organic compounds

1,2-Bis(diphenylphosphino)benzene and two related mono-methiodides, [o-C₆H₄(PR₂)(PR₂Me)]I (R = Ph or Me)

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The structures of the compounds 1,2-bis(diphenylphosphino)-benzene, $C_{30}H_{24}P_2$, [2-(diphenylphosphino)phenyl]methyl-diphenylphosphonium iodide, $C_{31}H_{27}P_2^+ \cdot I^-$, and [2-(dimethyl-phosphino)phenyl]trimethylphosphonium iodide, $C_{11}H_{19}P_2^+ \cdot I^-$, show that quaternization only occurs at one P centre and results in significantly shorter P—C bonds and larger C—P—C angles, consistent with the formal oxidation from P^{III} to P^{V}.

Comment

Diphosphines, o-C₆H₄(PR₂)₂ (R = Ph, Me, *etc.*), are widely used in coordination and organometallic chemistry. The rigid o-phenylene backbone pre-organizes the ligands for chelation and its rigidity resists dissociation from metal centres (the 'o-phenylene backbone' effect; Levason, 1990). A combination of these effects, especially when combined as in the case of R = Me with small steric requirements and exceptionally strong σ donation, produces ligands that can form robust complexes with most transition metals, even hard 3d-metal centres, such as Mn^{II}, Fe^{IV} or Ni^{IV}, or oxophilic early metals including Zr^{IV} and Hf^{IV} (Warren & Bennett, 1976; Levason, 1990; Levason *et al.*, 2004). Complexes with p-block Lewis acids, including the halides of Ga, Sb and As, are also readily prepared (Hill *et al.*, 2002; Genge *et al.*, 2001; Sigl *et al.*, 1998a). A further consequence of the o-phenylene backbone is that, in contrast to diphosphinoalkanes, quaternization of o-C₆H₄(PR₂)₂ with MeI in acetone or alcohols affords exclusively the mono-phosphonium salts [o-C₆H₄(PR₂)(PR₂Me)]I, since the nucleophilicity of the second P atom is markedly reduced by the positive charge on the neighbouring phosphonium centre. Phosphonium salts, [PR₄]⁺, are widely used as large cations to stabilize a variety of anionic species and to phase-transfer anions into low polarity organic media. The (2-di-R-phosphinophenyl)phosphonium species behave similarly but also have the potential to function as positively charged ligands, binding through the phosphane function to metals leading to zwitterionic products. A related example involving mono-quaternized Ph₂PCH₂PPh₂H⁺ has been structurally characterized in [TiCl₅(Ph₂PCH₂PPh₂H)] (Hart *et al.*, 2001).

During the course of studies on the coordination chemistry of o-C₆H₄(PR₂)₂ (R = Ph or Me), we obtained crystals of the three title materials and report their structures here.
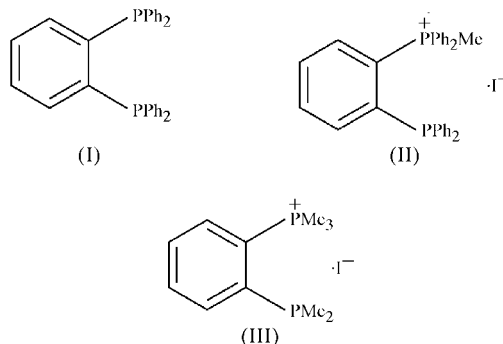
o-C₆H₄(PPh₂)₂, (I) (Fig. 1 and Table 1), has P—C distances of 1.836 (3)–1.851 (3) Å; addition of the Me group in the phosphonium salt (II) results in shortening of the P1—C distances to 1.787 (2)–1.814 (2) Å, consistent with formal oxidation from P^{III} to P^{V}, leaving the P2—C distances essentially unchanged (Fig. 2 and Table 2). Although even with excess MeI quaternization only occurs at one P centre (evidence of transmitted electronic effects), there are no significant differences in the P—C bond lengths and the C—P—C angles at P2 in (II) [the average of the three angles is 102.2 (19)°] compared with those in (I) [the average of the six angles is 101.8 (16)°]. The P⋯P distance of the neutral ligand [3.166 (1) Å] increases in the methiodide to 3.300 (1) Å, and the C—P—C angles increase by about 7° at the phosphonium P atom. The observed structural changes on quaternization generally parallel those observed by Dunne *et al.* (1991) in PPh₃ derivatives, although the presence of P^{III} and P^{V} within the same molecule in [o-C₆H₄(PPh₂)(PPh₂Me)]I provides a particularly clear example. Comparison of (I) with the crystal structure of o-C₆H₄[P(O)Ph₂]₂ (Davis *et al.*, 2006) reveals similar changes in the geometry at both P atoms.

o-C₆H₄(PMe₂)₂ is a liquid at ambient temperatures and has not been obtained in crystalline form; thus, comparisons with the mono-methiodide [o-C₆H₄(PMe₂)(PMe₃)]I, (III), are not possible. However, the same trends as observed in (II) are
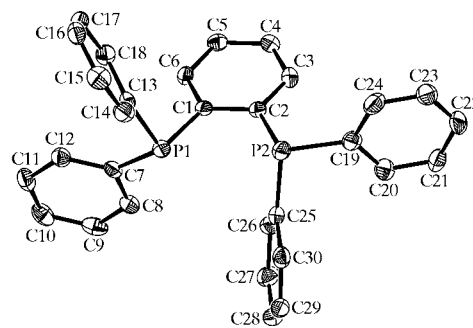

Figure 1
The discrete molecule of o-C₆H₄(PPh₂)₂, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

apparent in the cation, with the P1—C distances shorter by *ca* 0.04 Å than the P2—C distances and with the C—P—C angles at P1 some 8° larger than those at P2 (Fig. 3 and Table 3). While *o*-C$_6$H$_4$(PMe$_2$)$_2$ very readily oxidizes in air, the P$^{\text{III}}$ centre in the mono-methiodide appears to be stable to air oxidation. The shortest anion–cation distance in the methio-dides is 3.04 Å (I···H), indicating no unusual interactions. Related compounds in the literature include *o*-C$_6$H$_4$(PMePh)$_2$ (Roberts *et al.*, 1980) and [*o*-C$_6$H$_4$(PPh$_2$)(PPh$_2$H)]$^+$ (Sigl *et al.*, 1998*b*)

Figure 2
The structure of [*o*-C$_6$H$_4$(PPh$_2$)(PPh$_2$Me)]I, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.
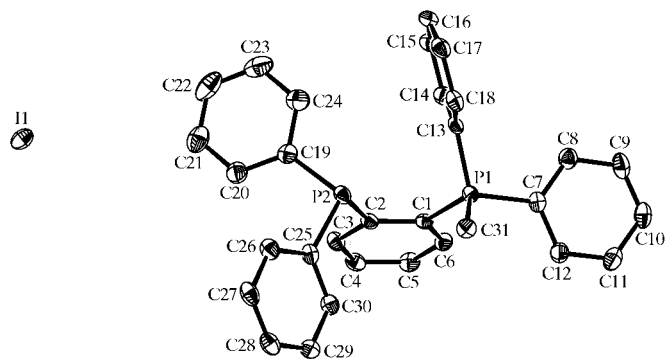

Figure 3
The structure of [*o*-C$_6$H$_4$(PMe$_2$)(PMe$_3$)]I, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.
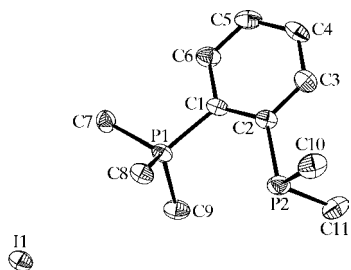
Experimental

o-C$_6$H$_4$(PR$_2$)$_2$ (R = Ph or Me) were prepared according to published procedures (McFarlane & McFarlane, 1983; Kyba *et al.*, 1983). [*o*-C$_6$H$_4$(PR$_2$)(PR$_2$Me)]I (R = Me or Ph) were prepared by reaction of the diphosphanes with excess MeI in gently refluxing acetone. White microcrystalline products separated on cooling. *o*-C$_6$H$_4$(PPh$_2$)$_2$: m.p. 458 K; ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$ relative 85% H$_3$PO$_4$): δ −13.0; EI–MS (*m/z*) = 446 a.m.u. (*M*$^+$). [*o*-C$_6$H$_4$(PPh$_2$)(PPh$_2$Me)]I: ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$): δ −14.8 (*d*, $^3J_{\text{PP}}$ = 26 Hz), 22.6 (*d*, $^3J_{\text{PP}}$ = 26 Hz); ES–MS (*m/z*) = 461 a.m.u. (*M*$^+$). [*o*-C$_6$H$_4$(PMe$_2$)(PMe$_3$)]I: ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$): δ −53.4 (*d*, $^3J_{\text{PP}}$ = 22 Hz), 22.0 (*d*, $^3J_{\text{PP}}$ = 22 Hz); ES–MS (*m/z*) = 213 a.m.u. (*M*$^+$). Crystals of *o*-C$_6$H$_4$(PPh$_2$)$_2$ were obtained by slow evaporation from a CH$_2$Cl$_2$ solution in an inert atmosphere. Crystals of the other two compounds were obtained directly from the preparations.

Compound (I)

Crystal data

C$_{30}$H$_{24}$P$_2$	$V = 1159.6$ (4) Å^3
$M_r = 446.43$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.279$ Mg m^{-3}
$a = 8.1930$ (15) Å	Mo $K\alpha$ radiation
$b = 12.442$ (2) Å	$\mu = 0.20$ mm^{-1}
$c = 12.584$ (3) Å	$T = 120$ (2) K
$\alpha = 109.846$ (5)°	Block, colourless
$\beta = 99.918$ (5)°	$0.12 \times 0.10 \times 0.06$ mm
$\gamma = 98.330$ (15)°	

Data collection

Nonius KappaCCD area-detector diffractometer	15781 measured reflections
φ and ω scans	5122 independent reflections
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)	2565 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.892$, $T_{\max} = 0.985$	$R_{\text{int}} = 0.132$
	$\theta_{\max} = 27.5°$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.056$	$w = 1/[\sigma^2(F_o^2) + (0.0398P)^2]$
$wR(F^2) = 0.132$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.93$	$(\Delta/\sigma)_{\max} = 0.001$
5122 reflections	$\Delta\rho_{\max} = 0.54$ e Å^{-3}
290 parameters	$\Delta\rho_{\min} = -0.33$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

P1—C1	1.851 (3)	P2—C19	1.846 (3)
P1—C7	1.839 (3)	P2—C25	1.838 (3)
P1—C13	1.836 (3)	C1—C2	1.420 (4)
P2—C2	1.849 (3)		
C13—P1—C7	104.17 (13)	C25—P2—C2	101.79 (13)
C13—P1—C1	102.65 (13)	C19—P2—C2	101.67 (13)
C7—P1—C1	100.67 (13)	C2—C1—P1	117.8 (2)
C25—P2—C19	99.70 (14)	C1—C2—P2	118.4 (2)

Compound (II)

Crystal data

C$_{31}$H$_{27}$P$_2^+$·I$^-$	$V = 1317.22$ (16) Å^3
$M_r = 588.37$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.483$ Mg m^{-3}
$a = 10.3323$ (5) Å	Mo $K\alpha$ radiation
$b = 11.8412$ (10) Å	$\mu = 1.36$ mm^{-1}
$c = 12.7828$ (10) Å	$T = 120$ (2) K
$\alpha = 69.536$ (3)°	Needle, colourless
$\beta = 67.260$ (3)°	$0.20 \times 0.08 \times 0.04$ mm
$\gamma = 70.847$ (4)°	

Data collection

Nonius KappaCCD area-detector diffractometer	20101 measured reflections
φ and ω scans	5956 independent reflections
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)	5063 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.855$, $T_{\max} = 0.945$	$R_{\text{int}} = 0.053$
	$\theta_{\max} = 27.5°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.036P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.031$	$+ 0.2511P]$
$wR(F^2) = 0.074$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{\max} = 0.001$
5956 reflections	$\Delta\rho_{\max} = 0.95$ e Å^{-3}
308 parameters	$\Delta\rho_{\min} = -1.08$ e Å^{-3}
H-atom parameters constrained	

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Table 2
Selected geometric parameters (Å, °) for (II).

P1—C1	1.814 (2)	P2—C2	1.858 (2)
P1—C7	1.801 (2)	P2—C19	1.838 (2)
P1—C13	1.789 (2)	P2—C25	1.834 (2)
P1—C31	1.787 (2)	C1—C2	1.406 (3)
C31—P1—C13	111.96 (11)	C25—P2—C19	104.26 (10)
C31—P1—C7	106.12 (11)	C25—P2—C2	100.67 (10)
C13—P1—C7	109.57 (10)	C19—P2—C2	101.50 (10)
C31—P1—C1	111.19 (11)	C2—C1—P1	120.79 (16)
C13—P1—C1	107.57 (10)	C1—C2—P2	121.29 (17)
C7—P1—C1	110.46 (10)		

Compound (III)

Crystal data

$C_{11}H_{19}P_2^+ \cdot I^-$	$Z = 4$
$M_r = 340.10$	$D_x = 1.532$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.2002$ (16) Å	$\mu = 2.36$ mm^{-1}
$b = 11.846$ (3) Å	$T = 150$ (2) K
$c = 13.566$ (2) Å	Rhomb, colourless
$\beta = 94.312$ (14)°	$0.2 \times 0.2 \times 0.05$ mm
$V = 1474.3$ (5) Å^3	

Data collection

Rigaku AFC-7S diffractometer	1772 reflections with $I > 2\sigma(I)$
$\omega/2\theta$ scans	$R_{int} = 0.120$
Absorption correction: ψ scan	$\theta_{max} = 25.0°$
(North *et al.*, 1968)	3 standard reflections
$T_{min} = 0.596$, $T_{max} = 0.890$	every 150 reflections
5375 measured reflections	intensity decay: none
2587 independent reflections	

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.046$	$w = 1/[\sigma^2(F_o^2) + (0.0668P)^2]$
$wR(F^2) = 0.121$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.97$	$(\Delta/\sigma)_{max} = 0.001$
2587 reflections	$\Delta\rho_{max} = 2.21$ e Å^{-3}
128 parameters	$\Delta\rho_{min} = -2.89$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (III).

P1—C1	1.820 (5)	P2—C2	1.858 (5)
P1—C7	1.794 (6)	P2—C10	1.832 (6)
P1—C8	1.795 (6)	P2—C11	1.843 (7)
P1—C9	1.792 (5)	C1—C2	1.390 (8)
C9—P1—C8	110.4 (3)	C10—P2—C11	100.4 (3)
C9—P1—C7	106.4 (3)	C10—P2—C2	101.3 (3)
C8—P1—C7	106.5 (3)	C11—P2—C2	100.5 (3)
C9—P1—C1	111.4 (3)	C2—C1—P1	123.3 (4)
C8—P1—C1	112.2 (3)	C1—C2—P2	121.4 (4)
C7—P1—C1	109.6 (3)		

H atoms were placed in calculated positions [C—H = 0.95 (aromatic) and 0.98 Å (methyl)]. For (I) and (II), a common refined $U_{iso}(H)$ value was used for all the H atoms. For (III), $U_{iso}(H)$ values

for phenyl H atoms were set at $1.2U_{eq}(C)$ of the bonded C atoms, whilst the methyl H atoms were given a common refined $U_{iso}(H)$ value. The largest peak and trough in the difference electron-density map for [*o*-C$_6$H$_4$(PMe$_2$)(PMe$_3$)]I were less than 1 Å from the I atom.

For compounds (I) and (II), data collection: *COLLECT* (Hooft, 1998) and *DENZO* (Otwinowski & Minor, 1997); cell refinement: *COLLECT* and *DENZO*; data reduction: *COLLECT* and *DENZO*. For compound (III), data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). For all compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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