

Homoatomic P → P coordination: A versatile synthetic approach to polyphosphorus dications

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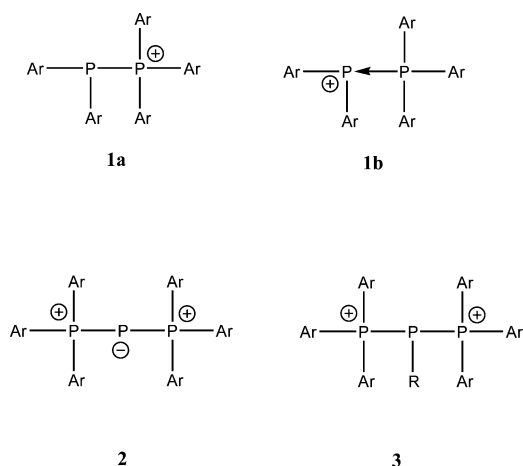
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Received (in West Lafayette, IN, USA) 2nd May 2003, Accepted 16th June 2003

First published as an Advance Article on the web 10th July 2003

Polyphosphorus dications have been synthesised and comprehensively characterised as diphosphine (dppe, dmpe and dpvh) linked Ar₂P⁺ Lewis acids (Ar = C₆H₅); this application of unique homoatomic coordination chemistry provides important building blocks for extended systems.

The allotropes of phosphorus as well as polyphosphines¹ and polyphosphorus anions² demonstrate a preference for P–P bonds that has not yet been extrapolated to cationic systems. Rare examples of polyphosphorus cations include ‘diphosphonium’[†] (1),³ ‘triphosphonium’[†] (2)^{4,5} and ‘triphosphonium’[†] (3).⁶ Derivatives of 1 exhibit structural features that are best described by the term ‘phosphinophosphonium’,⁷ but their developing chemistry (reactivity) primarily involves P–P dissociation implicating a phosphine → phosphonium coordination complex (illustrated by 1b).^{3,8,9} We have exploited this novel homoatomic P → P coordinate bonding model and the opportunity for ligand exchange as a versatile¹⁰ synthetic methodology¹¹ to obtain polyphosphorus dications composed of the diphosphines bis-(1,2-diphenylphosphino)ethane (dppe), bis-(1,2-dimethylphosphino)ethane (dmpe) or bis-(1,2-diphenylphosphino)hexane (dpvh), which link Ar₂P⁺ Lewis acids (Ar = C₆H₅).[‡]



³¹P{¹H} NMR spectra of reaction mixtures containing a 2:1 stoichiometric combination of [Ar₃P–PAR₂][OTf] or [Ar₂PCl–PAR₂][GaCl₄] with dppe, dmpe or dpvh show two new signals with δ values consistent with those observed for isolated materials listed in Table 1, and a third assigned to the free phosphines Ar₃P (–5 ppm) or Ar₂PCl (81 ppm), respectively. In most cases, the signals are broad (1000–1500 Hz) indicating dynamic behaviour at room temperature. Isolated solids have been comprehensively characterised as [4dppe][OTf]₂, [4dmpe][OTf]₂ and [4dpvh][GaCl₄]₂ (Table 1).

The ionic formulations for all derivatives of 4 are confirmed by the solid state structures, which reveal dications (Figs. 1–3) that can be viewed as complexes of two Ar₂P⁺ cations tethered through a bifunctional ligand 4b, and contrast the monocationic chelate structures that are possible with such ligands.

Table 1 compares P–P bond lengths and NMR data for derivatives of 4 with those in Ar₂P–PAR₂¹² and salts of 1,⁷ 2⁴ and 3.⁶ The P–P bond lengths are independent of molecular charge and coordination number of each phosphorus center. The chemical shifts are distinctive for the phosphonium centers and are consistent with the characteristic shift for Ar₄P⁺ (≈ 20 ppm).

Table 1 P–P bond lengths, δ³¹P{¹H} and ¹J_{PP} for Ar₂P–PAR₂, derivatives of 1[Anion], 2[Anion], 3[Anion] and 4[Anion]₂

Compound	P–P (Å)	δ ³¹ P (ppm)	¹ J _{PP} (Hz)	Ref.
Ar ₂ P–PAR ₂	2.217(1)	–14	—	12
[Ar ₃ P–PAR ₂] (1) [OTf]	2.230(1)	15, –10	343	7
[Ar ₃ P–PAR ₂] (1) [GaCl ₄]	2.220(6)	15, –10	341	7
[Ar ₃ P–P–PAR ₃] (2) [AlCl ₄]	2.137(6)	30, –174	502	4
	2.128(6)			
[Ar ₃ P–PH–PAR ₃] (3) [AlCl ₄]	2.205(1)	23, –120	286	6
[4dppe][OTf] ₂	2.219(1)	21, –33	322	This work
[4dmpe][OTf] ₂	2.217(2)	21, –32	300	This work
	2.209(2)			
[4dpvh][GaCl ₄] ₂	2.211(1)	20, –24	318	This work

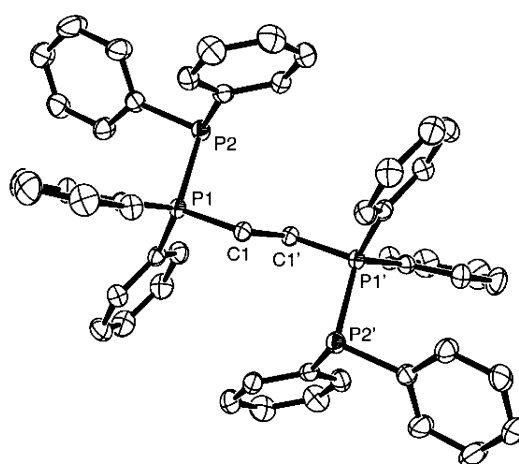
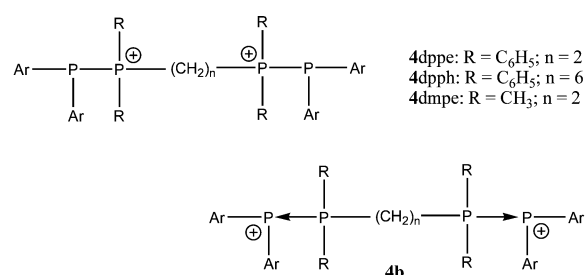


Fig. 1 View of one of the crystallographically-independent cations in the solid state structure of [4dppe][OTf]₂. Ellipsoids are 50% probability, hydrogen atoms have been omitted for clarity. Primed atoms are related to unprimed atoms via the crystallographic inversion centre ($\frac{1}{2}, 0, \frac{1}{2}$) at the midpoint of the C1–C1' bond.

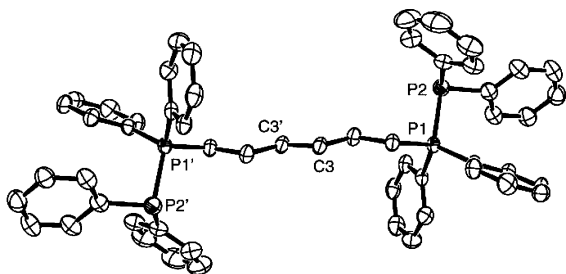


Fig. 2 Solid state structure of the cation in $[4dpph][GaCl_4]_2$. Ellipsoids are 50% probability, hydrogen atoms have been omitted for clarity. Primed atoms are related to unprimed ones *via* the crystallographic inversion centre $(0, -\frac{1}{2}, 0)$ at the midpoint of the C3–C3' bond.

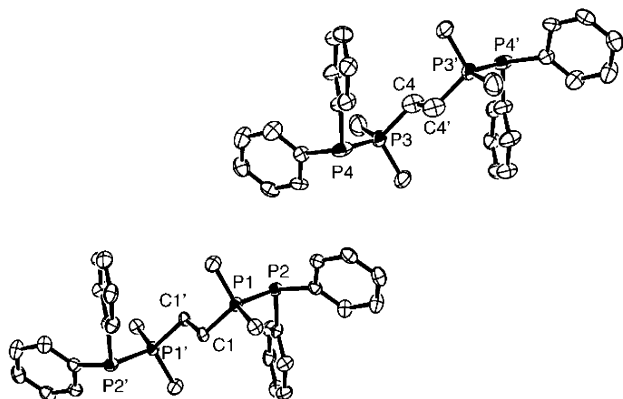


Fig. 3 Solid state structure of the two crystallographically distinct cations in $[4dmpe][OTf]_2$. Ellipsoids are 50% probability, hydrogen atoms have been omitted for clarity. Primed atoms are related to unprimed ones *via* the crystallographic inversion centre $(\frac{1}{2}, 0, \frac{1}{2})$ at the midpoint of the C1–C1' and C4–C4' bond.

The chemical shift values for the phosphine centers are likewise consistent with those of Ar_3P and Ar_2P-PAr_2 , with a somewhat broader range than those of the phosphonium centers. The shift of the central phosphorus center in **2** is predictably unique, as is the $^1J_{PP}$ value, which are consistently in the range of 300 Hz for phosphinophosphonium derivatives.¹³

Bifunctional amines have been used to tether neutral phosphines,¹¹ but cationic phosphorus centers have previously been observed to form chelate complexes.¹⁴ Therefore, the isolation and characterisation of otherwise synthetically inaccessible polyphosphorus dications highlights the versatility of ligand exchange at the Ar_2P^+ Lewis acceptor. Moreover, association of phosphonium centers using coordination chemistry offers opportunities for supramolecular organophosphorus chemistry.

We thank the Natural Sciences and Engineering Research Council of Canada, the Killam Foundation, the Canada Research Chairs Program, the Canada Foundation for Innovation, the Nova Scotia Research and Innovation Trust Fund, and the Walter C. Sumner Foundation for funding, and the Atlantic Region Magnetic Resonance Centre for use of instrumentation.

Notes and references

† Common, non-IUPAC nomenclature.

‡ *Experimental.* All manipulations were performed in a nitrogen dry box with solvents distilled prior to use. CH_2Cl_2 was dried at reflux over CaH_2 , P_2O_5 and again over CaH_2 . Hexane was dried at reflux over K and Et_2O was dried at reflux over Na/benzophenone. All IR spectra were collected on a Bruker Vector 22 FT-IR spectrometer using nujol mulls. Solution (CD_2Cl_2)

NMR spectra were obtained on a Bruker AC-250 spectrometer. X-ray crystallographic data were obtained on a Bruker PLATFORM/SMART 1000 CCD diffractometer, using graphite-monochromated Mo K_{α} ($\lambda = 0.71073$) radiation. CCDC 207172–207175. See <http://www.rsc.org/supp-data/cc/b3/b304984a/> for crystallographic data in .cif or other electronic format

In a typical experiment, the diphosphine in CH_2Cl_2 (3 mL) was added dropwise (5 min) to two equivalents of $[Ar_3P-PAr_2][OTf]$ or $[Ar_2CIP-PAr_2][GaCl_4]$ in CH_2Cl_2 (2 mL). After stirring for 12 hours at RT, solvent was removed *in vacuo*, and addition of hexanes (5 mL) gave a fine white precipitate; crystals were obtained by vapour diffusion (CH_2Cl_2/Et_2O).

§ **[4dmpc][OTf]₂·CH₂Cl₂**: 0.09 g, 74%; m.p. 193–195 °C; clear, colourless, needle-shaped crystals; Elemental Analysis Calcd. (found): C 55.27 (57.26), H 4.03 (4.30)%; IR (cm^{-1}) ranked intensity: 633(11), 658(15), 694(5), 723(1) 801(13), 881(14), 973(9), 996(8), 1028(4), 1097(6), 1150(3), 1263(2), 1584(12), 2670(10), 2726(7); $^{31}P\{^1H\}$ NMR: RT, 21 (s, br), –26 (s, br), 193 K, 21 (d, $^1J_{PP} = 322$ Hz), –33 (d, $^1J_{PP} = 322$ Hz); Crystal Data for $C_{53}H_{46}Cl_2F_6O_6P_4S_2$: $M = 1151.80$ g mol^{–1}, triclinic, $P\bar{1}$, $a = 9.3972(8)$, $b = 12.863(1)$, $c = 13.668(1)$ Å, $\alpha = 119.801(2)$, $\beta = 95.700(2)^\circ$, $\lambda = 104.239(2)$, $V = 1340.5(2)$ Å³, $T = 193(2)$, $Z = 1$, $\mu(Mo K_{\alpha}) = 0.388$ mm^{–1}, 6741 measured reflections, (5392 unique), 329 refined parameters, $R_1(F)[4092$ reflections with $I > 2\sigma(I)$] = 0.060, $wR_2(F^2)$ [all data] = 0.168.

¶ **[4dmpe][OTf]₂**: 0.03 g, 63%; m.p. 167–170 °C; clear, colourless, needle-shaped crystals; Elemental Analysis Calcd. (found): C 46.95 (46.67), H 4.43 (4.54)%; IR (cm^{-1}) ranked intensity: 516(18), 571(20), 634(7), 693(15), 704(19), 723(13), 744(8), 912(11), 959(14), 997(17), 1028(5), 1088(16), 1152(19), 1183(6), 1201(12), 1221(10), 1249(3), 1283(4), 1377(2), 1462(1); $^{31}P\{^1H\}$ NMR: RT, 21 (d, br), –21 (d, br, $^1J_{PP} \approx 274$ Hz), 193 K, 21d, –32d ($^1J_{PP} = 300$ Hz); Crystal Data for $C_{32}H_{36}F_6O_6P_4S_2$: $M = 818.61$ g mol^{–1}, triclinic, $P\bar{1}$, $a = 8.637(1)$, $b = 13.544(2)$, $c = 15.742(2)$ Å, $\alpha = 96.528(3)^\circ$, $\beta = 93.131(3)^\circ$, $\gamma = 99.431(2)^\circ$, $V = 1799.8(4)$ Å³, $T = 193(2)$, $Z = 2$, $\mu(Mo K_{\alpha}) = 0.400$ mm^{–1}, 11460 measured reflections (7168 unique), 451 refined parameters, $R_1(F)[4743$ reflections with $I > 2\sigma(I)$] = 0.074, $wR_2(F^2)$ [all data] = 0.201.

|| **[4dpph][GaCl₄]₂**: 0.049 g, 79%; m.p. 64–67 °C; clear, colourless, needle-shaped crystals; Elemental Analysis Calcd. (found): C 51.98 (51.01), H 4.20 (4.25)%; IR (cm^{-1}) ranked intensity: 279(10), 356(9), 373(8), 688(7), 722(4), 742(3), 1104(5), 1377(2), 1461(1), 1670(3); $^{31}P\{^1H\}$ NMR: RT, 20 (d), –24 (d, $^1J_{PP} \approx 318$ Hz); Crystal Data for $C_{54}H_{52}Cl_8Ga_2P_4$: $M = 1247.88$ g mol^{–1}, monoclinic, $I2/a$, $a = 30.395(4)$, $b = 10.119(1)$, $c = 19.465(2)$ Å, $\beta = 105.829(2)^\circ$, $V = 5760.2(1)$ Å³, $T = 193(2)$, $Z = 4$, $\mu(Mo K_{\alpha}) = 1.453$ mm^{–1}, 15467 measured reflections (unique 5895), 307 refined parameters, $R_1(F)$ [4077 reflections with $I > 2\sigma(I)$] = 0.050, $wR_2(F^2)$ [all data] = 0.132.

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