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_4^3P(PhP)_3C]H][OTf] (4a,b[OTf]) and [L_3^3P(PhP)_3]H][OTf] (5b[OTf]) were prepared from the reaction of imidazolium-substituted dipyrazolophosphine trflate salts [L_4^3P(pyr)]_2[OTf] (3a,b[OTf]; a = R = Me, b = iPr; L = 1,3-dialkyl-4,5-dimethylimidazol-2-yl; pyr = 3,5-dimethylpyrazol-1-yl) with the secondary phosphanes PhP- (H)C,H,P(H)Ph and Ph3PH. A stepwise double P–N/P–P bond metathesis to catena-tetraphosphan-2,3-diium triflate salt [(PhP)_3LMeP]_2[OTf] (7a[OTf], 7b[OTf]) is observed when reacting 3a[OTf] with diphasphane P2Ph2. The coordination ability of 5b[OTf] was probed with selected coinage metal salts [(Cu(CH_3CN)_2]OTf, AgOTf and AuCl(tht)] (tht = tetrahydrothiophene). For AuCl(tht), the helical complex [(PhP)_3LMeP]Au[OTf] (9)[OTf] 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)L(M-(CH_3CN)_2)]OTf] (M = Cu, Ag) (10)[OTf] and 11[OTf] (3).

Introduction

Next to carbon, phosphorus has the strongest tendency to form homoatomic frameworks.[1] As shown by the pioneering work of Baudler,[2] von Schnerring,[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 sources are typically based on salt metathesis of a halophosphate with a metal phosphate,[2-4] the reaction of chlorophosphanes with silyl- or silylimidophosphanes,[7] or the reduction of a halophosphate 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] Phosphonylmethylphosphonium 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 phosphorus such as 1 as readily accessible P units (Scheme 1).[13] Pyrazolyl substituents are excellent leaving groups, which enable clean condensation reactions with primary and secondary phosphanes for the construction of...
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 phosphate 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 (1) with the imidazoliumyl substituent Lc[R] (Lc[R] = 1,3-dialkyl-4,5-dimethyl-imidazol-2-yl; a: R = Me; b: R = iPr) gives trflate salts [Lc[R]Ppyr]2[OTf] (3a,b[OTf]). Since imidazoliumyl substituents such as Lc[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 P3 building blocks. Herein, we describe the facile synthesis of cationic triphosphorus (4a,b[OTf], 5b[OTf]) and tetraphosphorus (7a[OTf]) compounds via the condensation of dipyrazolylphosphanes 3a,b[OTf] with secondary phosphates and via a stepwise P–N/P–P bond metathesis in the reaction of 3a[OTf] with PPh2H. A detailed NMR spectroscopic investigation provides mechanistic insight into the unusual P–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]), 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] and 11[OTf], 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)-1H-pyrazole (pyrSiMe3) under release of two equiv Me2SiCl (Scheme 2). The addition of n-hexane to the reaction mixture leads to the precipitation of analytically pure, colorless salts 3a[OTf] (96% yield) and 3b[OTf] (88% yield).[21] The 31P[H] NMR resonances of 3a,b[OTf] in CD2Cl2 (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)C6H4(P(H)Ph, one equiv) to give 1,2,3-triphospholanium salts 4a,b[OTf] under release of 3,5-dimethyl-1H-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 CH2Cl2 solution of 4a[OTf] and

![Figure 1](image)

**Figure 1.** Molecular structure of cations 3b–, 4b–, and 5b– of the respective trflate salts;[21] 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 1.734(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).

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by diffusion of Et₂O into a CH₂CN 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-triphospholene derivatives,[16−23] both cations show an envelope conformation of the five-membered ring in the solid state in which the phenyl and the imidazoliyl 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-triphospholenes.[24] The P2−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 31P NMR spectra of 4a[OTf] reveals at room temperature two sharp resonances of an AX, spin system (4af[OTf]: δ(P₈) = −47.4 ppm, δ(P₉) = 5.5 ppm; 1J(P,P₈) = −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[OTf] with diphenylphosphine to form triphosphanes 5a,b[OTf] is less selective (Scheme 3, I). The 31P NMR spectrum of a 1:2 reaction mixture of 3a[OTf] and Ph₂PH (Figure S6)[21] reveals the formation of several compounds, where 5a[OTf] is only the minor product (δ(P₈) = −57.1 ppm, δ(P₉) = −22.4 ppm; 1J(P,P₈) = −157 Hz). The 31P NMR spectrum of the crude reaction mixture additionally shows the presence of cation L₅M⁶P(H)PPh₂ (6a⁺: δ(P₈) = −52.4 ppm, δ(P₉) = −17.8 ppm, 1J(P,P₈) = −158 Hz, 1J(P,P₉) = −230 Hz, pyrPPh₂ (δ(P) = 39.3 ppm), pyrH, Ph₂H, δ(P) = −15.3 ppm) and catena-tetraphosphane 7a[OTf] (see below). Cations 5a⁻ and 6a⁺ are the result of a stepwise condensation of 3a[OTf] and Ph₂PH (Scheme 3, I) accompanied by the formation of 1,3-(dimethylpyrazolyl)triphenylphosphine (pyrPPh₂) and 3,5-dimethyl-1H-pyrazole (pyrH). Diphenylphosphorus P₂H₂ is the condensation product of Ph₂PH and pyrPPh₂ (Scheme 3, II). Catena-tetraphosphane-2,3-dimium trflate 7a[OTf] can be isolated in 29% yield by filtration of the reaction mixture and washing with C₆H₆.

The formation of P₂Ph₃ 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⁺++. Indeed, 7a[OTf] is formed selectively in this reaction in C₂H₂F₂, where the triflate salt of 7a⁺++ 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 P₂Ph₃ to give 8a⁻ and 5a⁺ under concomitant formation of pyrPPh₂ (Scheme 3, III), which is confirmed by 31P NMR investigations of the reaction mixture showing 8a⁻ (AX spin system, δ(P₈) = −23.6 ppm, δ(P₉) = 34.1 ppm, 1J(P,P₈) = −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⁺++ via the release of another equivalent of pyrPPh₂ (Scheme 3, III). Dication 7a⁺++ gives rise to an AAX′X′ spin system in the 31P NMR spectrum with resonances at δ(P₈) = −66.5 ppm and δ(P₉) = −22.6 ppm (1J(P,P₈) = −132 Hz, 1J(P,P₉) = −138 Hz, 2J(P,P₈) = 80 Hz and 2J(P,P₉) = −7 Hz; Supporting Information, Figure S5); detailed 31P NMR parameters are included in Table S1.[21]

The molecular structure of 7a⁺++ reveals a catena-P₈ structural motif with two imidazoliyl substituents L₅Me attached to the inner P atoms (Figure 2). In the solid state, 7a⁺++ adopts a meso-configuration. The rac-isomer is likely energetically unfavorable due to the steric bulk of the imidazoliyl 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.[25,27]

When the analogous condensation reaction is performed with compound 3b[OTf] and Ph₂PH, the related dication 7b⁺++ 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 Ph group in 3b⁻ prevents the formation of the P₄ 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 Ph₂PH (2 equiv.), resulting in a mixture of 5b[OTf] (δ(P₈) = −55.8, δ(P₉) = −47.4 ppm, 1J(P,P₈) = −221 Hz) and 7b[OTf] (δ(P₈) = −58.6 ppm, δ(P₉) = −15.3 ppm, 1J(P,P₈) = −132 Hz, 1J(P,P₉) = −138 Hz, 2J(P,P₈) = −22 Hz, 2J(P,P₉) = −7 Hz; Supporting Information, Figure S5). Subsequent treatment with 2 equiv. of Ph₂PH affords 7b[OTf].
The molecular structure of 7a in 7a[OTf];[30] 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 94.47(2).

Figure 2. Molecular structure of 7a[OTf];[30] 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 94.47(2).

Scheme 4. Synthesis of triphosphane 5b[OTf]; i) –pyrH, CH₂CN, r.t., 16 h, then n-Ph₂P–pyr, –pyrH, THF, r.t., 16 h; 5b[OTf], yield (NMR): 52%, yield (isolated): 21%.

-19.1, $^1J(P,P_3) = -154$ Hz and 6b[OTf] ($\delta(P)= -108.7$ ppm, $\delta(P_X) = -23.5$ ppm, $^1J(P,P_3) = 141$ Hz), which can be detected by $^{31}$P NMR spectroscopy (Supporting Information, Figure S8). In the second step, pyrPPh₂ (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[32,33] or salt metathesis[31] from the dichlorophosphane 2b[OTf] were unsuccessful which underlines the advantageous use of pyrazolylphosphines.[21] X-ray-quality crystals are obtained by slow diffusion of Et₂O 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.[12,25]

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]; 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[¹H] NMR spectrum of the filtrate shows one sharp resonance which is assigned to Ph₂P(δ(P) = 82.5 ppm; Supporting Information, Figure S15).[21] The $^{31}$P[¹H] NMR spectrum of the solid material dissolved in CD₂CN shows a highly symmetric, higher order spin system which can be attributed to the helical cationic tetragold complex [(Ph₂PPh₂)Au₄][OTf]ₙ (9[OTf]ₙ). The two major resonances are at $\delta(P_X) = -86.6$ 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″′ 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 Ph₂P moiety. The resonances of the ligand are significantly high-field shifted with a much larger $^3J(P,P_3)$ coupling constant of –328 Hz compared to related free diphosphane compounds (compare (cAAC)P–PPh₂, cAAC = cyclic (alkyl)(amino)carbene $\delta(P_X) = -27.3$ ppm and $\delta(P_X) = 41.2$ ppm, $^3J(P,P_3) = -242$ Hz),[25] which is caused by Au coordination. The unusually large $^3J(P,P_3)$ 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.[21]

Recrystallization of the precipitate by diffusion of benzene into a saturated CH₂CN solution of 9[OTf] gave yellow-orange colored crystals suitable for X-ray analysis, which revealed the tetranuclear, helical structure of the tetracation 9[OTf]⁺. The homometallic core features three short Au–Au distances of 2.2222(5) Å and 2.2311(5) Å, a Au–Au–Au distance of 3.4343(1) Å, and an Au–Au–Au–Au angle of 108.7°. The Au–Au–Au–Au angle is slightly larger than that of the diphenyl phosphanyl atoms (P2, P4, P6 and P8) (2.2908(9) Å). The Au–Au–Au–Au angle in 9[OTf] is 108.7°, which we attribute to the presence of a minor diastereomer (Supporting Information, Figure S16). The two major resonances are at $\delta(P_X) = -86.6$ 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). 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″′ spin system (Figure 3, left; see the Supporting Information, Table S2 for further details). The A part of the spin system is assigned to the phosphorus atoms carrying the imidazoliumyl substituents and the X part to the Ph₂P moiety. The resonances of the ligand are significantly high-field shifted with a much larger $^3J(P,P_3)$ coupling constant of –328 Hz compared to related free diphosphane compounds (compare (cAAC)P–PPh₂, cAAC = cyclic (alkyl)(amino)carbene $\delta(P_X) = -27.3$ ppm and $\delta(P_X) = 41.2$ ppm, $^3J(P,P_3) = -242$ Hz),[25] which is caused by Au coordination. The unusually large $^3J(P,P_3)$ 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.[21]
chloride anions to give Ph₃PCI and the diphenosphate ligand Ph₃PP₄ [38], which subsequently aggregates to complex 9+ [38]. To evaluate the chloride-induced fragmentation in the aforementioned reactions, we further reacted compound 5b[OTf] with one equivalent CuCl, CuOTf·4CH₃CN and AgOTf, respectively (Scheme 6). The equimolar reaction of 5b[OTf] with CuCl is rather unselective as judged by the 31P NMR spectrum of the reaction mixture, indicating again a chloride induced P–P bond cleavage reaction in 5b+ (Supporting Information, Figure S14). [21]

This notion is supported by reactions of 5b[OTf] with one equivalent CuOTf·4CH₃CN and AgOTf; δ C₆H₄Cl/CH₃CN (ν/ν = 1:1), 1h, 10[OTf]₂; 46%; 11[OTf]₂; 52%.

Scheme 6. Reaction of 5b[OTf] with CuOTf·4CH₃CN and AgOTf; δ C₆H₄Cl/CH₃CN (ν/ν = 1:1), 1h, 10[OTf]₂; 46%; 11[OTf]₂; 52%.

Figure 3. Left: 31P[H] NMR spectrum of 9+ (CD2CN, 235 K); insets show the zoom in of the experimental (upwards) and the iteratively fitted (downwards) AAA’X’X’’X’’’ spin system; right: Molecular structure of gold complex 9+ in 6[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).

Conclusion

An efficient method for the synthesis of cationic polyporphosphorus compounds using imidazoliumyl-substituted dipryzolophosphate salts 3a,b[OTf] as suitable P₁ precursors is presented. Our approach using P–P condensation and P–N/P–P bond metathesis enables the formation of cationic polyphosphines with excellent selectivity. Thereby, the very small family of cationic polyphosphines (Pₙ; 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-triporpholanium salts (4a,b[OTf]), a dicatonic catena-tetraphosphate salt 7a[OTf]₄.
was isolated and fully characterized. The potential use of these polyphosphorus cations as multidentate ligands is illustrated by the reaction of $\text{5b}(\text{OTf})$ with $\text{AuCl(tht)}$ leading to the unusual cationic tetranuclear, helical gold complex $[\text{(Ph}_2\text{P}_3\text{L}_2\text{P}_2\text{Au})\text{Au}][\text{OTf}]_2[\text{9}(\text{OTf})]_2$ as a result of a chloride induced P–P bond cleavage reaction. Classical coordination complexes ($\text{10}(\text{OTf})_2$ and $\text{11}(\text{OTf})_2$) 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 polyphosphines 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.

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**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** cationic polyphosphines - gold complex - phosphorus ligands - P–P bond metathesis - reductive coupling

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