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Phosphanylidenes

Synergistic Binding of Both Lewis Acids and Bases to Phosphinidenes[**]

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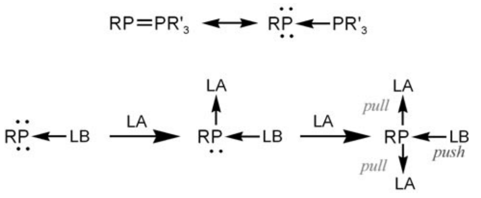
Free phosphinidenes or phosphanylidenes (RP), the heavier analogues of carbenes, remain unisolable owing to their extreme reactivity.[1] Although a significant body of stable transition metal complexes having terminal PR functionalities now exists, simple main group adducts of phosphinidenes are by comparison rare. Phosphanylidene-σ^4-phosphoranes ($RP{=}PR'_3$) are a fundamental type of base-stabilized adducts of phosphinidenes[2] First recognized in 1961 with the synthesis of $CF_3P{=}PMe_3$,[3] and later studied in more detail,[4] these early derivatives were thermally unstable and not structurally characterized. Derivatives bearing additional phosphorus atoms and lone pairs, such as $R_2P{-}P{=}P(X)R'_2$ are also an important class of such materials, and they have received attention as phosphinidene precursors and transfer reagents.[1c,e,5] The more recent discovery of thermally stable $ArP{=}PR_3$, where Ar is a sterically demanding aryl group, allowed for structural identification and more detailed studies.[6,7] Phosphanylidene-σ^4-phosphoranes can be pictorially represented by various resonance forms (Scheme 1, top) and, as in their lighter analogue Wittig reagents ($R'_2C{=}PR_3$), there are added bonding interactions between the phosphorane and the phosphinidene or carbene entity through negative hyperconjugation.[8–11] Also by analogy to Wittig reagents, $ArP{=}PR_3$ have been shown to undergo "phospha-Wittig"[12] reactions with C=O bonds to form phosphaalkenes.[6,13] These unique reagents have also served as convenient sources of free phosphinidenes.[14]



Scheme 1. Resonance structures for $RP{=}PR_3$ (top) and Lewis acid (LA) and base (LB) adducts of phosphinidene (bottom).

Mathey's pioneering work has shown that phosphanylidene-σ^4-phosphoranes are more readily handled if complexed to metal centers, such as $[W(CO)_5]$.[15] Little work has appeared on the binding of other Lewis acids to $RP{=}PR_3$, despite the fact that $CF_3P{=}PMe_3$ yields $CF_3P(BH_3)_2PMe_3$ upon addition of BH_3.[3] This system is especially interesting, as the phosphorus atom bound to the CF_3 group bonds to both a Lewis base donor (PMe_3) and two Lewis acid acceptors (BH_3), generating a "push-pull" system on the phosphanylidene center (Scheme 1). This particular example, however, has not been structurally authenticated, and thus it would be of fundamental interest to assess the importance of simultaneous Lewis acid/Lewis Base (push/pull) binding on such species.

Previous attempts to generate well-characterized adducts using BH_3 with $DmpP{=}PMe_3$ ($Dmp = 2,6\text{-}Mes_2C_6H_3$) met with limited success, with spectroscopic data being determined for a mono-BH_3 adduct.[7] Here we report the successful syntheses of Lewis acid diadducts using the sterically unhindered Lewis acids AuCl and AgOTf, and examine their impact on phosphorus–phosphorus bonding. Two different types of structures have been characterized.

The reaction of $ArP{=}PMe_3$ (**1**, Ar = Dmp; **2**, Ar = Mes* = 2,4,6-tri-*tert*-butylphenyl) with two equivalents of [Au(tht)Cl] in toluene (tht = tetrahydrothiophene) proceeds to provide products of the form $[ArP(AuCl)_2PMe_3]$ (**3**, Ar = Dmp; **4**, Ar = Mes*) as depicted in Scheme 2.

The result of a single crystal X-ray diffraction study on a crystal of **3** is shown in Figure 1.[16] The two {AuCl} fragments feature linear coordination at the gold centers, and the gold–gold distance in **3** (> 3.5 Å) is too far to suggest any significant Au···Au interactions.[17] Each gold atom, however, is within possible interaction distance of a carbon atom of a mesityl ring (Au1−C7 = 3.066 Å; Au2−C17 = 3.123 Å) and may be considered three-coordinate. Binding of this type and of similar gold–carbon distance has been reported previously with gold and vicinal aryl rings.[18]

The most noteworthy aspect of the structure of **3** is the significant lengthening of the P1−P2 bond to 2.205(1) Å from the distance of 2.084(2) Å determined for $DmpP{=}PMe_3$. The nature of the multiple bonding and short P−P bond length in $ArP{=}PR_3$ had been ascribed to negative hyperconjugation involving donation of electron density on the phosphanylidene phosphorus atom into symmetry-adapted combinations of the phosphorane P−R σ* orbitals.[8–11] Sequestration of both lone pairs by the gold Lewis acid molecules appears to affect this type of multiple bonding and thus the phosphorus–

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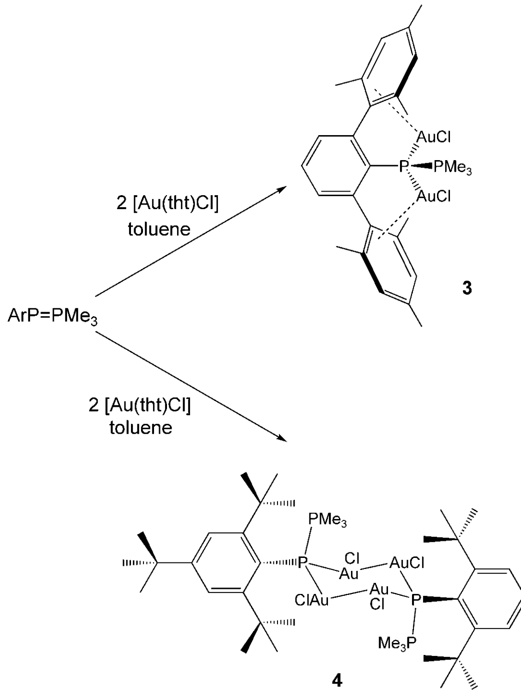


Scheme 2. Synthesis of complexes **3** and **4**. tht = tetrahydrothiophene.

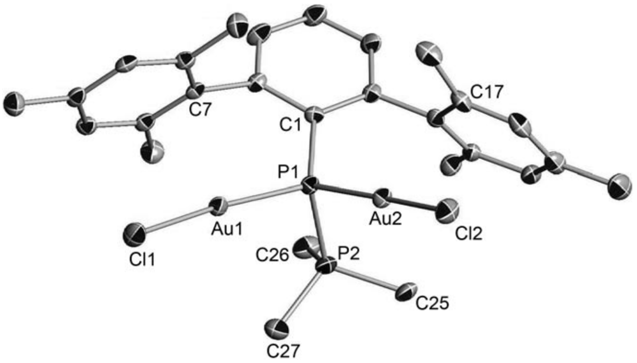


Figure 1. ORTEP representation of **3** with ellipsoids set at 50% probability; hydrogen atoms have been omitted for clarity. Selected bond lengths [Å]: Au1–P1 2.247(1), Au2–P1 2.244(1), Au1–Cl1 2.230(1), Au2–Cl2 2.291(1), P1–P2 2.205(1). Selected bond angles [°]: P1-Au1-Cl1 171.03(3), P1-Au2-Cl2 173.88(4), C1-P1-P2 103.78(1), C1-P1-Au2 119.71(1), P2-P1-Au2 104.15(5), C1-P1-Au1 118.86(1), Au1-P1-Au2 103.19(4).

phosphorus bond is returned to a "normal" value for a single bond (ca. 2.2 Å) between these two elements. The Au–P bond lengths more closely resemble those of structurally similar phosphine-ligated gold(I) chlorides[18] than the bond lengths of structurally similar μ-phosphido-ligated gold(I) chlorides, which have longer Au–P bonds.[19] The structure of **3** makes for a fascinating comparison to the triaurated species [Mes*P-$(AuPPh_3)_3$]BF_4.[20] This remarkable molecule, by contrast to **3**, displays a short Au···Au interaction of 3.1546(3) Å between two of the three gold atoms, and longer Au–P bond lengths (2.293(1) to 2.328(1) Å). The latter feature may reflect the description of [Mes*P$(AuPPh_3)_3$]BF_4 as a gold phosphanido complex.

As there are often subtle and differing structural impacts imparted by sterically hindered terphenyl and Mes* units in low-coordinate and unusual molecules,[21] we have also prepared [Mes*P$(AuCl)_2$$PMe_3$] (**4**) and have determined its structure (Figure 2). The P–P bond length is again found to be longer than that determined in DmpP=PMe_3, albeit at the shorter end of the known scale for P–P single bonds. In contrast to complex **3**, compound **4** dimerizes in the solid state by gold–gold interactions (3.294(1) Å). The resulting large six-membered Au_4P_2 ring adopts a chair-like conformation. It could be speculated that **4**, lacking the electron-rich mesityl rings that lead to possible stabilizing Au···arene interactions in **3**, forms aurophilic interactions with neighboring molecules.

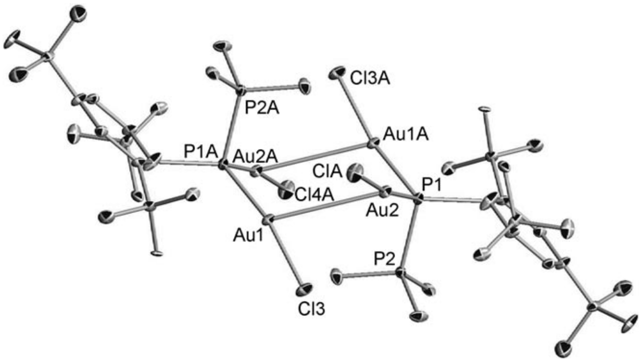


Figure 2. ORTEP representation of **4** with ellipsoids set at 50% probability; hydrogen atoms have been omitted for clarity. Selected bond lengths [Å]: Au1–Au2 3.294(1), Au1–P1A 2.236(2), Au2–P1 2.239(2), Au1–Cl3 2.299(3), Au2–Cl4 2.291(2), P1–P2 2.174(3). Selected bond angles [°]: P1A-Au1-Cl3 166.35(7), P1-Au2-Cl4 171.59(7), P1-Au2-Au1 109.51(5), Au1-Au2-Cl4 75.07(5), 119.71(1), P2-P1-Au2 105.33(9), Au1A-P1-Au2 98.93(8).

Compounds **3** and **4** are soluble and stable in chlorinated solvents, such as $CDCl_3$, with **4** displaying significantly more stability than **3** in solution. Both materials quickly decompose in THF. Phosphorus NMR spectroscopy reveals that upon binding two AuCl units, the chemical shifts are shifted considerably downfield relative to the resonances detected for **1** and **2**, and that the $J_{P\text{-}P}$ coupling constants are greatly reduced from ca 580 Hz to 125-183 Hz. The latter decreases are consistent with reduced phosphorus–phosphorus bonding interactions, and are notably smaller than values ascertained for the cations [DmpP(R)PMe_3]X (R = Me_3Si, H, CH_3; X = OTf or I; $J_{P\text{-}P}$ = 282–343 Hz).[7]

Attempts to extend this chemistry to the corresponding silver adducts have thus far proved more challenging. Addition of AgOTf to toluene solutions of **1** and **2** yielded materials consistent with the formulation of ArP-$(AgOTf)_2$$PMe_3$ (**5**, Ar = Dmp; **6**, Ar = Mes*). Interpretation of the NMR spectral data, however, is rendered difficult, owing to broadened resonances that might reflect exchange processes (Lewis base and/or acid) and unresolved coupling to NMR-active ^{107}Ag and ^{109}Ag nuclei.[22] Single crystals of [DmpP{Ag_2OTf_2(toluene)}PMe_3] (**5**) were grown (Figure 3).

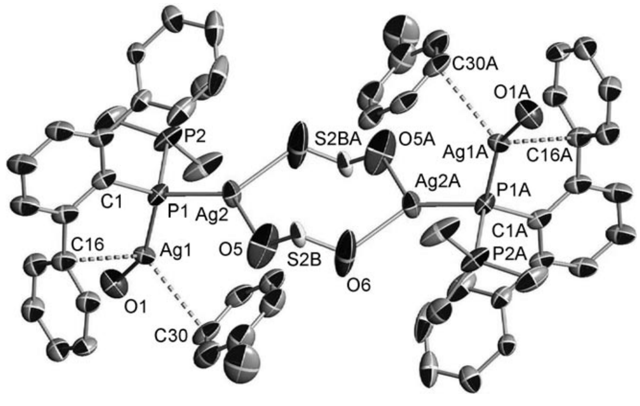
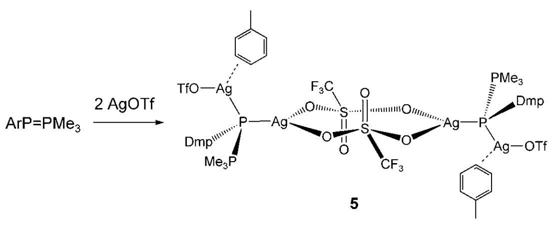


Figure 3. ORTEP representation of **5** with ellipsoids set at 50% probability for core structure; hydrogen atoms, CF_3 groups, nonbridging oxygen atoms of bridging triflate ligands, all atoms of the terminal triflates except the bound oxygen atom, and mesityl methyl groups have been omitted for clarity. Selected bond lengths [Å]: Ag1–O1 2.215(5), Ag1–P1 2.309(3), Ag2–O5 2.387(6), Ag2–O6A 2.308(12), Ag2–P1 2.2817(18), P1–P2 2.159(2), P1–C1 1.856(5). Selected bond angles [°]: O1-Ag1-P1 153.45(17), O6A-Ag2-O5 102.8(3), O5-Ag2-P1,130.7(2), O6A-Ag2-P1 126.3(3), Ag1-P1-Ag2 117.95(9), C1-P1-Ag2 116.49(18), C1-P1-P2 109.24(18), P2-P1-Ag1 93.18(7), P2-P1-Ag2 102.34(9).

The results of a preliminary structure determination by X-ray diffraction clearly show that complex **5** forms dimeric species having bridged AgOTf units, as depicted in Equation (1). As in compounds **3** and **4**, compound **5** has a P–P bond (2.159(2) Å) lengthened from that in precursor **1**, but the effect of AgOTf on this distance is notably less than that of AuCl. Whereas disorder in the AgOTf entities does not warrant a detailed discussion of the silver coordination environments, it is clear that the terminal AgOTf unit resides in a flattened tetrahedral geometry and is associated with a solvent molecule of toluene ($d_{Ag\cdots C}$ as close as 2.59 Å), and possibly more weakly with the vicinal mesityl ring.[23] The other silver ion can be considered distorted trigonal planar but also having possible weak interactions with a mesityl ring. The structures of **4** and **5** bear a resemblance to a tungsten phosphoranylidene phospholene CuCl-bridged dimer isolated as an intermediate in a CuCl-promoted phosphinidene-transfer process from the transient complex $[(CO)_5W{=}PPh]$.[24]



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(1)

In summary, we have synthesized the novel di-Lewis acid adducts of phosphanylidene-σ^4-phosphorane that are "push–pull" complexes of phosphinidenes. These new materials show parallels to Lewis acid-stabilized carbene-phosphinidenes,[25] and may find utility for catalytic applications.

Experimental Section

$[DmpP(AuCl)_2PMe_3]$ (**3**): In a glovebox, $DmpP{=}PMe_3$ (38.3 mg, 0.091 mmol) was dissolved in toluene (3 mL), and this yellow solution was added dropwise to a stirred suspension of [Au(tht)Cl] (59 mg, 0.18 mmol) in toluene (3 mL). The solution decolorized and then produced a suspension of a colorless solid in toluene. After 2 h the solution was concentrated in vacuo and pentane was added to precipitate **3** as a colorless solid, which was collected and dried. Yield: 60 mg (75%). ^{1}H NMR ($CDCl_3$): $\delta = 7.54$ (tq, 1H, $J = 1.2$, 7.6 Hz), 7.29 (qd, 2H, $J = 1.2$, 7.6 Hz), 7.05 (s, 4H), 2.39 (s, 6H), 2.15 (s, 12H), 1.64 ppm (dd, 9H, $J = 6.0$, 12.4 Hz). ^{31}P NMR ($CDCl_3$): $\delta = 23.5$ (d, 1P, $J = 183$ Hz), -23.2 ppm (d, 1P, $J = 183$ Hz).

$[Mes^*P(AuCl)_2PMe_3]$ (**4**):. In a glovebox, $Mes^*P{=}PMe_3$ (21 mg, 0.060 mmol) was dissolved in toluene (1.5 mL), and this yellow solution was added dropwise to a stirred suspension of Au(tht)Cl (38 mg, 0.12 mmol) in toluene (1.5 mL). The solution first decolorized and then produced a suspension of a colorless solid. After one hour, pentane was added to precipitate **4** as a colorless solid, which was then collected and dried. Yield: 47 mg (97%). ^{1}H NMR ($CDCl_3$): $\delta = 7.46$ (d, 2H, $J = 4.4$ Hz), 1.85 (s, 18H), 1.58 (dd, 9H, $J = 5.6$, 12.8 Hz), 1.31 ppm (s, 9H). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 22.8$ (d, 1P, $J = 125$ Hz), -23.6 ppm (d, 1P, $J = 125$ Hz). Elemental analysis [%] calcd for $C_{21}H_{38}Au_2Cl_2P_2$: C 30.86, H 4.69; found: C 30.58, H 4.39.

$[DmpP\{Ag_2OTf_2(toluene)\}PMe_3]$ (**5**): In a glovebox, $DmpP{=}PMe_3$ (22 mg, 0.051 mmol) was dissolved in toluene (1 mL), and a stirred solution of AgOTf (29 mg, 0.11 mmol) in toluene (1 mL) was added dropwise to this solution. The solution turned pale yellow and, after 1 hour, was concentrated in vacuo to the point that colorless material just began to precipitate from solution. Pentane was added to cause further precipitation of a white solid that was collected and dried. Upon drying the solid turned brown, and thus was extracted into toluene and filtered through celite. Diffusion of pentane into the toluene solution yielded white crystalline **5**. Yield: 8 mg (16%). ^{1}H NMR ($CDCl_3$): $\delta = 7.57$ (tq, 1H, $J = 4.4$, 7.6 Hz), 7.18 (dd, 2H, $J = 4.4$, 7.6 Hz), 7.15 (s, 4H), 2.38 (s, 6H), 2.09 (s, 12H), 1.63 ppm (q, 9H, $J = 6.0$, 12.8 Hz). ^{31}P NMR ($CDCl_3$): $\delta = 20.3$ ppm (d, $J = 295$ Hz), (other signal severely broadened near -70).

$[Mes^*P(AgOTf)_2PMe_3]$ (**6**): In a glovebox, $Mes^*P{=}PMe_3$ (41 mg, 0.12 mmol) was dissolved in toluene (1.5 mL), and this yellow solution was added dropwise to a stirred suspension of AgOTf (60 mg, 0.24 mmol) in toluene (1.5 mL). The $Mes^*P{=}PMe_3$ solution decolorized. After one hour, pentane was added to induce precipitation of a colorless solid. The suspension was placed in a freezer to maximize precipitation. The solid was collected and dried. Yield: 92 mg (91%). ^{31}P{^{1}H} NMR (THF): $\delta = 24.8$ ppm (d, 1P, $J = 252$ Hz), (other signal severely broadened and undetected). Elemental analysis [%] calcd for $C_{23}H_{38}Ag_2F_6O_6P_2$: C 31.89, H 4.42; found: C 32.72, H 4.08.

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[16] Crystal data for **3** at 100(2) K: $\mathrm{C_{27}H_{34}Au_2Cl_2P_2}$ ($M_r = 885.32$), $P2_1/n$; $a = 9.5512(15)$, $b = 15.087(2)$, $c = 19.767(3)$ Å, $\beta = 100.769(2)°$; $V = 2798.3(7)$ Å^3; $Z = 4$, Mo$_{K\alpha}$ radiation, $2\Theta_{max} = 55.0°$. Of 32212 reflections, 6390 were independent ($R_{int} = 0.0355$); $R1 = 0.0222$, $wR2 = 0.0511$ (based on F^2) for 307 parameters and 5667 reflections with $I > 2\sigma(I)$. Crystal data for **4** at 100(2) K: $\mathrm{C_{42}H_{76}Au_4Cl_4P_4}$ ($M_r = 1634.57$), $P2_1/c$; $a = 12.688(5)$, $b = 14.172(6)$, $c = 15.588(6)$ Å, $\beta = 101.771(5)°$; $V = 2744.0(2)$ Å^3; $Z = 2$, Mo$_{K\alpha}$ radiation, $2\Theta_{max} = 54.30°$. Of 29314 reflections, 5944 were independent ($R_{int} = 0.0525$); $R1 = 0.0409$, $wR2 = 0.0986$ (based on F^2) for 244 parameters and 5184 reflections with $I > 2\sigma(I)$. Crystal data for **6** at 100(2) K: $\mathrm{C_{72}H_{84}Ag_4F_{12}O_{12}P_4S_4}$ ($M_r = 2052.99$), $P2_1/c$; $a = 17.211(2)$, $b = 13.4966(16)$, $c = 17.495(2)$ Å, $\beta = 91.041(1)°$; $V = 4063.4(8)$ Å^3; $Z = 2$, MoKα radiation, $2\Theta_{max} = 55.0°$. Of 46602 reflections, 9261 were independent ($R_{int} = 0.0313$); $R1$ 0.0651, $wR2 = 0.1709$ (based on F^2) for 569 parameters and 6951 reflections with $I > 2\sigma(I)$. Silver atoms Ag1 and Ag1B were refined as having 50% occupancy, and silver atoms Ag2 and Ag2B were refined as having 63% and 37% occupancy respectively. CCDC 684214, 684215, 684216 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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