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Variable coordination chemistry of the phospha(III)guanidinate anion; application as a metal-functionalised phosphine ligand†

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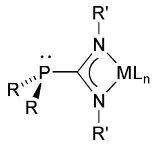
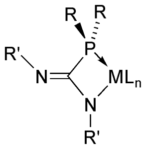
Structural investigation of Li-complexes of the phospha(III)-guanidinate anion $[Ph_2PC\{N^iPr\}_2]^-$ revealed variable coordination to lithium; synthesis of the dimethyl aluminium compound, $(Ph_2PC\{N^iPr\}_2)AlMe_2$, which behaves as a metal-functionalised phosphine ligand towards platinum, is reported.

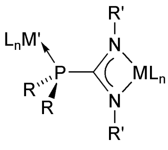
Tertiary phosphines, PR_3, have played a central role in the development of coordination chemistry and are currently employed as ancillary ligands in many catalytic transformations.[1] Amongst the properties that make them so appealing is the ease with which their steric and electronic properties can be systematically varied through introduction of different R-substituents at the phosphorus atom. With a view to developing a novel class of phosphine ligand, we have initiated a study of the ligating properties of phospha(III)guanidinate anions, $[R_2PC\{NR'\}_2]^-$. In contrast to their conventional nitrogen analogues where delocalisation across the central 'CN_3' core of the molecule is normally observed,[2] retention of the lone-pair at phosphorus is predicted, due to unfavourable overlap with the sp^2-hybridised carbon. Thus in addition to *N*,*N*′-bonding (type **I**),[3] participation of the *P*-centre in either an *N*,*P*- (type **II**),[4] or ambidentate (type **III**) coordination mode is possible. The latter situation may be regarded as a new type of metal-functionalised phosphine ligand, where in addition to derivitisation directly at the nitrogen and phosphorus atoms, the potential for facile modification of the steric and electronic properties may be further achieved through the incorporation of a broad range of '**M**L$_n$' fragments at the amidinate moiety.



I



II



III

Reaction of Ph_2PLi with $^iPrN{=}C{=}N^iPr$ in THF proceeded *via* insertion of the carbodiimide into the P–Li bond, to afford the lithium salt $[Ph_2PC\{N^iPr\}_2Li]$ (**1**). Combustion analysis of the bulk sample indicated formation of the *bis*-THF adduct **1**(THF)$_2$;‡ however, X-ray structural data of crystals that formed upon removal of solvent from the reaction mixture showed formation of the monosolvated, centrosymmetric dimer, [**1**(THF)]$_2$ (Fig. 1),§ in which the ligand adopts a μ-η^1,η^2-bridge between two lithium centres, unique in phosphaguanidinate chemistry.[5] The core of the molecule consists of three, 4-membered ring-systems in a folded 'ladder-type' arrangement (angle between CN_2Li and N_2Li_2 planes = 124.4°). Bond lengths are consistent with unequal delocalisation across the 'CN_2' moiety, where the longer C(1)–N(2) distance reflects a charge localisation at the nitrogen atom, as a consequence of incorporation in the Li_2N_2 ring.[5a] The C(1)–P distance [1.915(2) Å] and pyramidal geometry at the phosphorus [Σ_{angles} = 315.61°] are consistent with a single P–C bond and retention of the lone pair at phosphorus.

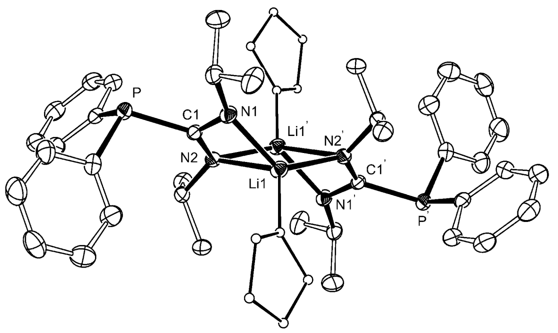


Fig. 1 Molecular structure of **1** (thermal ellipsoids 30%; ′: −x, −y + 1, −z). Selected bond lengths (Å) and angles (°): C(1)–N(1) 1.316(3); C(1)–N(2) 1.339(3); C(1)–P 1.915(2); N(1)–Li(1) 2.024(5); N(2)–Li(1) 2.175(5); N(2)–Li(1′) 2.078(5); N(1)–Li(1)–N(2) 65.28(15); Li(1)–N(2)–Li(1′) 70.30(19); N(1)–C(1)–N(2) 117.3(2).

Addition of TMEDA to a toluene solution of **1** afforded colourless crystals which analysed as $Ph_2PC\{N^iPr\}_2Li$(TMEDA) (**2**).‡ X-Ray diffraction data revealed that a major structural rearrangement had occurred in **2**, to afford the first structurally characterised example of a complex containing type **II** bonding (Fig. 2).§ The C–N bond distances indicate a considerably more localised bonding situation than for **1**, with the C(1)–N(2) distance [1.299(4) Å] close to the value found for C=N double bonds. As a consequence, the N(1)–Li bond [1.927(5) Å] is appreciably shorter than in **1**, and overall the CN_2PLi core of the molecule is essentially planar.[6] It is noteworthy that, although the mean P–Li bond distance in **2** [2.611 Å] is comparable to those reported in the closely related lithium phosphide complex $[Ph_2PLi(TMEDA)]_2$ (2.523–2.629 Å),[7] severe distortion from ideal tetrahedral geometry results at both the P- and Li-atoms [angles at Li: 66.54–140.3°; angles at P: 74.49–139.88°], suggesting that such an interaction is weak in compound **2**.

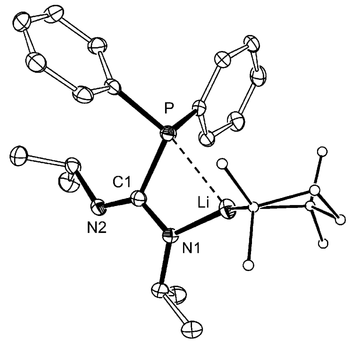


Fig. 2 Molecular structure of **2** (thermal ellipsoids 30%). Selected bond lengths (Å) and angles (°) for one of two independent molecules in the unit cell. C(1)–N(1) 1.354(4); C(1)–N(2) 1.299(4); C(1)–P 1.892(3); N(1)–Li 1.927(5); P–Li 2.625(5); N(1)–Li–P 66.54(16); Li–P–C(1) 74.49(14); N(1)–C(1)–N(2) 126.4(3).

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† Electronic supplementary information (ESI) available: simulated and observed NMR spectra. See http://www.rsc.org/suppdata/cc/b2/b209026k/

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Compounds **1** and **2** reacted with $AlMe_2Cl$ to generate the aluminium dimethyl compound, $(Ph_2PC\{N^iPr\}_2)AlMe_2$ (**3**).‡ X-Ray analysis, revealed a monomeric complex incorporating type **I** bonding of the phospha(III)guanidinate ligand (Fig. 3).§ The planar, four-membered metallacycle displays metrical parameters typical for conventional aluminium amidinate complexes,[8] with carbon–nitrogen bond distances commensurate with delocalised bonding across the 'CN_2' moiety. The carbon–phosphorus distance [1.869(2) Å] is significantly shorter than in **1**, which, in conjunction with a reduction in the Σ_{angles} at phosphorus [309.63°] suggests greater delocalisation of the P-lone pair into the ring system, a likely consequence of the greater electronegativity of Al *vs.* Li. In solution however, free rotation around the C–P bond is observed upon cooling to low temperature (198 K), indicated by equivalent ^iPr resonances (^1H NMR spectroscopy), suggesting that the P-lone pair may remain available for coordination to an additional metal fragment (type **III** bonding).

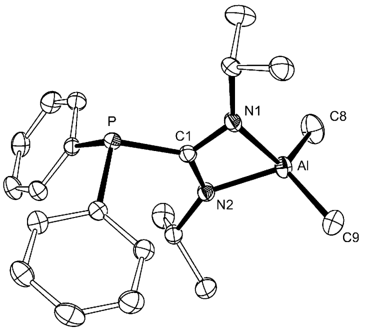
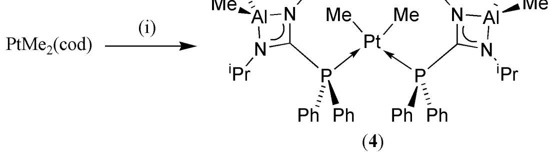


Fig. 3 Molecular structure of **3** (thermal ellipsoids 30%). Selected bond lengths (Å) and angles (°): C(1)–N(1) 1.337(3); C(1)–N(2) 1.336(3); C(1)–P 1.869(2); N(1)–Al 1.928(2); N(2)–Al 1.9270(19). N(1)–Al–N(2) 68.95(8); N(1)–C(1)–N(2) 109.43(19).

Accordingly, the NMR scale reaction between two equivalents of **3** and $PtMe_2(cod)$ indicated that quantitative displacement of the diene had occurred, resulting in formation of the mixed Pt/Al compound, $[(Ph_2PC\{N^iPr\}_2)AlMe_2]_2PtMe_2$ (**4**, Scheme 1). ^{31}P NMR spectroscopy was able to confirm coordination of **3** *via* the phosphorus atom ($^1J_{PtP} = 1780$ Hz) and the presence of two phosphine ligands was established by the presence of a triplet in the ^{195}Pt NMR spectrum. Despite the inability to observe a peak in the ^{27}Al NMR spectrum (presumably due to quadrapolar broadening), both the ^1H and ^{13}C NMR spectra exhibited characteristic high field peaks for the Al-*Me* groups (δ −0.15 and −8.7 respectively), clearly showing retention of the aluminium methyl moiety in the resultant complex. In addition, the EI^+ mass spectrum exhibited a signal corresponding to the molecular ion with loss of one methyl group. The overall geometry at platinum was established as *cis*-square planar through simulation of the platinum methyl (^1H and ^{13}C),¶ and the PCN_2 signals of the phospha(III)guanidinate ligand (^{13}C),¶ in the proton and carbon NMR spectra.[9]

In summary we have demonstrated the highly versatile coordination chemistry exhibited by the phospha(III)guanidinate anion $[Ph_2PC\{N^iPr\}_2]^-$ in lithium and aluminium complexes, including the first structurally characterised examples of μ-η^1,η^2-bridging (**1**) and *N,P*-chelating modes (**2**). Formation of the aluminium complex $(Ph_2PC\{N^iPr\}_2)AlMe_2$ (**3**) was achieved by salt metathesis, and it was demonstrated that the resultant complex retained sufficient electron density at the P-atom to coordinate to a '$PtMe_2$' fragment as a novel class of metal-functionalised phosphine ligand in $[Ph_2PC\{N^iPr\}_2AlMe_2]_2PtMe_2$ (**4**). NMR spectroscopic methods were used to establish a *cis*-square planar geometry at platinum in **4**.



(**4**)

Scheme 1 *Reagents and conditions*: (i) 2 equiv. **3**, C_6D_6.

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Notes and references

‡ Selected data for **1**$(THF)_2$: **Yield** 72%. **Anal.** Calc. for $C_{27}H_{40}N_2LiO_2P$: C, 70.11; H, 8.72; N, 6.06. Found C, 70.12; H, 8.69; N, 6.13%. Selected data for **2**: **Yield** 91%. **Anal.** Calc. for $C_{25}H_{40}N_4LiP$: C, 73.86; H, 9.92; N,6.89. Found C, 73.79; H, 9.79; N, 6.81%. Selected data for **3**: **Yield** 64%. **Anal.** Calc. for $C_{21}H_{30}N_2AlP$: C, 68.46; H, 8.21; N, 7.60. Found: C, 68.53; H, 8.27; N, 7.52%. **NMR** (C_6D_6, 298 K): ^1H (300 MHz), δ 7.46 (m., 4H, P*Ph$_2$*), 7.00 (m, 6H, P*Ph$_2$*), 3.81 (d sept, $^3J_{HH} = 6$ Hz, $^4J_{PH} = 4$ Hz, 2H, C*H*Me$_2$), 0.89 (d, $^3J_{HH} = 6$ Hz, 12H, CH*Me$_2$*), −0.16 (s, 6H, Al*Me$_2$*). ^{13}C (75.5 MHz), δ 172.7 (d, $^1J_{PC} = 51$ Hz, P*C*N$_2$), 132.7 (d, $J_{PC} = 50$ Hz, *C$_6$*H$_5$), 132.9 (d, $J_{PC} = 19$ Hz, *C$_6$*H$_5$), 129.2 (d, $J_{PC} = 7$ Hz, *C$_6$*H$_5$), 129.0 (s, *C$_6$*H$_5$), 46.7 (d, $^3J_{PC} = 13$ Hz, *C*HMe$_2$), 25.4 (CH*Me$_2$*), −9.1 (br, Al*Me$_2$*). ^{31}P (121.5 MHz) δ −19.8. Selected data for **4**: **NMR** (C_6D_6, 298 K): ^1H (300 MHz), δ 7.79 (m, 8H, P*Ph$_2$*), 6.79 (m, 12H, P*Ph$_2$*), 3.81 (sept, $J_{HH} = 5.9$, 4H, C*H*Me$_2$), 1.64 (m, $J_{PtH} = 69.9$, $J_{PH} = 6.0$, 6H, Pt*Me$_2$*), 0.80 (d, br, $J_{HH} = 5.2$, 24H, CH*Me$_2$*), −0.15 (s, 12H, Al*Me$_2$*). ^{13}C NMR (75.5 MHz), δ 167.6 (m, P*C*N$_2$), 136.0 (m, P*Ph$_2$*), 131.4 (P*Ph$_2$*), 130.8 (P*Ph$_2$*), 128.2 (P*Ph$_2$*), 45.9 (m, *C*HMe$_2$), 25.2 (CH*Me$_2$*), 8.6 (m, $J_{PtC} = 633$ Hz, $J_{PC} = 98$ Hz, $J_{PC} = 8$ Hz, Pt*Me*), −8.7 (s, br, Al*Me$_2$*). ^{31}P NMR (121.5 MHz), δ 27.8 ($J_{PtP} = 1780$ Hz). ^{195}Pt NMR (107 MHz) δ −4881 ($J_{PtP} = 1780$ Hz). Mass spec. (EI^+, *m/z*): 946 $[M-Me]^+$, 930 $[M-Me_2]^+$, 874 $[M-AlMe_4]^+$.

§ *Crystal data*: for $C_{46}H_{64}Li_2N_4O_2P_2$ ([**1**$(THF)]_2$): $M = 780.83$, monoclinic, $P2_1/n$ (no. 14), $a = 9.9739(7)$, $b = 19.6236(13)$, $c = 11.6860(8)$ Å, $\beta = 94.531(3)°$, $V = 2280.1(3)$ Å^3, $T = 173(2)$ K, $Z = 2$, μ(Mo-Kα) = 0.14 mm^{-1}, independent reflections = 3937 ($R_{int} = 0.088$), $R1$ [for 3047 reflections with $I > 2\sigma(I)$] = 0.063, $wR2$ (all data) = 0.177. *Crystal data*: for $C_{25}H_{40}LiN_4P$ (**2**): $M = 434.52$, triclinic, $P1$ (no. 2), $a = 9.5099(2)$, $b = 11.9348(2)$, $c = 28.6122(6)$ Å, $\alpha = 98.125(1)$, $\beta = 75.908(1)$, $\gamma = 122.665(3)°$, $V = 2651.37(9)$ Å^3, $T = 173(2)$ K, $Z = 4$, μ(Mo-Kα) = 0.12 mm^{-1}, independent reflections = 7271 ($R_{int} = 0.065$), $R1$ [for 5713 reflections with $I > 2\sigma(I)$] = 0.058, $wR2$ (all data) = 0.156. *Crystal data* for $C_{21}H_{30}AlN_2P$ (**3**): $M = 368.42$, monoclinic, $P2_1/n$ (no. 14), $a = 16.0218(9)$, $b = 8.3303(6)$, $c = 17.6419(9)$ Å, $\beta = 107.443(4)°$, $V = 2246.3(2)$ Å^3, $T = 173(2)$ K, $Z = 4$, μ(Mo-Kα) = 0.17 mm^{-1}, independent reflections = 3095 ($R_{int} = 0.041$), $R1$ [for 2623 reflections with $I > 2\sigma(I)$] = 0.041, $wR2$ (all data) = 0.101. CCDC reference numbers 182193, 182194 and 193950. See http://www.rsc.org/suppdata/cc/b2/b209026k/ for crystallographic data in CIF or other electronic format.

¶ *Coupling constants (Hz) for simulated NMR data*: PtC*H$_3$* ($A_3A'_3$ part of an $A_3A'_3XX'$ spin system) $J_{XY} = \pm 7$; $J_{AX} = J_{A'X'} = -8.7$; $J_{AX'} = J_{A'X} = +13.2$; $J_{AA'} = 1.4$. Pt*C*H$_3$ (A part of AXX′ spin system) $J_{XY} = \pm 7$; $J_{AX} = 96.4$; $J_{AX'} = 7.4$. P*C*N$_2$ (A part of AXY spin system) $\Delta\delta_{XY} = 0.08$ ppm; $J_{XY} = \pm 7$; $J_{AX} = 14.9$; $J_{AY} = 3.0$.

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