Synthesis and structure of [{$(Me_3Si)_2N$}$_2$Cd{$(PhN)_3C$}$Li_2\cdot 3thf$]; an unusual heterobimetallic co-complex containing three different metal coordination environments

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Dilithio-1,2,3-triphenylguanidide, [{$(PhN)_3C$}Li_2], reacts with [Cd{$N(SiMe_3)_2$}] to give [{$(Me_3Si)_2N$}$_2$Cd{$(PhN)_3$}$Li_2\cdot 3thf$] 1; a novel co-complex containing three different metal coordination environments.

We are currently undertaking a study of the ligand properties of guanidine and N-substituted guanidines. Our interest in this area initially stemmed from the fact that guanidide dianions, $[C(NR)_3]^{2-}$, are isoelectronic with the trimethylenemethane dianion, $[C(CH_2)_3]^{2-}$, which is known to coordinate to a wide range of transition metals in an η^4-mode.[1] We have previously shown that 1,2,3-triphenylguanidine, [PhN=C$(NHPh)_2$], may be dilithiated to provide $Li_2[C(NPh)_3]$ as a thf solvated dimer,[2] containing the nitrogen analogue of the tribenzylidenemethane dianion, $[C(CHPh)_3]^{2-}$.[3] In addition we have synthesised rhodium and ruthenium complexes containing the chelating monoanion of 1,2,3-triphenylguanidine, $[(PhNH)C(NPh)_2]^-$,[4] and the quadruply bonded Mo dimer [Mo_2{η^2-$(NPh)_2CNHPh$}$_4$] containing the same ligand in a bridging mode of coordination.[5] We have recently employed the nucleophilic substitution reactions of metal trimethylsilylamides of group 12 (Zn–Hg) and 13 (Al–Tl) as a novel, halide-free method of synthesis of homoleptic metallo-organic complexes.[6] This method successfully eliminates the problem of preferential crystallisation of the alkali-metal halide by-products present in the nucleophilic substitution reactions of group 12 or 13 metal halides[6a] and avoids the incorporation of halide ions into the product complexes. Thus, the homoleptic cadmium phosphide complex $2[Li(thf)_4]^+[Cd_4(PPh_2)_{10}]^{2-}$, containing an adamantoid dianion, is the product of the reaction of [Cd{$N(SiMe_3)_2$}$_2$] with [$LiPPh_2$]; a complex which can not be prepared by conventional synthetic approaches.[6c] We now report that the reaction of [Cd{$N(SiMe_3)_2$}$_2$] with the dianion $[C(NPh)_3]^{2-}$ results in the novel co-complex [{$(Me_3Si)_2N$}$_2$Cd{$(PhN)_3C$}$Li_2\cdot 3thf$] **1** which contains three different metal coordination environments.

The reaction of dilithio-1,2,3-triphenylguanidide, [{$(PhN)_3C$}Li_2], with [Cd{$N(SiMe_3)_2$}$_2$] (1 : 1 molar ratio) in thf produces a yellow solution from which colourless crystals of [{$(Me_3Si)_2N$}$_2$Cd{$(PhN)_3C$}$Li_2\cdot 3thf$] **1** are isolated [eqn. (1)].[†]

$$\begin{array}{c}[Cd\{N(SiMe_3)_2\}_2] + [Li_2\{C(NPh)_3\}] \\ \Big\downarrow \text{thf} \\ [\{(Me_3Si)_2N\}_2Cd\{(PhN)_3C\}Li_2\bullet 3thf] \quad (1)\end{array}$$

A low-temperature X-ray crystallographic study of **1** shows that the product is a co-complex of the two components of the reaction rather than a product of nucleophilic subsitution of the $N(SiMe_3)_2$ groups of [Cd{$N(SiMe_3)_2$}$_2$] by [{$(PhN)_3C$}Li_2] (Fig. 1).[‡] In addition, there is half a disordered toluene molecule for each formula unit of **1** in the lattice.

The distorted trigonal-planar Cd centre of **1** (av. N–Cd–N 119.6°) is attached asymmetrically to two $N(SiMe_3)_2$ groups [Cd(1)–N(1) 2.216(4), Cd(1)–N(2) 2.138(4) Å] and to one N atom of the guanidine ligand [Cd(1)–N(11) 2.213(4) Å]. As a result of the bonding of this N centre to the Cd atom, the associated C$\overset{...}{-}$N bond within the [{$(PhN)_3C$}] moiety [C(10)–N(11) 1.376(7) Å] is longer than the remaining C$\overset{...}{-}$N bonds (av. 1.354 Å). The three phenyl groups of the [{$PhN)_3C$}]$^{2-}$ dianion assume a *trans*, *trans*, *cis* conformation about the central carbon atom. This arrangement leaves the lone pairs on N(12) and N(13) free to interact with the two Li^+ cations, Li(1) and Li(2) [N(12)–Li(1) 1.97(1), N(13)–Li(2) 1.98(1) Å]. The coordination sphere of Li(1) is completed by Lewis base solvation by two thf ligands and by Li···C interactions with the *ipso*- and *ortho*-carbon atoms of the Ph ring attached to N(11) [2.73(1),

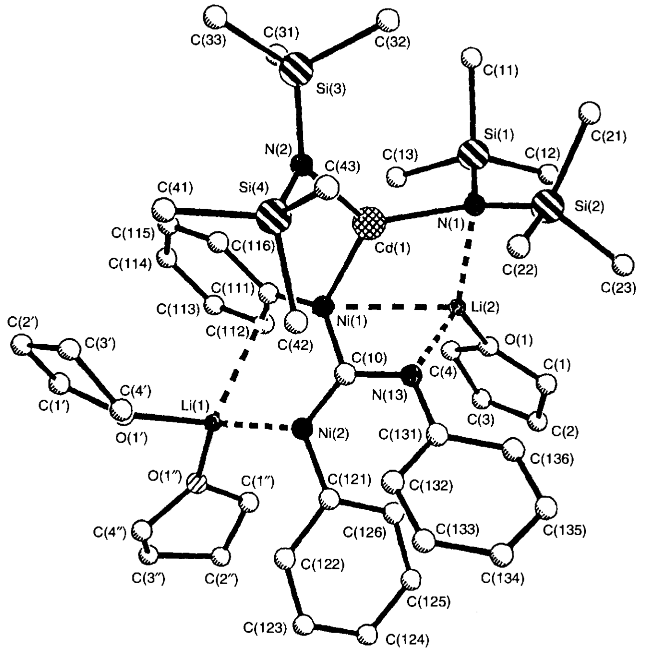

Fig. 1 Molecular structure of **1**. Hydrogen atoms and the lattice-bound disordered toluene have been omitted for clarity. Key bond lengths (Å) and angles (°): Cd(1)–N(1) 2.216(4), Cd(1)–N(2) 2.138(4), Cd(1)–N(11) 2.213(4), av. Si–N 1.71, C(10)–N(11) 1.376(7), C(10)–N(12) 1.350(7), C(10)–N(13) 1.358(7), Li(1)–N(12) 1.97(1), Li(1)···C(111) 2.73(1), Li(1)···C(112) 2.47(1), *av.* Li(1)–O 1.91, Li(2)–N(13) 1.98(1), Li(2)–N(11) 2.58(1), Li(2)–N(1) 2.08(1), Li(2)–O(1) 1.93(1); N(1)–Cd(1)–N(2) 134.9(2), N(2)–Cd(1)–N(11) 121.1(2), N(1)–Cd(1)–N(11) 102.9(2), Si(1)–N(1)–Si(2) 122.9(3), Si(3)–N(2)–Si(4) 128.4(3), C(10)–N(11)–Cd(1) 112.9(3), N(11)–C(10)–N(12) 118.5(5), N(11)–C(10)–N(13) 111.8(4), N(12)–C(10)–N(13) 129.7(5).

2.47(1) Å, respectively]. These interactions are similar to those which have been observed in a variety of organometallic and metallo-organic Li complexes.[7] A highly irregular pseudo-tetrahedral geometry occurs for Li(2). In addition to being bonded to the guanidide N(13) atom, this Li^+ cation is coordinated by one of the $N(SiMe_3)_2$ groups of the $[Cd\{(SiMe_3)_2\}_2]$ moiety [Li(2)–N(1) 2.08(1)], by the O atom of a thf ligand and by a long-range interaction with the Cd-attached guanidide N centre [Li(2)–N(11) 2.58(1) Å].

It is interesting to note that complex **1** is formed by nucleophilic addition to a main group metal trimethylsilamide, and not substitution as has been observed previously for group 12 and 13 trimethylsilamides.[6] That the observed adduct **1** is stable with respect to elimination of $[LiN(SiMe_3)_2]$, and consequent formation of the substitution product, may be associated with the extensive resonance stabilisation of the guanidide system. Further studies of the reactions of the cadmium reagent with substituted guanidines would be of interest as the complexes formed would have potential as ligand-transfer reagents.

We gratefully acknowledge the EPSRC for studentships (L. A. M., M.-A. R., K. L. V.), The Royal Society (P. J. B., D. S. W.), The Leverhulme (Trust P. J. B.), The Nuffield Foundation (P. J. B., D. S. W.), The Associated Octel Co. Ltd., Ellesmere Port, UK (K. L. V), and the Cambridge Crystallographic Data Centre (M.-A. R.) for financial support.

Footnotes

† All the compounds described are air- and moisture-sensitive. They were prepared and handled under an inert argon atmosphere. $LiBu^n$ (3.13 cm^3, 1.6 mol dm^{-3} in hexanes, 5.0 mmol) was added to a solution of $[PhN{=}C(NHPh)_2]$ (.072 g, 2.5 mmol) in thf (10 cm^3), $[Cd\{N(SiMe_3)_2\}_2]$ (1.0 cm^3, 2.5 mmol) and toluene (5 cm^3) were added and a yellow solution was produced. The solution was stirred at room temp. (5 min) and the volume reduced *in vacuo* to 10 cm^3. Subsequent storage of the yellow solution (20 °C, 12 h) yielded air-sensitive colourless crystals of **1** (1.0 g, 40% first batch). The complex crystallises with one toluene molecule per unit cell (*i.e.* half per formula unit); mp 135 °C; ^1H NMR (+25 °C, 250 MHz, 0.2 mol dm^{-3}, $[^2H_8]$thf) δ 7.19–6.95 (overlapping m, 17.5 H, $[(PhN)_3C]^{2-}$ and $C_6\mathit{H}_5Me$), 3.60 (m, 12 H, thf), 2.28 (m, 1.5 H, $C_6H_5\mathit{Me}$), 1.75 (m, 12 H, thf), 0.03 (36 H, $SiMe_3$); ^{13}C NMR (+25 °C, 62.85 MHz, 0.2 mol dm^{-3}, $[^2H_8]$thf) δ 169.0 $[(PhN)_3\mathit{C}]$, 155.6–115.7 $[(\mathit{Ph}N)_3C, \mathit{C}_6H_5]$, 67.8 (thf), 21.5 ($C_6H_5\mathit{Me}$), 7.0 ($SiMe_3$). Satisfactory elemental analyses (C, H, N) were obtained.

‡ *Crystal data for* **1**: $C_{47}H_{77}CdLi_2N_5O_2Si_4$, M_w = 982.78, triclinic, space group $P\bar{1}$ (no. 2), a = 11.3112(2), b = 12.075(2), c = 22.033(4) Å, α = 97.67(3), β = 103.22(3), γ = 106.88(3) °, U = 2738.0(8) $Å^3$, Z = 2, λ = 0.71073 Å, D_c = 1.192 Mg m^{-3}, μ(Mo-Kα) = 0.524 mm^{-1}. Data were collected on a Siemens-Stoe AED diffractometer using an oil-coated crystal[9] of dimensions 0.32 × 0.25 × 0.24 mm using the θ–ω method (6.04 $< 2\theta <$ 45.12°). Of a total of 8030 reflections collected 7139 were independent. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of $R1$ = 0.054 (for 7132 data with $F > 4\sigma F$) and $wR2$ = 0.146 (all data) $[R1 = \Sigma|F_o - F_c|/\Sigma|F_o|$, $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma wF_o^4\}^{0.5}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2/3)]$.[10] Largest peak, hole in the final difference map = 1.611, 0.755 e $Å^{-3}$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/92.

References

1 M. D. Jones and R. D. W. Kemmit, *Adv. Organomet. Chem.*, 1987, **27**, 279 and references therein.

2 P. J. Bailey, A. J. Blake, M. J. Kryszczuk, S. Parsons and D. Reed, *J. Chem. Soc. Chem. Commun.*, 1995, 1647.

3 D. Wilhelm, T. Clark, P. von R. Schleyer, K. Buckl and G. Boche, *Chem. Ber.*, 1983, **116**, 1669.

4 P. J. Bailey, L. A. Mitchell and S. Parson, *J. Chem. Soc., Dalton Trans.*, submitted (comm. 6/02963I/DCC).

5 P. J. Bailey, S. F. Bone, L. A. Mitchell, S. Parsons, K. J. Taylor and L. J. Yellowlees, *J. Chem. Soc., Dalton Trans.*, in the press (paper 6/00586A/DAP).

6 (*a*) D. Barr, A. J. Edwards, P. R. Raithby, M.-A. Rennie, K. Verhorevoort and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1994, 1627; (*b*) A. J. Edwards, A. Fallaize, P. R. Raithby, M-A. Rennie, A. Steiner, K. L. Verhorevoort and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, 1996, 133; (*c*) M. A. Beswick, P. R. Raithby, A. Steiner, K. L. Verhorevoort, G. N. Ward and D. S. Wright, *Angew. Chem.*, 1995, **107**, 2891; *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2662.

7 W. Setzer and P. von R. Schleyer, *Adv. Organomet. Chem.*, 1985, **24**, 353; K. Gregory, P. von R. Schleyer and R. Snaith, *Adv. Inorg. Chem.*, 1991, **37**, 47; R. E. Mulvey, *Chem. Rev.*, 1991, **20**, 167; M. A. Beswick and D. S. Wright, Alkali metals, in *Comprehensive Organometallic Chemistry II*, vol. 1, ch. 1, Pergamon, Oxford, 1995.

8 A similar step-wise process is implicated in the nucleophilic substitution reactions of $[(C_5H_5)_2Sn]$: M. A. Paver, C. A. Russell, D. Stalke and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1993, 1349.

9 D. Stalke and T. Kottke, *J. Appl. Crystallogr.*, 1993, **26**, 615.

10 SHELXL-93, G. M. Sheldrick, a package for crystal structure refinement, Göttingen, 1993.

Received, 8th March 1996; Com. 6/01646D