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**Phosphanide Ligands**

# Accessing the Coordination Chemistry of Phosphorus(I) Zwitterions**

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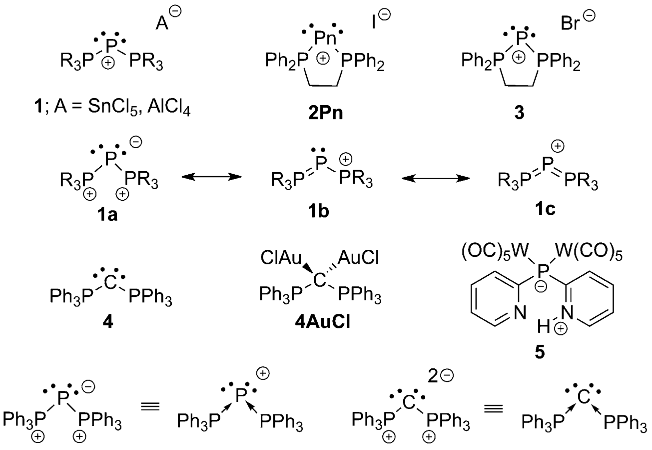
*In memory of Adam "MCA" Yauch*

Triphosphenium cations (**1**) have a rich history dating back to pioneering work in 1982 from Schmidpeter et al.[1] This work has since served as the cornerstone for the synthesis of related derivatives featuring various substitutions and ring sizes.[2] Three canonical structures (**1a**–**c**; Scheme 1) can be considered for these compounds, where the phosphanide-like structure **1a** is the most curious and tantalizing, as the two non-bonding pairs of electrons make these species candidates as ideal ligands for a wide variety of Lewis acids. Despite this intuitive application, there remains an obvious absence of examples of these electron-rich compounds playing this role. This dearth can be explained in part by the presence of an ion pair, wherein the counteranion is often more reactive than the phosphorus(I) center, thus inhibiting the study of any donor chemistry the central phosphorus atom might exhibit. The electronic structure for derivatives of **1** has been investigated in detail and confirms the presence of two "lone pairs" on the two-coordinate phosphorus atom. The HOMO typically constitutes the π-type "lone pair", while the σ-type "lone pair" is primarily attributed to a somewhat more stable occupied orbital.[2b,3] However, even if the complication of a reactive anion is removed (**2**, **3**),[4] further rationale for the poor donor ability of these cations are provided by the computational work. The non-bonding electrons in the frontier orbitals participate in significant π-backbonding (negative hyperconjugation) with the flanking phosphorus centers, thus they become too stabilized to participate in Lewis basic chemistry. The positive charge on the cation may further contribute to the relative inertness of the non-bonding electrons. This behavior is in stark contrast to the analogous neutral carbon(0) compounds, the carbodiphosphoranes (**4**), which were first developed in 1961[5] and have seen widespread use as a ligand for transition metals (**4**AuCl).[6] Recently, Bertrand et al. have demonstrated substantial donor ability from carbodicarbenes,[7] while in related work the coordination chemistry of the two-coordinate carbon in electron rich allenes and heterocumulenes, was extensively investigated by Alcarazo et al.[8] In these cases, the magnitude of any π-backbonding is diminished as the π-acidity of the flanking NHC groups are substantially less than that of the ligating phosphanes.[9] The particularly electron-rich nature of the two-coordinate carbon atom in both Bertrand's and Alcarazo's systems is emphasized by their ability to bind either one or two Lewis acids simultaneously.[8,10] Electronically similar "inverse carbodiphosphoranes" (that is, C-P-C vs. P-C-P) have been reported by Stalke et al.[11] with the subsequent chemical and electronic studies showing behavior consistent with a phosphanide Lewis structure. The two-coordinate phosphorus atom in such systems can act as a four-electron donor to two supported metal fragments (Cs, Mn), and also to two unsupported $\{W(CO)_5\}$ fragments (**5**).[12] Elegant charge-density studies have been performed and reveal two distinct valence-shell charge concentrations (VSCC) in the non-bonding region, which are consistent with two "lone pairs" of electrons on the phosphorus atom.[12,13] This parallels the calculated bonding environment for the triphosphenium systems (**1a**), which themselves have no experimental evidence for the equivalent Lewis structure.



***Scheme 1.*** Representations of triphosphenium cations and the isovalent carbodiphosphoranes.

Nevertheless, some basic/nucleophilic reactivity has been demonstrated with derivatives of **1** using strong electrophiles ($H^+$, $CH_3^+$),[14] but coordination to neutral Lewis acids or transition metals has remained less extensively explored.[15] One particularly noteworthy example of the unique possibilities of such compounds was reported by Driess and coworkers, who showed that the phosphanide complexes can

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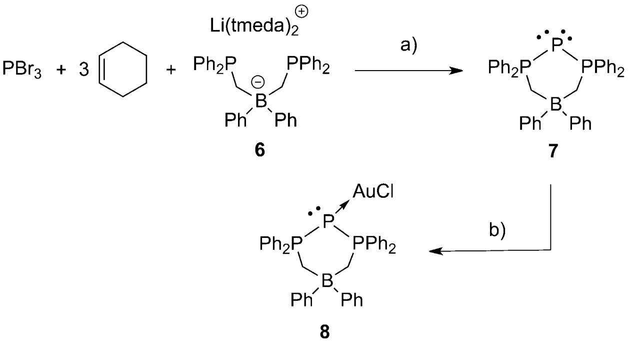
function as sources of "free" Pn(I) for planar four-coordinate phosphonium and arsonium salts.[16]

To expand and exploit the donor chemistry of triphosphenium species in a manner analogous to the well-established carbon(0) chemistry (carbodiphosphoranes and carbodicarbenes), we rationalized that two modifications to derivatives of **1** might prove fruitful: 1) the counteranion and cationic charge should be eliminated; and 2) a more electron-rich supporting ligand may attenuate the backbonding component within the system, and instead promote electron donation from both of the "lone pairs" on the central phosphorus atom. A convenient solution that addresses both of these aims is to employ a zwitterionic approach, which is used extensively by the d-block chemists to promote greater solubility for their catalytic systems.[17] In particular, the bis(phosphino)borate class of ligands developed by Peters et al.[18] are ideal candidates to address the deficiencies of triphosphenium salts because they carry a remote anionic charge but still allow one to exploit the well-established and convenient P→P coordination and redox chemistry used to generate such species.[19] The resulting phosphorus(I) zwitterion was anticipated to have greater solubility, increased electron density and thus much better donor properties relative to analogues **1**–**3**. In this context, we report the synthesis and comprehensive characterization of new zwitterionic P(I) centers and their ability to act as neutral phosphanide ligand in binding not only one, but two {AuCl} fragments. Computational investigations provide insights into the electronic structures of these compounds and pave the way for the comprehensive understanding of this new ligand set and how it can be further modified for wider application. These results represent, for the first time, the structural authentication of a complex in which both lone pairs on the phosphorus(I) atom simultaneously bind two metal centers, therefore acting as a novel neutral phosphanide-like four-electron μ-type ligand.[20]

The 1:1:3 stoichiometric addition of the bis(phosphino)-borate $[Li(tmeda)_2][(Ph_2PCH_2)_2BPh_2]$ (**6**)[21] to $PBr_3$ and cyclohexene results in the facile formation of a yellow solution and white precipitate. Analysis of the reaction mixture by $^{31}P\{^1H\}$ NMR spectroscopy reveals a doublet and triplet ($\delta_P = 32$ and $\delta_P = -220$, respectively; $^1J_{P\text{-}P} = 414$ Hz; Supporting Information, Figure S17), which is consistent with the quantitative formation of a triphosphenium compound. The volatile components were removed in vacuo and the product was extracted into a 80:20 pentane/dichloromethane mixture, which upon concentration and standing at −30 °C provides colorless crystals. Single crystal X-ray diffraction studies revealed the solid state structure to be the zwitterionic phosphorus(I) species, **7**, isolated in 75 % yield (Scheme 2). As anticipated by the zwitterionic nature of the compound, compound **7** was readily soluble in non-polar solvents such as diethyl ether, benzene, and large portions of pentane.

It should be noted that **7** can also be prepared by simple ligand-exchange reaction of **2P** with the bis(phosphino)borate ligand, **6**. The quantitative formation of **7** is observed in the $^{31}P\{^1H\}$ NMR spectrum within 5 min in conjunction with the presence of free dppe ($\delta_P = -12$). The increased donor strength of the bis(phosphino)borate compared to neutral phosphines is also evident in the fact that **2P** will readily undergo ligand exchange stronger electron donors (for example $PMe_3$; NHC),[22] while **7** shows no reaction with these strong Lewis bases.

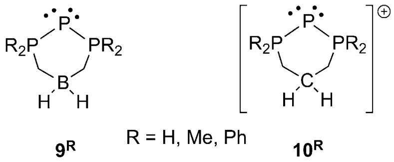


***Scheme 2.*** Synthesis of the phosphorus(I) zwitterion **7** and its {AuCl} complex **8**. Reagents and conditions (% yield): a) THF, RT, 10 min (75 %); b) $[AuCl(SMe_2)]$ (1 equiv), $CH_2Cl_2$, RT, 10 min (64 %).

Upon confirming the identity and structure of **7**, we then sought to explore its coordination chemistry. Treatment of **7** with one or two equivalents of $[AuCl(SMe_2)]$ results in a significant shift in the $^{31}P\{^1H\}$ NMR spectrum ($\delta_P = 30$ and $\delta_P = -110$; $^1J_{P\text{-}P} = 314$ Hz; Supporting Information, Figure S17) consistent with the binding of the central phosphorus to an electrophilic center. The $^1H$ NMR spectrum showed a slight downfield shift of the methylene protons ($\Delta\delta_H = 0.11$). Single crystals were grown from the vapor diffusion of a dichloromethane/hexane solution into toluene and were suitable for X-ray diffraction, which confirmed the product to be the triphosphenium zwitterion bound to one {AuCl} Lewis acid by the central phosphorus atom (compound **8**), isolated in 64 % yield (Scheme 2).

While the geometry about phosphorus clearly suggests the presence of a second "lone pair" of electrons, further addition of $[AuCl(SMe_2)]$ to **8** did not result in the formation of the diaurinated species. To further understand the reluctance of the second "lone pair" of electrons to simultaneously bind to a second metal center, DFT calculations were conducted on a series of models of compound **7** and related species. The model complexes reproduce the geometrical features of the experimental structures quite accurately and attest to the validity of the method used; extensive results are presented in the Supporting Information and only the most pertinent insights are described herein.

NBO and Molden analyses confirm the presence of two "lone pairs" on the di-coordinate phosphorus atoms in all of the model compounds. The zwitterionic model complexes $\mathbf{9^R}$ (R = H, Me, Ph; Scheme 3) are all predicted to be considerably more reactive electron donors than the corresponding cationic triphosphenium models $\mathbf{10^R}$. The energies of the frontier MOs, NBO "lone pair" orbitals, proton affinities, and the larger negative charge on the central phosphorus atom are all consistent with this assessment and the trend in reaction energies for the complexation of {AuCl} by the model ligands support that conclusion. Within each group, *P*-methyl substituents are predicted to generate more reactive donors than



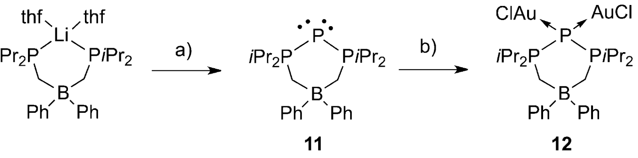
*Scheme 3.* Structures of the model complexes used for the calculations.

the *P*-phenyl ligands. The reaction energies for the complexation of {AuCl} by the model ligands are found to be very exothermic (−213 to −238 kJ mol$^{-1}$ in every instance) and the coordination of a second {AuCl} fragment is exothermic by a somewhat smaller amount (ca. −170 kJ mol$^{-1}$). Consequently, the formation of the diaurinated complex is clearly favorable. These reaction energies are comparable to the −235 kJ mol$^{-1}$ calculated for the complexation of {AuCl} and $PMe_3$ at the same level of theory. In stark contrast, the complexation energies calculated for the cationic variants $\mathbf{10^R}$ are considerably smaller (ca. −150 kJ mol$^{-1}$ for attachment of a single {AuCl} fragment).

In light of the predicted favorability of the ligation of a second {AuCl} fragment for the zwitterionic model complexes, we surmised that the reason for the contrasting experimental observation is almost certainly ascribable to the steric bulk of the phenyl substituents. In fact, examination of the structural features of the optimized model of $\mathbf{9^H}$ bound to two {AuCl} fragments reveals that replacement of the H atoms on boron with Ph groups would result in a sterically impossible structure. Likewise, a space-filling representation of the X-ray structure of **8** also shows the intrusion of a Ph group into the region in which a second {AuCl} fragment would be bound.

Given the results of the computational work we sought to mitigate some of the steric bulk on the bis(phosphino)borate ligand by substituting the $P_{(aryl)}$ groups with $P_{(alkyl)}$ groups. The bis(diisopropyl)phosphino analogue has already been prepared by Peters and Thomas[21] and this ligand reacts cleanly with $PBr_3$ and excess cyclohexene to give the zwitterionic phosphorus(I) species **11**. The $^{31}P\{^1H\}$ NMR spectrum reveals the characteristic doublet and triplet ($\delta_P = 57.1$ and $\delta_P = -268.3$, respectively; $^1J_{P\text{-}P} = 420$ Hz; Supporting Information, Figure S17) with the latter being shifted significantly upfield ($\Delta\delta_P = 48$) when compared to **7**. Single crystals, grown from a saturated $Et_2O$ solution at −30 °C, confirm the identity of the product and the solid-state structure reveals similar metrical parameters to **7**.

The reaction of **11** with two stoichiometric equivalents of $[AuCl(SMe_2)]$ results in a drastic downfield shift of the central phosphorus atom in the $^{31}P\{^1H\}$ NMR spectrum ($\delta_P = -81.7$; Supporting Information, Figure S17). There is also a dramatic difference in the P–P coupling constant ($^1J_{P\text{-}P} = 153$ Hz cf. $^1J_{P\text{-}P} = 314$ Hz in **8**) consistent with a significant decrease in the P−P bond strength and diminished π-backbonding from the phosphorus(I) lone pairs of electrons. Single crystals were grown from a $CH_2Cl_2$ solution layered with pentane and confirm the identity of the product to be the triphosphenium zwitterion with the central phosphorus being simultaneously ligated by two {AuCl} fragments (Compound **12**; Scheme 4).



*Scheme 4.* Synthesis of the phosphorus(I) zwitterion **11** and the diaurinated complex **12**. Reagents and conditions (% yield): a) $PBr_3$ (1 equiv), cyclohexene (6 equiv), $Et_2O$, −78 °C, 16 h (68 %); b) [AuCl-$(SMe_2)$] (2 equiv), $CH_2Cl_2$, RT, 10 min (74 %).

The solid-state structures are shown in Figure 1. The most noteworthy feature of the free ligands is the absence of a halide counterion, thus verifying the zwitterionic nature of **7** and **11**.[23] The metrical parameters of **7** reveal an average P−P bond length of 2.135 Å, which is slightly longer than other triphosphenium cations (2.11–2.13 Å), consistent with slightly mitigated π-backbonding. The P2-P1-P3 angle is 95.70(3)°, comparable to the literature precedent for six-membered cyclic triphosphenium cations (94–97°). While unligated **7** exists in a twist-boat conformation, upon coordination to {AuCl} the ring adopts an almost boat-like conformation in the solid state. The phosphorus(I) center in compound **8** is trigonal-pyramidal ($\Sigma_{angles} = 307°$), which is consistent with an $AX_3E$ VSEPR geometry, confirming the presence of an

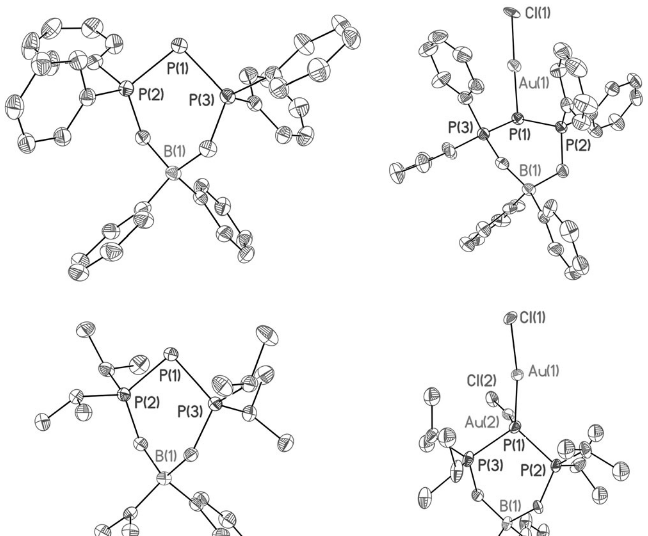


*Figure 1.* The solid-state structures of **7** (top left), **8** (top right), **11** (bottom left), and **12** (bottom right). Ellipsoids are set to 50 % probability and hydrogen atoms and solvent molecules have been removed for clarity. For **12**, the one disordered {AuCl} fragment is removed for clarity. Selected bond lengths [Å] and angles [°] for **7**: P1–P2 2.1371(9), P1–P3 2.1328(9); P2-P1-P3 95.70(3); **8**: P1–Au1 2.2512(17), Au1–Cl1 2.3170(15), P1–P2 2.174(2), P1–P3 2.200(2); P1-Au1-Cl1 177.76(6), P2-P1-P3 94.59(9); **11**: P1–P2 2.1349(9), P1–P3 2.1341(9); P2-P1-P3 96.50(4); **12**: P1–Au1 2.257(3), P1–Au1A 2.255(3), P1–Au2 2.249(3), Au1–Cl1 2.316(6), Au1A–Cl1A 2.310(5), Au2–Cl2 2.297(3), P1–P2 2.215(3), P1–P3 2.216(4), Au1–Au2 3.332(5); P1-Au1-Cl1 171.41(18), P1-Au1-Cl1A 172.0(2), P1-Au2-Cl2 167.61(10), P2-P1-P3 100.55(14).

additional non-bonding pair of electrons on phosphorus. The metrical parameters reveal longer P–P bond lengths as compared to **7** (2.174(2), 2.200(2) Å; compare with av. 2.135 Å) and a smaller P2-P1-P3 angle of 94.59(9)°. The P–Au bond length is 2.2512(17) Å, which is comparable to the average phosphine–gold(I) bonds (av. 2.22 Å), while the P-Au-Cl angle is nearly linear at 177.76(6)°.[24] Therefore, the solid-state structure of **8** shows **7** acting as a two-electron donor to {AuCl} with parameters consistent with resonance form **1a**. For the dinuclear gold species **12**, the phosphorus(I) center has a distorted-tetrahedral $AX_4$ geometry, while the P–P bond lengths are 2.215(3) and 2.216(4) Å. These are somewhat longer than those in compound **11** (2.1341(9) and 2.1349(9) Å), but remain consistent with single bonds as well as the $^{31}P\{^{1}H\}$ NMR data. The P–Au bonds are nearly identical at 2.249(3) and 2.257(3) Å, showing the equal donor ability of the each of the lone pairs of electrons on the central phosphorus. The P2-P1-P3 angle has expanded to 100.55(14)°, while the P-Au-Cl angles are slightly bent at a 167.61(10) and 171.41(18)°. There are notable, albeit small, intra- and intermolecular Au···Au contacts in the solid state that are 3.6–3.9 Å and 3.332(5) Å, respectively, forming a planar $Au_4$ parallelogram. These gold–gold bond distances are both greater than the standard range for considerable aurophilic interactions (2.7–3.3 Å)[25] and are also greater than the analogous diaurinated carbodiphosphorane **4**AuCl (3.1432(2) Å).[10b] Furthermore, the gold–gold bond lengths in **12** are both longer than the short Au–Au bonds in a triaurinated phosphido complex $[Mes^{*}P(AuPPh_3)_3][BF_4]$ (3.1546(3) Å).[26]

In conclusion, a new type of zwitterionic phosphorus(I) compound has been isolated in good yields and fully characterized. These species show high solubility in solvents that are typically unsuitable for their ionic relatives. The derivative with phenyl substituents on the flanking phosphorus atoms is able to form a stable, isolable complex with {AuCl}. Unfortunately, the steric bulk in the ligand backbone prevents a second coordination. Simple modification of the organic groups on the backbone phosphorus centers to isopropyl adjusts the nature of the phosphorus(I) center to allow access to both "lone pairs" of electrons. This is represented in the first example of simultaneous ligation of two Lewis acids (metal centers) by a triphosphenium based complex; a feat not achieved until now, in spite of significant previous investigations of such compounds. The electronic structure calculations suggest that the use of the anionic bis(phosphino)borate ligand provides access to new structures and coordination chemistry about the two-coordinate phosphorus atom that cannot be observed with the neutral phosphine ligands ($PPh_3$, dppe, dppp). This discovery opens a door to the use of these compounds as a new class of sterically demanding neutral phosphorus-based ligands that are strong sigma donors that cannot behave as π-acceptors.

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