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# Synthesis and structural characterisation of the first tris(diacylpnictido)phosphines, $P[E\{C(O)R\}_2]_3$, $E = P$ or As, $R = Bu^t$ or Ph

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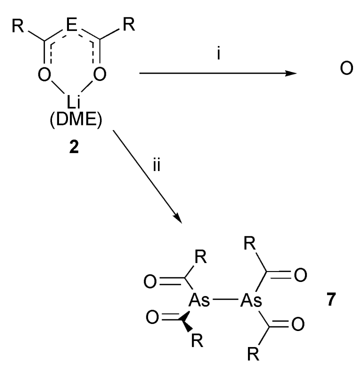
**The reactions of the 2-phospha- or 2-arsa-dionatolithium complexes, $[Li(DME)\{\eta^2\text{-O,O-OC(R)EC(R)}\}]$, E = P or As, R = $Bu^t$ or Ph, with $PCl_3$ have afforded the first examples of tris(diacylpnictido)phosphines, $P[E\{C(O)R\}_2]_3$, two of which have been structurally characterised.**

A great deal of attention has been paid to the chemistry and applications of low coordination phosphorus compounds over the past 20 years.[1] In more recent times this area has been extended to compounds containing the heavier pnictogens, As, Sb or Bi, in a low coordinate state,[2] though the stability of these decreases significantly as the molecular weight of the incorporated Group 15 element increases. Despite this we have developed a number of ligand systems containing multiply bonded As or Sb centres which include the 2-arsa- and 2-stibadionates, $[RC(O)EC(O)R]^-$ **1**, E = As or Sb, R = alkyl or aryl, which are valence isoelectronic to the ubiquitous β-diketonate class of ligand.[3] Whereas β-diketonates generally ligate both transition and main group metals in an $\eta^2$-O,O-chelating fashion we have shown that ligands such as **1** can coordinate transition metals in a variety of fashions which include $\eta^2$-O,O; $\eta^1$-E; $\eta^1$-E:$\eta^1$-O:$\eta^2$-CO; $\eta^1$-E:$\eta^2$-O,O and μ-$\eta^1$:$\eta^1$-E.[4] To date the only main group complexes of **1** are their lithium salts in which the metal is chelated by both oxygen centres of the ligand, as in **2**.[3] We were eager to extend the main group element coordination chemistry of **1** due to the variety of coordination modes it can adopt and saw the lithium salts, **2**, as potentially excellent transfer reagents for this task. Herein we report the preliminary results of this study, namely the preparation and structural characterisation of the first tris(diacylpnictido)phosphines.

The reactions of $PCl_3$ with **2**, E = As or P, in a 3 : 1 stoichiometry led cleanly to the tris(pnictido)phosphines, **3**–**6**, though only low to moderate yields of the compounds could be obtained upon crystallisation (Scheme 1). Interestingly, when **2**, E = As, was reacted with either $AsCl_3$ or $SbCl_3$ in a 3 : 1 stoichiometery high yields of the known diacylarsines, **7**,[4,5] were obtained, presumably by oxidative coupling reactions. Similarly, in the reaction of **2**, E = Sb, with $PCl_3$ a facile decomposition process occurred which involved the deposition of elemental antimony.



**Scheme 1** Reagents and conditions: i, $1/3PCl_3$, DME, $-LiCl$; ii, E = As, $1/3AsCl_3$ or $SbCl_3$, DME.

The spectroscopic data† for the thermally robust compounds, **3**–**6**, are consistent with their proposed structures in that the $^{31}P\{^1H\}$ NMR spectra of **3** and **4** display singlets at $\delta$ −78.9 and −73.4 ppm respectively, whilst those of **5** and **6** exhibit $AX_3$ patterns with large one bond PP couplings and high field shifts for the central phosphorus atoms (**5** $\delta$ $P_A$ −111.3 ppm, $P_x$ 4.9 ppm, $^1J_{PP}$ = 429 Hz; **6** $\delta$ $P_A$ −99.8 ppm, $P_x$ 23.3 ppm, $^1J_{PP}$ = 398 Hz). Similar shifts have been observed in related substituted *iso*-tetraphosphines, *e.g.* $P(PC_4Me_4)_3$.[6] The $^1H$ and $^{13}C$ NMR data are also compatible with the symmetry of these molecules.

X-Ray crystal structure analyses‡ of **3** and **6** have been carried out and their molecular structures are depicted in Figs. 1 and 2, respectively. They are both monomeric and **3** possesses three-fold crystallographic symmetry. The central P-atom in each has a pyramidal geometry [**3** As–P–As angles 108.39(11)°, **6** av. P–P–P angle 107.4°] similar to that in $P(C_4Me_4)_3$ [av. PPP angle 104.2°] but different to the trigonal planar central P-atom in the closely related compound, $P(PBu^t_2)_3$.[7] There are no structurally characterised trisarsino-

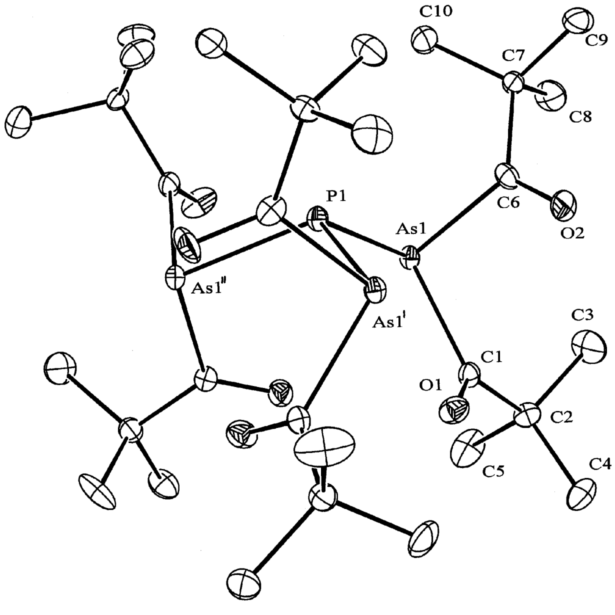


**Fig. 1** Molecular structure of **3**. Selected bond lengths (Å) and angles(°): As(1)–C(6) 2.046(10), As(1)–C(1) 2.053(10), As(1)–P(1) 2.3054(19), O(1)–C(1) 1.201(12), O(2)–C(6) 1.203(13); C(6)–As(1)–C(1) 94.3(4), As(1)–P(1)–As(1)′ 108.39(11), C(6)–As(1)–P(1) 88.2(3), C(1)–As(1)–P(1) 103.4(3).

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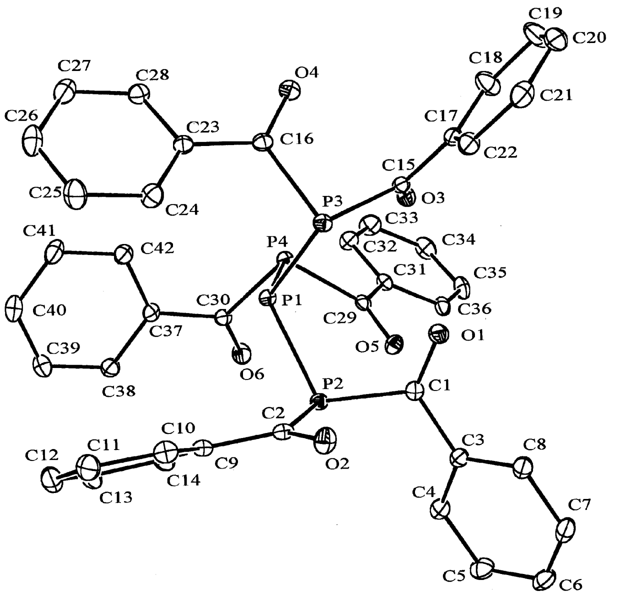

**Fig. 2** Molecular structure of **6**. Selected bond lengths (Å) and angles(°): P(1)–P(2) 2.1759(8), P(1)–P(4) 2.1819(15), P(1)–P(3) 2.1819(9), P(2)–C(2) 1.886(2), P(2)–C(1) 1.8928(17), P(3)–C(16) 1.8995(18), P(3)–C(15) 1.904(2), P(4)–C(30) 1.8874(17), P(4)–C(29) 1.906(2), O(1)–C(1) 1.214(2), O(2)–C(2) 1.221(2); P(2)–P(1)–P(4) 106.47(5), P(2)–P(1)–P(3) 108.75(3), P(4)–P(1)–P(3) 106.85(4), C(2)–P(2)–C(1) 94.25(8), C(2)–P(2)–P(1) 95.66(7), C(1)–P(2)–P(1) 108.96(6), C(16)–P(3)–C(15) 92.62(8), C(16)–P(3)–P(1) 95.13(6), C(15)–P(3)–P(1) 107.61(7), C(30)–P(4)–C(29) 96.73(8), C(30)–P(4)–P(1) 95.64(6), C(29)–P(4)–P(1) 106.92(7).

phosphines, $P(AsR_2)_3$, for comparison. The As–P distances in **3** [2.3054(19) Å] and the average P–P distance in **6** (2.18 Å) are shorter than the means for all crystallographically determined As–P [2.33 Å] and P–P [2.21 Å][8] bonds but still in the normal range for single bonded interactions. In addition, the E–C interactions in **3** and **6** are normal for single bonds but significantly longer than the delocalised E–C double bonds in the reaction precursors, **2**.[3] This, combined with the fact that the peripheral E-centres in **3** and **6** have distorted pyramidal geometries suggests that, unlike **2**, there is no delocalisation over the OCECO fragments.

In conclusion, we have prepared the first tris(diacylpnictido)-phosphines, the formation of which suggests that 2-pnictidodionato ligands will display a similar range of coordination modes with main group elements as they do with transition metals. We are currently systematically exploring these possibilities in addition to investigating the potential use of **3**–**6** as multidentate ligands. The outcomes of these investigations will be presented in a future publication.

## Acknowledgements

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## Notes and references

† Selected data for **3**: (yield 21%); mp 184–186 °C (dec.). $^1H$ NMR (400 MHz, $C_6D_6$, 300 K): $\delta$ 1.29 (s, 54H, $Bu^t$); $^{13}C$ NMR (101.6 MHz, $C_6D_6$, 300 K): $\delta$ 25.4 ($CH_3$), 49.4 ($CMe_3$), 225.2 (CO); $^{31}P\{^1H\}$ NMR (121.7 MHz, $C_6D_6$) $\delta$ −78.9 (s); MS APCI: *m*/*z* (%) 767 ($M^+$, 100); IR (Nujol) $\nu$/cm$^{-1}$: 1708 (s), 1660 (s), 1475 (m), 1363 (m). Found: C, 46.67; H, 7.11; $C_{30}H_{54}O_6PAs_3$ requires: C, 47.0; H, 7.10%.

For **4**: (yield 18%); mp 130–132 °C (dec.). $^1H$ NMR (400 MHz, $C_6D_6$, 300 K): $\delta$ 6.65–6.75 (m, 12H, *m*-ArH), 6.85 (t, 6H, *p*-ArH, $^3J_{HH} = 8$ Hz), 7.85 (d, 12H, *o*-ArH, $^3J_{HH} = 8$ Hz); $^{13}C$ NMR (101.6 MHz, $C_6D_6$, 300 K): $\delta$ 128.9 (*m*-Ar), 129.3 (*o*-Ar), 133.7 (*p*-Ar), 140.8 (*ipso*-Ar), 210.0 (CO); $^{31}P\{^1H\}$ NMR (121.7 MHz, $C_6D_6$) $\delta$ −73.4 (s); MS APCI: *m*/*z* (%) 317 [$PAs(OCPh)_2^+$, 100], 286 [$As(OPh)_2$, 45]; IR (Nujol) $\nu$/cm$^{-1}$: 1655 (s), 1629 (s), 1460 (m), 1444 (m). Found: C, 55.45; H, 3.41; $C_{30}H_{42}O_6PAs_3$ requires: C, 56.9; H, 3.4%.

For **5**: (yield 20%); mp 195–197 °C (dec.). $^1H$ NMR (400 MHz, $C_6D_6$, 300 K): $\delta$ 1.21 (s, 54H, $Bu^t$); $^{13}C$ NMR (101.6 MHz, $C_6D_6$, 300 K): $\delta$ 25.8 ($CH_3$), 48.5 ($CMe_3$), 221.8 (CO); $^{31}P\{^1H\}$ NMR (121.7 MHz, $C_6D_6$) $\delta$ −111.3 (q, $P_A$, $^1J_{PP} = 429$ Hz), 4.9 (d, $P_X$, $^1J_{PP} = 429$ Hz); MS APCI: *m*/*z* (%) 635 ($M^+$, 100); IR (Nujol) $\nu$/cm$^{-1}$: 1680 (s), 1644 (s), 1475 (m), 1454 (m).

For **6**: (yield 15%); mp 278–280 °C (dec.). $^1H$ NMR (400 MHz, $C_6D_6$, 300 K): $\delta$ 6.71–6.80 (m, 12H, *m*-ArH), 6.90 (t, 6H, *p*-ArH, $^3J_{HH} = 8$ Hz), 7.90 (d, 12H, *o*-ArH, $^3J_{HH} = 8$ Hz); $^{13}C$ NMR (101.6 MHz, $C_6D_6$, 300 K): $\delta$ 129.0 (*m*-Ar), 129.8 (*o*-Ar), 133.8 (*p*-Ar), 140.1 (*ipso*-Ar), 215.0 (CO); $^{31}P\{^1H\}$ NMR (121.7 MHz, $C_6D_6$) $\delta$ −99.8 (q, $P_A$, $^1J_{PP} = 398$ Hz), 23.3 (d, $P_X$, $^1J_{PP} = 398$ Hz); MS APCI: *m*/*z* (%) 754 ($M^+$, 100); IR (Nujol) $\nu$/cm$^{-1}$: 1695 (s), 1633 (s), 1455 (m).

‡ Crystal data for **3**: $C_{30}H_{54}As_3O_6P$, $M = 766.46$, hexagonal, space group $R3_c$, $a = b = 17.372(4)$, $c = 21.520(8)$ Å, $V = 5624(3)$ Å$^3$, $Z = 6$, $D_c = 1.358$ g cm$^{-3}$, $F(000) = 2376$, $\mu$(Mo-K$\alpha$) = 2.74 mm$^{-1}$, $T = 223(2)$ K, 1469 unique reflections [$R$(int) = 0.0473], $R$ (on $F$) = 0.0529, $wR$ (on $F^2$) = 0.1342 [$I > 2\sigma(I)$].

For **6**·$Et_2O$: $C_{46}H_{40}O_7P_4$, $M = 828.66$, triclinic, space group $P\bar{1}$, $a = 12.930(3)$, $b = 14.012(3)$, $c = 14.939(3)$ Å, $\alpha = 97.21(3)$, $\beta = 112.28(3)$, $\gamma = 116.39(3)°$, $V = 2097.8$ Å$^3$, $Z = 2$, $D_c = 1.312$ g cm$^{-3}$, $F(000) = 864$, $\mu$(Mo-K$\alpha$) = 0.23 mm$^{-1}$, $T = 150(2)$ K, 9595 unique reflections [$R$(int) = 0.0676], $R$ (on $F$) = 0.0416, $wR$ (on $F^2$) = 0.0877 [$I > 2\sigma(I)$]. CCDC reference numbers 184013 and 184014. See http://www.rsc.org/suppdata/dt/b2/b203709m/ for crystallographic data in CIF or other electronic format.

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