The effect of *P*-cyclohexyl groups on the coordination chemistry of phosphaguanidinates

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The anion of *P*-dicyclohexylphosphaguanidine, Cy_2PC- {NⁱPr}{NHⁱPr}, forms a *P*,*N*-chelate at lithium and cobalt(II); bridging through the N_{imine} atom forms cyclic hexamers in the former complex.

Chelating ligands which combine disparate donor-groups are attractive in catalytic chemistry as they offer a degree of selectivity due to the inherent differences in metal–ligand bonding parameters. Amongst the most widely applied combination of atoms is that based around the κ^1 -*P*,*N*-donor set,¹ with a major feature of interest being the potential for hemilability within the system.² Many areas of applied chemistry have been explored, focussing mainly on the late transition elements with, for example, recent reports on systems active for alkene hydrocarboxylation,³ asymmetric C–C bond forming reactions⁴ and copolymerization of olefins and carbon monoxide.⁵

Previous work has shown that the Li-salt of N,N'-diisopropyl-*P*diphenylphospha(III)guanidine crystallizes from THF as the dimer [Li(Ph₂PC{NⁱPr}₂)(THF)]₂ (**I**), which deaggregates to afford the monomeric species Li(Ph₂PC{NⁱPr}₂)(TMEDA) (**II**) on reaction with the appropriate base (Fig. 1).⁶ In **I**, the ligand adopts a $\kappa^{1,2}$ -N- κ^{1} -N'-bonding mode to generate a central 'Li₂N₂' core. In contrast, within compound **II** the ligand adopts a κ^{1} -N,*P*-chelating mode, with the resultant monomeric compound containing an uncomplexed imine group.



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We have recently extended the family of phospha(III)guanidines to include the *P*-dicyclohexyl derivatives, $Cy_2PC\{NR'\}\{NHR'\}$ $(R' = Cy, {}^{i}Pr).^{7}$ Deprotonation of the neutral compound was achieved with "BuLi in THF and the product of the reaction was crystallised from toluene at -30 °C, to afford colourless crystals (1). Full characterisation by NMR spectroscopy was not possible due to difficulty in redissolving the isolated crystals. However, the

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compound was sparingly soluble in C_6D_6 enabling limited NMR data to be obtained, which confirmed the presence of lithium (⁷Li NMR: broad singlet at δ 1.87), and indicated the absence of THF. In agreement with these data, elemental analysis was consistent with the base-free formula, $[Li(Cy_2PC\{N^iPr\}_2)]_n$.†

Single crystal X-ray diffraction of 1[‡] revealed two distinct molecules within the unit cell which differ slightly in their bond lengths and angles. Each molecule is comprised of the cyclic hexamer, $[Li(Cy_2PC{N^iPr}_2)]_6$ (Fig. 2); four disordered molecules of toluene are also present in the unit cell. Both hexameric molecules consists of three unique forms of the basic "Li(Cy₂PC{NⁱPr}₂)" component (referred to as A, B and C) with the remaining three units being symmetry generated equivalents. In each case the lithium is P,N-bound by the ligand, as noted in II,⁶ and the spectroscopically characterized rhodium compound, $Rh(\kappa^1-N, P-Ph_2PC{NAr}_2)(PPh_3)_2$.⁸ However, in contrast to these monomeric compounds, the imine group of 1 is bonded to the lithium atom of an adjacent unit in a unique $\kappa^1 - N, P - \kappa^2 - N'$ bridging mode, with N_{imine} -Li distances in the range 1.974(12)-1.987(12) Å. Examination of the bond lengths of each unit (Fig. 3) show that these values are largely indistinguishable from the $N_{\rm amine}$ -Li bond within the metallacycle, suggesting that the hexameric core is tightly bound into a cohesive entity. The remaining bond lengths associated with each unit are comparable to those of the TMEDA adduct, despite the distorted trigonal planar metal centres in 1 $[\sum_{\text{angles}} \text{ at Li: } A, 352.8^\circ; B, 359.1^\circ; C, 356.8^\circ]$ compared to the four-coordinate lithium in compound II.



Fig. 2 ORTEP representation of one of the independent molecules of $[Cy_2PC{N^iPr}_2Li]_6$ in compound 1 (' = -x, -y, -z; " = -x + 1, -y + 1, -z + 1; ellipsoids at the 30% probability level; hydrogen atoms omitted).



Fig. 3 Selected bond lengths (Å) within the three 'Li(Cy₂PC- $\{N^iPr\}_2$)' units of 1, together with corresponding values from compound II.

The 'N=CNPLi' atoms of each unit form an approximate plane (max. deviation: A, 0.02 Å; B, 0.20 Å; C, 0.11 Å) with a small bite angle for the ligand in each case [P–Li–N: A, 66.5(4)°; B, 64.5(4)°, C, 66.3(3)°]. These metallacycles form a 'puckered' system throughout the hexamer, with the phosphine moieties arranged alternatively above and below the plane defined by the six lithium atoms (Fig. 4); the interplanar angles are +26.9°, -60.5° and +48.7° for units A, B and C, respectively, where positive and negative values indicate the phosphine moiety positioned above and below the Li₆-plane. The angle at which the N_{imine} atom from each unit bonds to the lithium, as measured by the N– Li–N angle, varies considerably from 151.2(7)° [N(4)–Li(1)–N(5)] to 139.2(7)° [N(1)–Li(2)–N(3)]. Both of these features contribute towards generating the curvature necessary to form the observed cyclic structure.



Fig. 4 Hexameric core of one of the independent molecules of 1. Cyclohexyl and isopropyl substituents, except the α -carbons, omitted.

Generation of 1 in the presence of TMEDA in an attempt to isolate the *P*-dicyclohexyl analogue of compound II failed, with the hexamer once again crystallizing preferentially from the reaction solution. This indicates a strong preference for the oligomerisation within 1, in contrast to the *P*diphenylphospha(III)guanidines previously reported. We believe that through changing the phosphorus substituents from phenyl to the relatively electron rich cyclohexyl substituent, the electron density within the PCN₂-core becomes substantially greater, increasing the likelihood that the N_{imine} will become involved in bonding.

The targeted application of the lithium phosphaguanidinate described is as a ligand transfer reagent. The reactivity of 1 (typically generated in situ to facilitate homogeneous reaction conditions) with metal halide salts has therefore been studied, concentrating on the mid- to late-transition elements where it is felt likely that the phosphine group is more likely to participate in the bonding. Accordingly, reaction of two equiv. of the Lisalt with CoCl₂ and subsequent work-up afforded the homoleptic compound $Co(Cy_2PC{N^iPr}_2)_2$ (2) as forest green crystals.[†] The solution magnetic moment (Evan's method⁹) was determined in C₆D₆ (298–333 K), affording data consistent with a single unpaired electron ($\mu_{eff} = 1.85 \,\mu_{B}$), indicative of a square planar metal centre. It is known that homoleptic amidinate complexes of cobalt(II) adopt N, N'-bonding with a highly distorted tetrahedral geometry in the solid-state,¹⁰ with bond angles in the range $\sim 66^{\circ}$ (amidinate bite angle) to 137°; where reported, the magnetic moments of these compounds are consistent with three unpaired electrons, corresponding to the retention of a tetrahedral geometry in solution.

X-Ray diffraction analysis of **2**[‡] was in agreement with the solution-state data, revealing a *trans*-square planar cobalt(II) complex with a κ^1 -*N*,*P*-chelating mode (Fig. 5). This geometry closely matches that of the recently reported homoleptic cobalt(II) bis(diphenylphosphino)anilide, Co(Ph₂PC₆H₄NH)₂,¹¹ with the expected reduction in bite angle in **2** [72.65(4)°] resulting from the smaller, four-membered metallacycle. The carbon–nitrogen distances within **2** are more localized than in **1** (Δ_{CN} values¹²: **1** unit A = 0.020; **1** unit B = 0.030; **1** unit C = 0.027; **2** = 0.094 Å) and as a result of increased electron density at the amido nitrogen the Co–N distance [1.8729(14) Å] is notably shorter than in the homoleptic amidinate complexes [av. 2.00 Å]. However, no intermolecular close contacts were noted in this case. Further studies of the coordination chemistry of the *P*-dicyclohexylphosphaguanidinate



Fig. 5 ORTEP representation of 2(' = -x + 1, -y + 1, -z + 1; ellipsoids at the 30% probability level; hydrogen atoms omitted). Selected bond lengths (Å) and angels (°): Co–N(1) 1.8729(14), Co–P 2.2181(4), C(13)–N(1) 1.375(2), C(13)–N(2) 1.281(2), C(13)–P 1.8619(17); N(1)–Co–P 72.65(4), N(1)–Co–P' 107.35(4), N(1)–Co–(N1') 180.0, P–Co–P' 180.0.

are ongoing in the research group and will be reported in due course.

Notes and references

† Selected data for 1: Crystallized yield 67%. Anal. calc. for $C_{19}H_{36}N_2LiP$: C, 69.07; H, 10.98; N, 8.48%. Found: C, 69.00; H, 11.00; N, 8.32%. Selected data for 2: Crystallized yield 53%. Anal. calc. for $C_{38}H_{72}N_4CoP_2$: C, 64.66; H, 10.28; N, 7.94%. Found: C, 64.75; H, 10.32; N, 7.48%. Solution magnetic moment (C₆D₆, 273–333 K): $\mu_{eff} = 1.85 \mu_B$.

‡ Selected crystallographic data for 1: C₁₁₄H₂₁₆Li₆N₁₂P₆·4(C₇H₈), M = 2350.98, T = 173(2) K, triclinic, space group P1 (No.2), a = 14.9993(4), b = 15.3885(3), c = 32.7501(7) Å, a = 89.639(1), $\beta = 85.970(1)$, $\gamma = 87.721(1)^{\circ}$, U = 7534.6(3) Å³, Z = 2, $D_c = 1.04$ Mg m⁻³, μ (Mo-Ka) = 0.12 mm⁻¹, independent reflections = 20864 ($R_{int} = 0.112$), R1 [for 10921 reflections with $I > 2\sigma(I)$] = 0.106, wR2 (all data) = 0.290 (NOTE very weak limited diffraction. Carbon atoms for the toluene solvates were left isotropic and for the two disordered solvate molecules the H-atoms were omitted). Selected crystallographic data for 2: C₃₈H₇₂CON₄P₂, M = 705.87, T = 173(2) K, monoclinic, space group $P_2 I/c$ (No.14), a = 11.9830(3), b = 10.8349(3), c = 16.3276(4) Å, $\beta = 108.076(2)^{\circ}$, U = 2015.26(9) Å³, Z = 2, $D_c = 1.16$ Mg m⁻³, μ (Mo-Ka) = 0.54 mm⁻¹, independent reflections = 3944 ($R_{int} = 0.056$), R1 [for 3215 reflections with $I > 2\sigma(I)$] = 0.033, wR2 (all data) = 0.080. CCDC reference numbers 296234 and 296235.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b601235c

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