Phosphine Ligand Exchange at a Phosphine Lewis Acceptor: The First Structural Characterization of Homoleptic Phosphinophosphonium Salts

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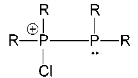
Coordination chemistry usually refers to bonding interactions involving donation from electron-rich nonmetals (ligands) to electron-deficient metals (Lewis acceptors). Reports of metal complexes behaving as ligands toward other metals[1] and of compounds involving electron-rich (lone-pair bearing) phosphinic centers as Lewis acceptors[2−21] introduce novel bonding possibilities and new synthetic opportunities. In this context, a phosphinophosphonium[2,3,6,16,22] **1** cation can be represented by **2**, involving a coordinate (phosphine)P → P(phosphine) interaction.



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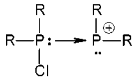

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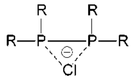

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The distinct ^{31}P chemical shifts[16] indicate that chlorine cation exchange and access to a chloronium cation **3** are restricted. Therefore, R_2(Cl)P of **2** is available for ligand exchange, which has facilitated the synthesis and structural characterization of the first penta-phenylphosphinophosphonium salts.

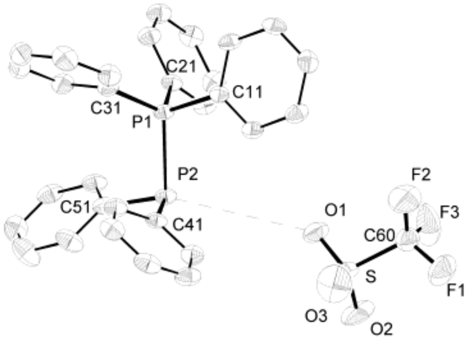
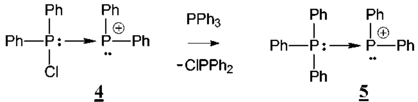


Figure 1. Crystallographic view of $[Ph_3P-PPh_2][SO_3CF_3]$, **5**$[SO_3CF_3]$; selected bond lengths (Å): P1−P2 2.2302(13), P2−O1 4.415(16), S1−O1 1.432(3), S1−O2 1.423(3), S1−O3 1.430(3); and angles (deg): C11−P1−P2 108.86(12), C21−P1−P2 105.46(11), C31−P1−P2 116.20(12), C41−P2−P1 100.38(11), C51−P2−P1 100.73(12), C41−P2−C51 104.25(16).



4 **5**

Phosphorus-31 NMR spectra[23] of reactions between **4**[A] (A = $GaCl_4$ or OSO_2CF_3) and Ph_3P indicate quantitative formation of **5**[A] and free Ph_2(Cl)P (δ = 80.5 ppm). Isolated solids have been characterized as **4**$[GaCl_4]$, **5**$[GaCl_4]$,[24] and **5**$[OSO_2CF_3]$,[25] which was also isolated from the reaction mixture of Ph_2PCl, $Me_3SiOSO_2CF_3$ and Ph_3P. Long interatomic distances between counterions are observed in the crystal structures of **5**$[GaCl_4]$ and **5**$[OSO_2CF_3]$ (Figure 1), indicating that they are best described as ionic in the solid state. Moreover, the structure of the

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(23) Using general procedures,[30] solutions of **4**[A] [A = $GaCl_4$, OSO_2CF_3] (0.25 g) in CH_2Cl_2 (10 mL) were prepared in situ,[16] and 1.3 equiv of Ph_3P in CH_2Cl_2 (10 mL) was introduced. NMR data are listed in Table 1.

(24) **4**$[GaCl_4]$: Using general procedures,[30] $GaCl_3$ (0.9 g 5.2 mmol) in CH_2Cl_2 (10 mL) added to Ph_2PCl (2.3 g, 10 mmol), stirred for 1 h. at rt, removal of solvent gave white solid (2.5 g, 77%); mp 103−105 °C; Anal. Calcd for $C_{24}H_{20}Cl_5GaP_2$: C, 46.69; H, 3.27; Found: C, 46.79; H, 3.33; IR cm^{-1} (ranked intensities): 367(4), 381(1), 496(7), 532(9), 681(5), 691(8), 745(3), 752(6), 1105(10), 1436(2). **5**$[GaCl_4]$: Using general procedures,[30] Ph_3P (0.25 g 0.97 mmol) in CH_2Cl_2 (15 mL) added to a solution of (0.60 g 0.97 mmol) in CH_2Cl_2 (20 mL), stirred for 1 h at rt, removal of solvent gave white solid (0.56 g, 88%); mp 153−155 °C; IR cm^{-1} (ranked intensities): 374(3), 489(7), 503(6), 550(9), 690(5), 720(4), 746(2), 1101(8), 1439(1); Crystal data for $C_{30}H_{25}P_2GaCl_4$: M = 659.01 g mol^{-1}, monoclinic, $C2/c$, a = 24.656(3) Å, b = 9.818(4) Å, c = 25.714(2) Å, β = 103.076(7)°, V = 6063(2) Å^3, T = 306 ± 1 K, Z = 8, μ(Mo Kα) = 0.562 mm^{-1}, 5403 measured reflections, 1281 unique, 260 refined parameters, $R[I^2 > 2\sigma(I^2)] = 0.049$, $wR2(F^2) = 0.056$.

(25) **5**$[OSO_2CF_3]$: Using general procedures,[30] Ph_2PCl (1.0 g, 4.5 mmol) added to $Me_3SiOSO_2CF_3$ (1.2 g 5.4 mmol 20% excess) in CH_2Cl_2 (20 mL), stirred for 45 min at rt, added to Ph_3P (1.5 g, 5.4 mmol), stirred for 45 min. White solid recrystallized from CH_2Cl_2, cubes; 2.14 g, 80%; mp 163−164 °C; Anal. Calcd for $C_{31}H_{25}O_3F_3P_2S$: C, 62.42; H, 4.22; Found: C, 62.20; H, 4.01. IR cm^{-1} (ranked intensities): 488(9), 636(2), 693(5), 741(6), 1029(4), 1124(8), 1150(7), 1222(10), 1260(1), 1439(3); Crystal data for $C_{31}H_{25}F_3O_3P_2S$: M = 596.51 g mol^{-1}, triclinic, P-1, a = 10.474(3) Å, b = 11.002(3) Å, c = 14.140(4) Å, α = 73.083(5)°, β = 73.302(5)°, γ = 68.632(5)°, V = 1421.5(7) Å^3, T = 193(2) K, Z = 2, μ(Mo Kα) = 0.278 mm^{-1}, 9489 measured reflections, 5723 unique, 361 refined parameters, $R[I^2 > 2\sigma(I^2)] = 0.0703$, $wR2(F^2) = 0.1723$.

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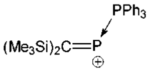
Table 1. Solid- and solution-state ^{31}P NMR spectroscopic data for **4**[A] and **5**[A] (A = $GaCl_4$ or OSO_2CF_3). $^1J_{PP}$ coupling was not observed for pure materials redissolved

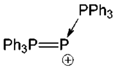
compound	in CH_2Cl_2 (CP-MAS)		reaction mix in CH_2Cl_2 (CP-MAS)
P_1-P_2	δ P_1	δ P_2	$^1J_{PP}$
$[Ph_2(Cl)P-PPh_2][GaCl_4]$	78 (77)	3 (3)	*b* (406)
$[Ph_2(Cl)P-PPh_2][SO_3CF_3]^a$	75 (*a*)	−4 (*a*)	*a*
$[Ph_3P-PPh_2][GaCl_4]$	15 (15)	−10 (−18)	340 (323)
$[Ph_3P-PPh_2][SO_3CF_3]$	15 (13)	−10 (−22)	*b* (350)

[a] Not isolated. [b] Not observed.

homoleptic phosphinophosphonium cation **5** is independent of the anion. The P−P bond length {e.g. **5**[OSO_2CF_3]: 2.220(6) and 2.2302(13) Å} compares with that of the parent diphosphine [Ph_2P-PPh_2, 2.217(1) Å],[26] as well as those observed for other Ph_3P complexes of phosphorus acceptors, **6** [2.267(2) Å],[8] **7** [2.137(6), and 2.128(6) Å][5] and **8** [2.206(1) Å].[10] An anomalously long interaction is observed for **9** [2.625(2) Å].[13]


$(Me_3Si)_2C{=}\overset{\oplus}{P}\leftarrow PPh_3$

6


$Ph_3P{=}\overset{\oplus}{P}\leftarrow PPh_3$

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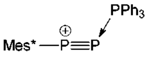
$Mes^*-\overset{\oplus}{P}{\equiv}P\leftarrow PPh_3$

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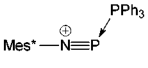
$Mes^*-\overset{\oplus}{N}{\equiv}P\leftarrow PPh_3$

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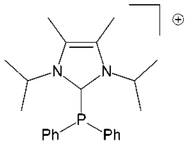
The solution- and solid-state[27] ^{31}P NMR chemical shifts correlate well for salts of **4** and **5** (Table 1), and are consistent with data obtained for reaction mixtures. Nevertheless, $^1J_{PP}$ coupling is observed in spectra of solid samples and in reaction mixture solutions, but not in solutions of isolated samples. An estimate of the P−P bond length (2.25 ± 0.02 Å) from the dipolar coupling constant measured for **5**[$GaCl_4$] and using first principle calculations[28] is consistent with 2.220(6) Å determined from X-ray diffraction data.

Phosphine exchange at a phosphorus center has been previously observed by NMR spectroscopy.[5] The isolation and characterization of otherwise synthetically inaccessible pentaphenylphosphinophosphonium salts described here highlights ligand exchange at a phosphine acceptor as a new synthetic methodology in phosphorus chemistry that is potentially applicable across the electron-rich elements of the p block. The versatility of coordinate element-P bond formation is further demonstrated by ^{31}P NMR spectra of reactions between **5**[OSO_2CF_3] and carbene (1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene), which show only Ph_3P and **10** (δ = −26.9 ppm, cf. −27.1 ppm[29]). We are currently assessing the potential extent and diversity of this synthetic procedure.



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Supporting Information Available: Atomic co-ordinates, isotropic displacement parameters, bond lengths and angles, and crystal data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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