is observed (Scheme 4). It appears that the increased steric requirement of the *i*Pr group in **3b**$^+$ prevents the formation of the P_4 chain from the condensation reaction of **6b**$^+$ and **8b**$^+$.

Triphosphane **5b**[OTf] can be isolated in a significantly higher yield when the reaction is performed stepwise. First, **3b**[OTf] (one equiv.) is reacted with Ph_2PH (2 equiv.), resulting in a mixture of **5b**[OTf] ($\delta(P_A) = -55.8$, $\delta(P_X) = $
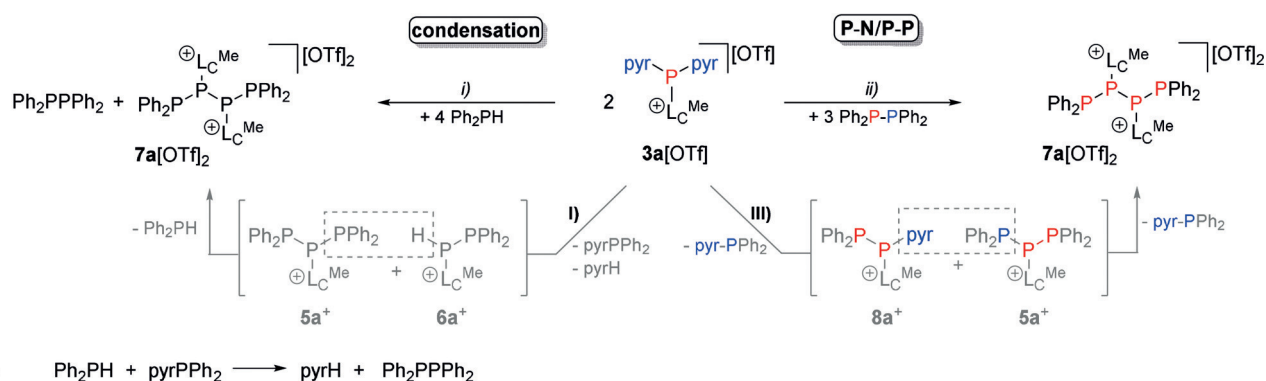
Scheme 3. I) Reaction of **3a**[OTf] with Ph_2PH giving *catena*-tetraphosphane **7a**[OTf]$_2$ along with P_2Ph_4 and intermediates **5a**$^+$ and **6a**$^+$ (gray); i) C_6H_5F, 45 min; II) formation of 3,5-dimethyl-1*H*-pyrazole (pyrH) and diphosphane (P_2Ph_4) from the reaction of sec. phosphane ($HPPh_2$) and the pyrazolylphosphane $pyrPPh_2$; III) ii) C_6H_5F, 3 d; formation of **7a**[OTf]$_2$ from the reaction of **3a**[OTf] with P_2Ph_4 and intermediates **8a**$^+$ and **5a**$^+$ (gray).
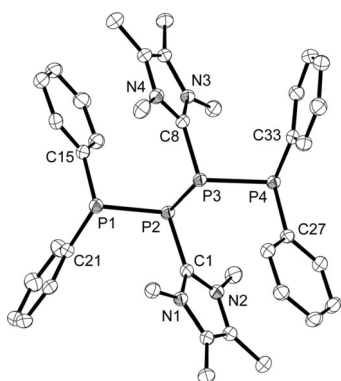
Figure 2. Molecular structure of **7a**$^{2+}$ in **7a**[OTf]$_2$;[33] hydrogen atoms, solvate molecules, and anions are omitted for clarity and ellipsoids are set at 50% probability; selected bond lengths [Å] and angles [°]: P1–P2 2.2364(5), P2–P3 2.2345(6), P3–P4 2.2397(5), P1-P2-P3 94.33(2), P2-P3-P4 99.47(2).
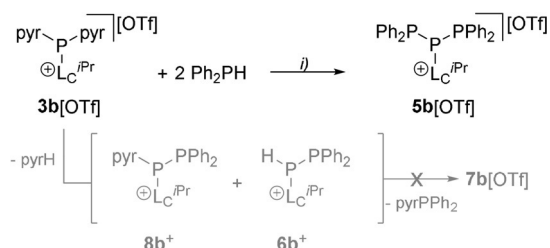
Scheme 4. Synthesis of triphosphane **5b**[OTf]; i) −pyrH, CH$_3$CN, r.t., 16 h, then + Ph$_2$Ppyr, −pyrH, THF, r.t., 16 h; **5b**[OTf], yield (NMR): 52%, yield (isolated): 21%.

−19.1, $^1J(P_AP_X) = -154$ Hz) and **6b**[OTf] ($\delta(P_A) = -108.7$ ppm, $\delta(P_X) = -23.5$ ppm, $^1J(P_AP_X) = 141$ Hz), which can be detected by ^{31}P NMR spectroscopy (Supporting Information, Figure S8). In the second step, pyrPPh$_2$ (0.7 equiv) is added. In this case, **5b**[OTf] can be obtained as crystalline crude material of 70% purity. Nevertheless, the compound can be isolated as a pure material in 21% yield after several recrystallization steps. Attempts to selectively synthesize **5b**[OTf] via dehalosilylation[7a,b] or salt metathesis[2] from the dichlorophosphane **2b**[OTf] were unsuccessful which underlines the advantageous use of pyrazolylphosphanes.[21] X-ray-quality crystals are obtained by slow diffusion of Et$_2$O into a saturated THF solution of **5b**[OTf] at −30°C (Figure 1). The P−P bond lengths of 2.2222(5) Å and 2.2311(5) Å compare well to those in comparable acyclic compounds.[12,27]

Realizing that the synthesized *oligo*-phosphorus compounds should have considerable potential as multidentate ligands, we explored their coordination chemistry towards gold(I) chloride. The reactions of **7a**[OTf]$_2$ and **4b**[OTf] with AuCl(tht) turned out to be rather unselective and result in complex mixtures of several products of currently unknown constitution.[21] However, the addition of one equivalent of AuCl(tht) to a solution of **5b**[OTf] in THF (Scheme 5) led to the formation of a pale yellow precipitate. The ^{31}P{^{1}H} NMR spectrum of the filtrate shows one sharp resonance which is
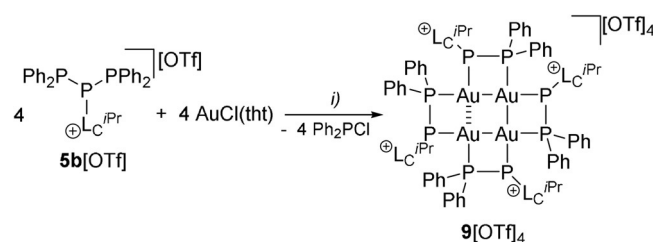

Scheme 5. Reaction of **5b**[OTf] with AuCl(tht); i) THF, r.t., 1 h; **9**[OTf]$_4$: 85%.

assigned to Ph$_2$PCl ($\delta(P) = 82.5$ ppm; Supporting Information, Figure S15).[21] The ^{31}P{^{1}H} NMR spectrum of the solid material dissolved in CD$_3$CN shows a highly symmetric, higher order spin system which can be attributed to the helical cationic tetragold complex [{(Ph$_2$PPL$_C$^{iPr})Au}$_4$][OTf]$_4$ (**9**-[OTf]$_4$). The two major resonances are at $\delta(P_A) = -86.6$ ppm and $\delta(P_X) = 29.0$ ppm next to additional signals which we attribute to the presence of a minor diastereomer (Supporting Information, Figure S16).[21] Upon cooling to 235 K, the resonances of this minor diastereomer vanish which allowed iterative fitting of the spectrum to an AA′A″A‴XX′X″X‴ spin system (Figure 3, left; see the Supporting Information, Table S2 for further details).[21] The A part of the spin system is assigned to the phosphorus atoms carrying the imidazoliumyl substituents and the X part to the Ph$_2$P moiety. The resonances of the ligand are significantly high-field shifted with a much larger $^1J(P_AP_X)$ coupling constant of −328 Hz compared to related free diphosphanide compounds (compare (cAAC)P−PPh$_2$, cAAC = cyclic (alkyl)(amino)carbene $\delta(P_A) = -27.3$ ppm and $\delta(P_X) = 41.2$ ppm, $^1J(P_AP_X) = -242$ Hz),[28] which is caused by Au coordination. The unusually large $^4J(P_AP_{A''})$ coupling constant of 314 Hz indicates a through space coupling path as a result of the orientation of the electron pairs of the imidazoliumyl-substituted phosphorus atoms.[29]

Recrystallization of the precipitate by diffusion of benzene into a saturated CH$_3$CN solution of **9**[OTf]$_4$ gave yellow–orange colored crystals suitable for X-ray analysis, which revealed the tetranuclear, helical structure of the tetracation **9**$^{4+}$. The homometallic core features three short Au−Au contacts (3.27349(12) Å, 3.16209(16) Å and 3.1926(3) Å) being well in the range of aurophilic interactions.[30] One large Au1−Au2 distance of 3.4341(3) Å is at the upper limit for a significant bonding contribution (Figure 3, right). The P−P bond lengths range from 2.1900(14) to 2.1958(13) Å as expected for P−P single bonds.[1] The average Au−P distance of the phosphanide atoms (P1, P3, P5 and P7) towards the gold atoms (2.3332(9) Å to 2.3557(9) Å) is slightly larger than for the diphenyl phosphanyl atoms (P2, P4, P6 and P8) (2.2908(9) Å to 2.3062(9) Å), indicating a stronger donor ability of the phosphanyl moiety. The diagonal Au−Au separations of 4.2052(2) Å and 4.2552(3) Å are significantly smaller compared to other square planar tetranuclear gold complexes.[31] This leads to a rhombic cluster with an angle of 132° between the planes Au1,Au2,Au3 and Au1,Au3,Au4.

Mechanistically, the formation of **9**[OTf]$_4$ is considered as a P−P bond cleavage reaction of **5b**[OTf] by nucleophilic
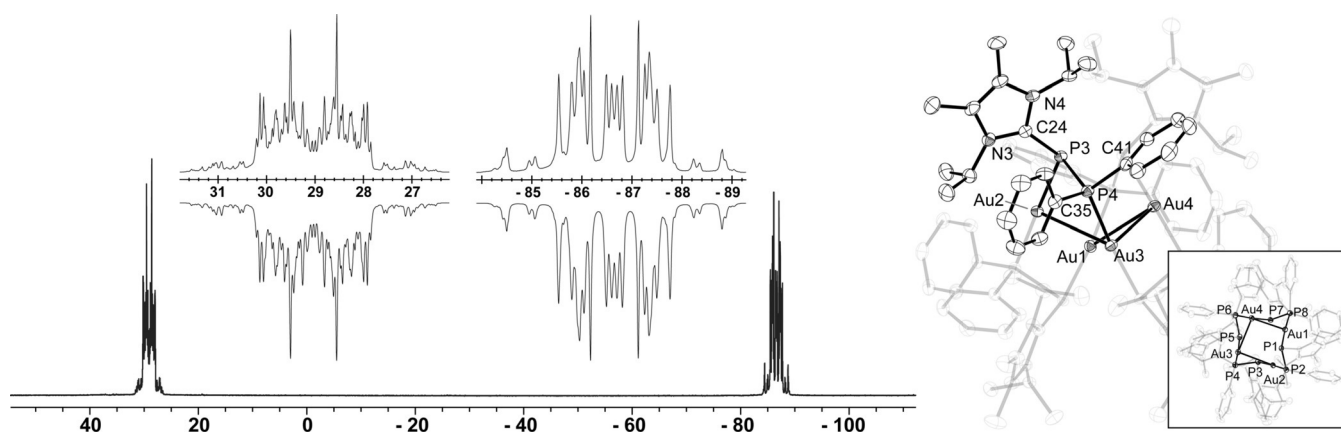
Figure 3. Left: ^{31}P{H} NMR spectrum of 9^{4+} (CD$_3$CN, 235 K); insets show the zoom in of the experimental (upwards) and the iteratively fitted (downwards) AA'A''A'''XX'X''X''' spin system; right: Molecular structure of gold complex 9^{4+} in 9[OTf]$_4$; hydrogen atoms, solvate molecules, and anions are omitted for clarity and ellipsoids are set at 50% probability; inset shows top view of the structure. Selected bond lengths [Å]: Au1–Au2 3.4341(3), Au2–Au3 3.27349(12), Au3–Au4 3.16209(16), Au4–Au1 3.1926(3), P1–P2 2.1958(13), P3–P4 2.1914(13), P5–P6 2.1900(14), P7–P8 2.1910(14).

chloride anions to give Ph$_2$PCl and the diphosphanide ligand Ph$_2$PPL$_C$^{iPr}, which subsequently aggregates to complex 9^{4+}. To evaluate the chloride-induced fragmentation in the afore-mentioned reactions, we further reacted compound $5b$[OTf] with one equivalent CuCl, CuOTf·4CH$_3$CN and AgOTf, respectively (Scheme 6). The equimolar reaction of $5b$[OTf] with CuCl is rather unselective as judged by the ^{31}P NMR spectrum of the reaction mixture, indicating again a chloride induced P–P bond cleavage reaction in $5b^+$ (Supporting Information, Figure S14).[21]
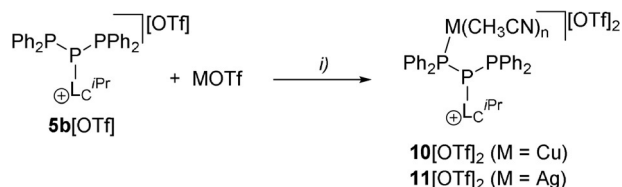
Scheme 6. Reaction of $5b$[OTf] with CuOTf·4CH$_3$CN and AgOTf; i) C$_6$H$_5$F/CH$_3$CN (v/v=1:1), r.t., 1 h; 10[OTf]$_2$: 46%; 11[OTf]$_2$: 52%.

This notion is supported by reactions of $5b$[OTf] with one equivalent CuOTf·4CH$_3$CN and AgOTf, which yield the expected coordination complexes 10[OTf]$_2$ and 11[OTf]$_2$, respectively. The molecular structures of these compounds contain the intact triphosphane $5b^+$.[32] The ^{31}P NMR spectra of the isolated complexes give rise to a broadened AX$_2$ spin system (10^{2+}: $\delta(P_A) = -56.4$, $\delta(P_X) = -16.5$, $^1J(P_AP_X) = -195$ Hz and 11^{2+}: $\delta(P_A) = -57.7$, $\delta(P_X) = -7.2$, $^1J(P_AP_X) = -191$ Hz), being only slightly shifted compared to the free ligand (see above).[21] Single crystals suitable for X-ray analysis were obtained by slow diffusion of Et$_2$O into a saturated CH$_3$CN solution of 10[OTf]$_2$ (Figure 4). The Cu atom is coordinated only to one terminal P atom of the triphosphane moiety, which contradicts the symmetrical spin system observed in solution by ^{31}P NMR spectroscopy. Presumably, a fast exchange of the metal atom between the
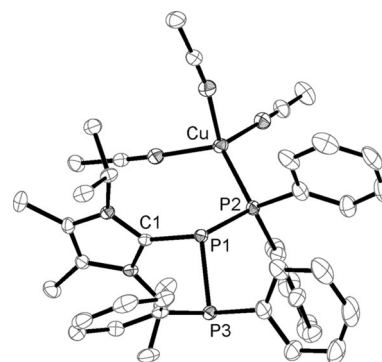
Figure 4. Molecular structure of 10^{2+} in 10[OTf]$_2$;[33] hydrogen atoms, solvate molecules, and anions are omitted for clarity and ellipsoids are set at 50% probability; selected bond lengths [Å] and angles [°]: C1–P1 1.836(2), P1–P2 2.2095(7), P2–P3 2.2326(7), P2–Cu 2.2190(6), P2-P1-P3 115.12(3).

two terminal P atoms of the ligand occurs in solution.[21] The bonding parameters in 10^{2+} are comparable to those of the free ligand $5b^+$, only the P2-P1-P3 bond angle is widened (10^{2+} P2-P1-P3 115.12(3)° vs. $5b^+$ P2-P1-P3 106.539(19)°) upon coordination to the Cu atom.

Conclusion

An efficient method for the synthesis of cationic poly-phosphorus compounds using imidazoliumyl-substituted di-pyrazoylphosphane salts $3a,b$[OTf] as suitable P$_1$ precursors is presented. Our approach using P–P condensation and P–N/P–P bond metathesis enables the formation of cationic polyphosphanes with excellent selectivity. Thereby, the very small family of cationic polyphosphanes (P$_n$; $n > 2$) has been considerably extended. The practical utility of this method is illustrated by the structural diversity of the synthesized compounds. Besides cationic 1,2,3-triphospholanium salts ($4a,b$[OTf]), a dicationic *catena*-tetraphosphane salt $7a$[OTf]$_2$

was isolated and fully characterized. The potential use of these polyphosphorus cations as multidentate ligands is illustrated by the reaction of **5b**[OTf] with AuCl(tht) leading to the unusual cationic tetranuclear, helical gold complex [{(Ph$_2$PPL$_C$^{iPr})Au}$_4$][OTf]$_4$ (**9**[OTf]$_4$) as a result of a chloride induced P—P bond cleavage reaction. Classical coordination complexes (**10**[OTf]$_2$ and **11**[OTf]$_2$) are observed when the nucleophilic chloride is substituted by a weakly coordinating anion such as triflate. The preliminary results presented in this study suggest that larger polyphosphanes with an asymmetric substitution pattern could likewise become accessible. Furthermore, the potential use of such ligands in coordination chemistry is a highly attractive objective. Investigations in this direction are in progress.

Conflict of interest

The authors declare no conflict of interest.

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[33] CCDC 1950491, 1950490, 1950495, 1950496, 1950492, 1950493, 1950494, and 1961363 (triflate salts of **3a**$^+$, **3b**$^+$, **4a**$^+$, **4b**$^+$, **7a**$^{2+}$, **5b**$^+$, **9**$^{4+}$, and **10**$^{2+}$) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.