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Dilithio-1,1,2-tris(diphenylphosphinoyl)ethane-1,2-diide: the first formal 1,2-dicarbanion stabilised by phosphorus?†

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Received (in Cambridge, UK) 17th July 2002, Accepted 18th September 2002
First published as an Advance Article on the web 30th September 2002

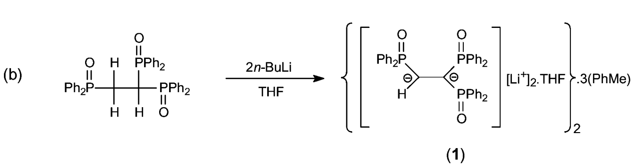
The tris(phosphine oxide) $\{Ph_2P(O)\}_2CHCH_2P(O)Ph_2$ readily undergoes double deprotonation to give the dimeric cluster $[(THF)Li(\{Ph_2P(O)\}_2CCH\{P(O)Ph_2\})Li]_2.3PhMe$ (1), after recrystallisation from toluene, the first example of a formal 1,2-dicarbanion stabilised by phosphorus.

Although the formation of 1,2-dicarbanions by the alkali metal mediated reduction of highly delocalised compounds such as acenaphthalene and 9,9′-bifluorene has been known for many years,[1] it is only in the last decade that significant progress has been made in the synthesis of non-conjugated 1,2-dicarbanions.[2] Several silicon-stabilised 1,2-dicarbanions have now been isolated and structurally characterised, each synthesised by the two-electron reduction of a silicon-substituted alkene by lithium (Scheme 1a).[3]

As part of an ongoing investigation into the chemistry of novel P-stabilised carbanions,[4] we have recently turned our attention to carbanions stabilised by an adjacent phosphoryl group. Phosphorus(V)-stabilised carbanions (Horner or Horner–Wadsworth–Emmons reagents) rank amongst the most versatile reagents available to the synthetic organic chemist, due in part to their ability to mediate the olefination of carbonyl compounds *via* a Wittig-type reaction.[5,6] Several lithium complexes of simple P(V)-stabilised carbanions have been structurally characterised;[7–9] however, since Horner reagents offer the opportunity for stereo-controlled carbonyl olefinations, a greater understanding of their structures is desirable.

We herein report the preparation of the first *formal 1,2-dicarbanion stabilised by phosphorus* and its structural characterisation.

The tris(phosphine oxide) $\{Ph_2P(O)\}_2CHCH_2P(O)Ph_2$[10] reacts with an excess of *n*-BuLi in THF to give the highly unusual cluster complex $[(THF)Li(\{Ph_2P(O)\}_2CCH\{P(O)Ph_2\})Li]_2.3PhMe$ (**1**), after recrystallisation from toluene (Scheme 1b).‡ As far as we are aware, **1** represents the first example of a formal 1,2-dicarbanion stabilised by phosphorus. We attribute the apparent readiness of the expected monocarbanion intermediate $[\{Ph_2P(O)\}_2CCH_2\{P(O)Ph_2\}]Li$ (**2**) to undergo a second deprotonation to the extensive delocalisation of charge from the initially formed carbanion centre by its two adjacent phosphoryl groups. Unfortunately, attempts to isolate the intermediate (**2**) have so far proved unsuccessful.



Scheme 1

X-ray crystallography reveals that **1** crystallises as a centrosymmetric dimer with three molecules of toluene solvent per dimer in the unit cell (Fig. 1).§ The dimer contains two distinct types of lithium atom: three-coordinate Li(1) is coordinated by two O atoms from opposite ends of one dianion ligand and one O atom from the other ligand, whilst four-coordinate Li(2) is coordinated by two O atoms from the second dianion, one from the first dianion and one molecule of THF. The four lithium atoms form a planar, parallelogram-shaped Li_4 core. The O(2) and O(3) atoms of the bis(phosphoryl)-substituted end of the dianion bridge the two different Li atoms, forming planar, parallel Li_2O_2 squares typical of α-metalated phosphonates, *etc.*;[7–9] the lithium atoms in these two squares are linked by the O(1) atoms from the mono(phosphoryl) ends of the dianions. There is no contact between the lithium atoms and the carbanion centres C(1) and C(2). In contrast, 1,2-dicarbanions which are solely substituted by SiR_3 groups typically adopt symmetrical *trans*-bridged structures in which the two lithium atoms lie either side of the C–C vector (see Scheme 1a).[2,3] In addition, **1** represents the first crystallographically characterised

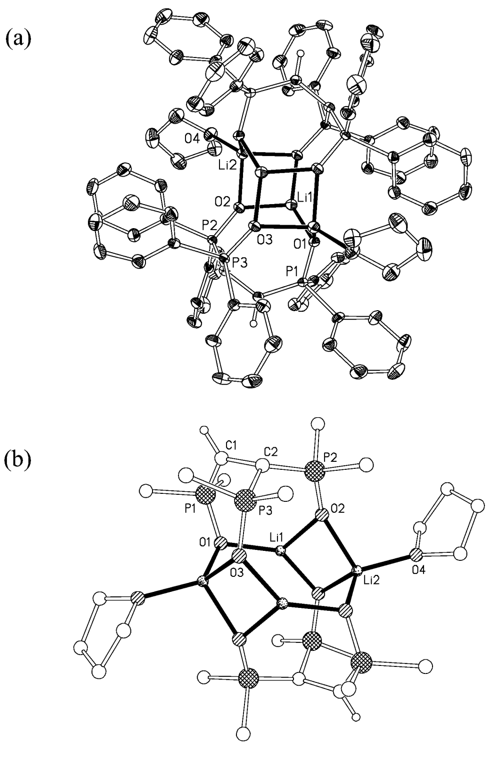


Fig. 1 (a) Molecular structure of **1** with 50% displacement ellipsoids. Toluene solvent, H atoms and parentheses in atom labels omitted for clarity. (b) Alternative view of the core of **1** without phenyl rings. Selected bond lengths (Å): C(1)–C(2) 1.509(4), C(1)–P(1) 1.686(3), C(2)–P(2) 1.720(3), C(2)–P(3) 1.722(3), P(1)–O(1) 1.545(2), P(2)–O(2) 1.539(2), P(3)–O(3) 1.538(2), Li(1)–O(1) 1.900(6), Li(1)–O(2) 1.879(6), Li(1)–O(3′) 1.893(6), Li(2)–O(1′) 1.964(6), Li(2)–O(2) 1.973(6), Li(2)–O(3′) 2.017(6), Li(2)–O(4) 1.933(6). Primes indicate symmetry-related atoms.

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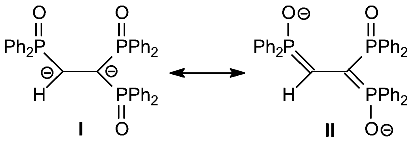
† Electronic supplementary information (ESI) available: atomic coordinates for **1** and calculated atomic coordinates for **3** along with calculated energies. See http://www.rsc.org/suppdata/cc/b2/b206963f/

DOI: 10.1039/b206963f

alkali metal complex of a bis(phosphoryl)-stabilised carbanion, *i.e.* $M[CR\{P(O)R'_2\}_2]$, although structural studies have recently been reported on alkali metal derivatives of bis(iminophosphoranes), $M[CH\{P(=NR)R_2\}_2]$.[11]

The two formal carbanion centres are close to orthogonal: the dihedral angle between the H(1)–C(1)–C(2) and P(2)–C(2)–P(3) planes is 82.4°. The C(1)–C(2) distance of 1.509(4) Å in **1** is the shortest such distance reported in a non-conjugated 1,2-dicarbanion; previously reported distances in Si-substituted dicarbanions lie in the range 1.534(9)–1.597(17) Å.[2,3] This short C–C distance may be a consequence of reduced repulsion between the formal carbanion centres due to more extensive delocalisation of charge to $P(O)R_2$ rather than to SiR_3 substituents. Calculations suggest that the carbanion stabilisation energies of $P(O)(OH)_2$ and SiH_3 are −46.4 and −23.7 kcal mol^{-1}, respectively,[12] so it is likely that a canonical form such as **II** makes a larger contribution to the electronic structure of the dianion in **1** than would a corresponding canonical form (containing Si=C) in an SiR_3 derivative. This view is also supported by the relatively long P–O bonds in **1**.



Preliminary *ab initio* calculations on the less sterically hindered model free dianion $[\{Me_2P(O)\}_2CCHP(O)Me_2]^{2-}$ (**3**) yield a global minimum for the equilibrium geometry in which the C_2P_3 skeletal core is remarkably similar to that observed in the solid state structure of **1** (Fig. 2a).¶ The calculated C(1)–C(2) distance in **3** is 1.515 Å (*cf.* 1.509(4) Å in **1**) and the C(1)–P and C(2)–P distances show a similarly close correspondence. The dihedral angle between the H(1)–C(1)–C(2) and P(2)–C(2)–P(3) planes of 88.61° in **3** compares well with that observed in the solid state for **1** (82.4°).

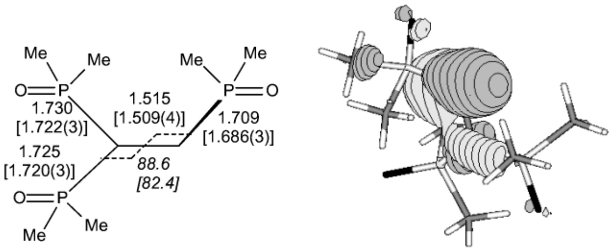


Fig. 2 (a) Calculated bond lengths (Å) and dihedral angle (°) for the model free dianion $[\{Me_2P(O)\}_2CCHP(O)Me_2]^{2-}$ (**3**) (Values for **1** in square brackets for comparison) . (b) Representation of the calculated HOMO of **3**.

The correspondence between the calculated geometry of **3** and the solid state structure of **1** suggests that the orthogonality of the two carbanion centers is not due to conformational preferences caused by formation of the dimeric cluster. Rather, this conformation minimises both steric buttressing between phosphoryl groups and overlap of the two adjacent carbanion lone pairs which the calculated HOMO for **3** shows to be *partially* delocalised towards the P atoms (Fig. 2b).

Compound **1** may be regarded as a ‘Siamese twin’ Horner reagent, in which the two formal carbanion centres are directly adjacent and, thus, offers intriguing prospects for the synthesis of novel organic compounds. The chemistry of **1** and its potential applications in the Horner–Wittig reaction are currently under investigation.

We thank the EPSRC and the Royal Society for support and Dr B. R. Horrocks for assistance with electronic structure calculations.

Notes and references

‡ **1** was prepared by the addition of *n*-BuLi (0.8 ml of a 2.5 M solution in hexanes, 2.00 mmol) to a solution of $\{Ph_2P(O)\}_2CHCH_2P(O)Ph_2$ (0.50 g, 0.792 mmol) in THF (10 ml). This mixture was stirred for 1 h and then solvent was removed under vacuum. The resulting red oil was recrystallised from cold (−5 °C) toluene as deep red prisms. Yield 0.32 g, 50%. Anal. Calcd. for $C_{84}H_{78}Li_4O_8P_6$ (molecular formula without PhMe of crystallisation): C, 70.60; H, 5.50. Found: C, 68.08; H, 5.34. ^{31}P NMR (22 °C, THF): δ = 33.7 (singlet $\nu_{1/2}$ 160 Hz, int. 2), 39.8 (singlet $\nu_{1/2}$ 50 Hz, int. 1). ^{31}P NMR (−81 °C, $C_6D_5CD_3$): numerous sharp signals in range 24–26 ppm showing splitting due to ^{31}P–^{31}P coupling (from ^{31}P COSY), but no splitting by ^7Li. ^7Li NMR (22 °C, THF): δ = 2.5 ($\nu_{1/2}$ 20 Hz, no splitting by ^{31}P). These data clearly show a dynamic equilibrium at room temperature and the presence of a number of oligomers at −81 °C.

§ *Crystal data* for $C_{84}H_{78}Li_4O_8P_6\cdot(C_7H_8)_3$ **1**: M = 1705.5, monoclinic, $P2_1/c$, a = 14.1978(6), b = 16.1487(7), c = 19.8548(8) Å, β = 97.956(2)°, U = 4508.4(3) Å^3, Z = 2, μ(Mo-Kα) = 0.177 mm^{-1}, T = 160 K. 35838 data, 10355 unique (R_{int} = 0.0402). w$R(F^2)$ = 0.1739 for all data, conventional R = 0.0780 for F values of 8725 reflections with $F_o^2 > 2\sigma(F_o^2)$. CCDC 177948. See http://www.rsc.org/suppdata/cc/b2/b206963f/ for crystallographic data in CIF or other electronic format.

¶ Equilibrium geometry optimisations were performed at the HF/6-31 + G* level using the PC Gamess suite of molecular modelling software (ref. 13). The HF/6-31 + G* level of theory is reported to be suitable for geometry optimisations on phosphoryl- and thiophosphoryl-stabilised carbanions, with little gain in accuracy when higher basis sets are employed (ref. 14).

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