

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

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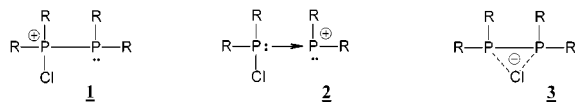
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Coordination chemistry usually refers to bonding interactions involving donation from electron-rich nonmetals (ligands) to electron-deficient metals (Lewis acceptors). Reports of metal complexes behaving as ligands toward other metals¹ and of compounds 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.



The distinct ³¹P chemical shifts¹⁶ indicate that chlorine cation exchange and access to a chloronium cation **3** are restricted. Therefore, R₂(Cl)P of **2** is available for ligand exchange, which

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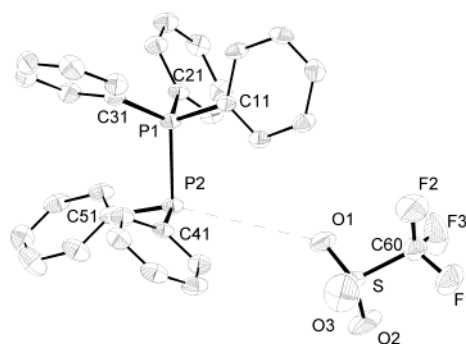
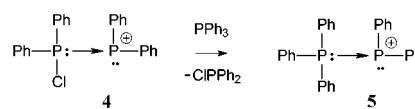


Figure 1. Crystallographic view of [Ph₃P–PPh₂][SO₃CF₃], **5**[SO₃CF₃]; selected bond lengths (Å): P1–P2 2.202(13), P2–O1 4.415(16), S1–O1 1.432(3), S1–O2 1.423(3), S1–O3 1.430(3); and angles (deg): C11–P1–P2 108.86(12), C21–P1–P2 105.46(11), C31–P1–P2 116.20(12), C41–P2–P1 100.38(11), C51–P2–P1 100.73(12), C41–P2–C51 104.25(16).

has facilitated the synthesis and structural characterization of the first penta-phenylphosphinophosphonium salts.



Phosphorus-31 NMR spectra²³ of reactions between **4**[A] (A = GaCl₄ or OSO₂CF₃) and Ph₃P indicate quantitative formation of **5**[A] and free Ph₂(Cl)P (δ = 80.5 ppm). Isolated solids have been characterized as **4**[GaCl₄], **5**[GaCl₄],²⁴ and **5**[OSO₂CF₃],²⁵ which was also isolated from the reaction mixture of Ph₂PCl, Me₃SiOSO₂CF₃ and Ph₃P. Long interatomic distances between counterions are observed in the crystal structures of **5**[GaCl₄] and **5**[OSO₂CF₃] (Figure 1), indicating that they are best described as ionic in the solid state. Moreover, the structure of the

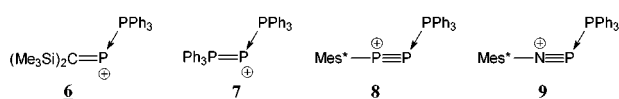
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- (23) Using general procedures,³⁰ solutions of **4**[A] [A = GaCl₄, OSO₂CF₃] (0.25 g) in CH₂Cl₂ (10 mL) were prepared in situ,¹⁶ and 1.3 equiv of Ph₃P in CH₂Cl₂ (10 mL) was introduced. NMR data are listed in Table 1.
- (24) **4**[GaCl₄]: Using general procedures,³⁰ GaCl₃ (0.9 g, 5.2 mmol) in CH₂Cl₂ (10 mL) added to Ph₂PCl (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 C₂₄H₂₀Cl₅GaP₂: 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**[GaCl₄]: Using general procedures,³⁰ Ph₃P (0.25 g, 0.97 mmol) in CH₂Cl₂ (15 mL) added to a solution of (0.60 g, 0.97 mmol) in CH₂Cl₂ (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 C₃₀H₂₅P₂GaCl₄: *M* = 659.01 g mol^{−1}, monoclinic, *C*2/*c*, *a* = 24.656(3) Å, *b* = 9.818(4) Å, *c* = 25.714(2) Å, β = 103.076(7)°, *V* = 6063(2) Å³, *T* = 306 ± 1 K, *Z* = 8, μ(Mo Kα) = 0.562 mm^{−1}, 5403 measured reflections, 1281 unique, 260 refined parameters, *R*[*I*² > 2σ(*I*)] = 0.049, w*R*2(*F*²) = 0.056.
- (25) **5**[OSO₂CF₃]: Using general procedures,³⁰ Ph₂PCl (1.0 g, 4.5 mmol) added to Me₃SiOSO₂CF₃ (1.2 g, 5.4 mmol 20% excess) in CH₂Cl₂ (20 mL), stirred for 45 min at rt, added to Ph₃P (1.5 g, 5.4 mmol), stirred for 45 min. White solid recrystallized from CH₂Cl₂, cubes; 2.14 g, 80%; mp 163–164 °C; Anal. Calcd for C₃₁H₂₅O₃F₃P₂S: 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 C₃₁H₂₅F₃O₃P₂S: *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) Å³, *T* = 193(2) K, *Z* = 2, μ(Mo Kα) = 0.278 mm^{−1}, 9489 measured reflections, 5723 unique, 361 refined parameters, *R*[*I*² > 2σ(*F*)] = 0.0703, w*R*2(*F*²) = 0.1723.

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

compound	in CH_2Cl_2 (CP-MAS)		reaction mix in CH_2Cl_2 (CP-MAS)
	δP_1	δP_2	$^1J_{\text{PP}}$
$\text{P}_1\text{--P}_2$			
$[\text{Ph}_2(\text{Cl})\text{P--PPh}_2][\text{GaCl}_4]$	78 (77)	3 (3)	<i>b</i> (406)
$[\text{Ph}_2(\text{Cl})\text{P--PPh}_2][\text{SO}_3\text{CF}_3]^a$	75 (<i>a</i>)	−4 (<i>a</i>)	<i>a</i>
$[\text{Ph}_3\text{P--PPh}_2][\text{GaCl}_4]$	15 (15)	−10 (−18)	340 (323)
$[\text{Ph}_3\text{P--PPh}_2][\text{SO}_3\text{CF}_3]$	15 (13)	−10 (−22)	<i>b</i> (350)

^a Not isolated. ^b Not observed.

homoleptic phosphinophosphonium cation **5** is independent of the anion. The P–P bond length {e.g. **5** $[\text{OSO}_2\text{CF}_3]$: 2.220(6) and 2.2302(13) Å} compares with that of the parent diphosphine $[\text{Ph}_2\text{P--PPh}_2]$, 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



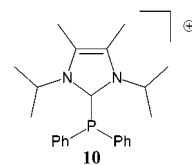
The solution- and solid-state²⁷ ^{31}P NMR chemical shifts correlate well for salts of **4** and **5** (Table 1), and are consistent with data obtained for reaction mixtures. Nevertheless, $^1J_{\text{PP}}$ coupling is observed in spectra of solid samples and in reaction mixture solutions, but not in 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** $[\text{GaCl}_4]$ and using first principle

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calculations²⁸ 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** $[\text{OSO}_2\text{CF}_3]$ and carbene (1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene), which show only Ph_3P and **10** ($\delta = -26.9$ ppm, cf. -27.1 ppm²⁹). 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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