A New Halide-free Route to Metallo-organic Cadmium Complexes; Syntheses and Structural Characterisations of $[Cd(PhC{\equiv}C)_2(tmeda)]$ and $[Cd(C_{12}H_8N)_4]^{2-}\cdot 2Li(thf)_4^+$ (tmeda = $Me_2NCH_2CH_2NMe_2$)

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The syntheses of the monomeric diorganocadmium complex $[Cd(PhC{\equiv}C)_2(tmeda)]$ **1**, the first structurally characterised Cd-acetylide, and of the ion-separated $[Cd(C_{12}H_8N)_4]^{2-}\cdot 2Li(thf)_4^+$ **2**, containing a metallo-organic Cd dianion, from the nucleophilic substitution reactions of $Cd(NSiMe_3)_2$ with $PhC{\equiv}CLi$ (1 : 1 or 1 : 2 equiv.) and with $C_{12}H_{18}NLi$ (1 : 1–4 equiv.) respectively, exemplify a new, halide-free and general route to metallo-organic complexes.

We have recently been interested in the use of nucleophilic addition and substitution of heavy p block metal cyclopentadienyl ($C_5H_5^-$) derivatives of groups 13 (E = Tl) and 14 (E = Sn, Pb) in the syntheses of a variety of organometallic complexes.[1,2] The metal centres within these species accept weak nucleophiles such as Cp^- and produce a range of complexes containing anionic organometallic fragments.[1] However, more potent nucleophiles such as imino anions and organometallics will substitute the C_5H_5 ligands of $(C_5H_5)_2E$ (E = Sn or Pb).[2]

More recently, we have become interested in group 12 organometallics (Zn, Cd, Hg).[3] Although cadmium organometallics have long been used in organic synthesis, most commonly in preparation of ketones by reaction with acid chlorides,[4] relatively little is known about their chemistry and there is a paucity of structural information. In general, organocadmium compounds can be prepared from Grignard reagents or organolithium compounds by reaction of cadmium(II) salts.[5] In the latter case, cadmium halides are most commonly used. However, we have found that this can lead to preferential crystallisation of an alkali metal halide, produced as the driving force byproduct, as opposed to the desired cadmium organometallic. We report the synthetic utility of the nucleophilic substitution reaction of $Cd[N(SiMe_3)_2]_2$[6] with organolithium compounds, and the full characterisation of $[Cd(PhC{\equiv}C)_2(tmeda)]$ **1** (tmeda = $Me_2NCH_2CH_2NMe_2$) and $2[Li(thf)_4]^+[Cd(C_{12}H_8N)_4]^{2-}$ **2** [$C_{12}H_8NH$ = carbazole]. Complex **1** is the first structurally characterised cadmium acetylide and **2** contains a metallo-organic cadmium dianion. The syntheses of **1** and **2** from the nucleophilic substitution reaction of $Cd[N(SiMe_3)_2]_2$ with $PhC{\equiv}CLi$ and $C_{12}H_8NLi$ respectively, exemplify a new halide-free and general route to metallo-organic complexes.

The reaction of $PhC{\equiv}CLi$ with $Cd[N(SiMe_3)_2]_2$ and tmeda (1 : 1 : 1 or 2 : 1 : 1) in toluene produces a yellow solution from which colourless crystals of **1** are isolated in good yield. The reaction of $C_{12}H_8NLi$ with $Cd[N(SiMe_3)_2]_2$ (1–4 : 1) in a toluene–thf solvent produces an orange solution from which colourless crystals of **2** are isolated in good yield.†

Low-temperature X-ray crystallographic studies were undertaken on **1** and **2**.‡ Complex **1** is shown to be a monomeric complex with four-coordinate cadmium, $[Cd(PhC{\equiv}C)_2(tmeda)]$ **1** (Fig. 1). The Cd centre is attached to two phenylacetylide groups [av. C≡C 1.209, av. Cd–C 2.140 Å; *cf.* Cd–C 2.194 Å in $Me_2Cd(tmeda)$][13] and rather asymmetrically to the two nitrogens of the bidentate tmeda ligand [Cd–N(1) 2.397(4), Cd–N(2) 2.510(4) Å; *cf.* 2.566(14) and 2.576(14) Å in $Me_2Cd(tmeda)$].[7] The resulting geometry around the Cd centre is distorted tetrahedral, with the most significant distortion occuring in the attachment of the two phenylacetylide ligands to Cd [C(8)–Cd–C(9) 142.8(2)°; *cf.* 165.6° in $(PhC{\equiv}C)_2Hg(phen)$ (phen = 1,10-phenanthroline).[8]

$$\begin{array}{c}
\mathrm{Cd[N(SiMe_3)_2]_2\ +\ 2\,PhC{\equiv}CLi} \\
\text{toluene}\ \Big\downarrow\ \text{tmeda} \\
\mathrm{[Cd(PhC{\equiv}C)_2(tmeda)]\ +\ 2\,LiN(SiMe_3)_2} \\
\mathbf{1} \\
\\
\mathrm{Cd[N(SiMe_3)_2]_2\ +\ 4\,C_{12}H_8NLi} \\
\text{Toluene–thf}\ \Big\downarrow\ \text{tmeda} \\
\mathrm{2[Li(thf)_4]^+[Cd(C_{12}H_8N)]^{2-}\ +\ 2\,LiN(SiMe_3)_2} \\
\mathbf{2}
\end{array}$$

Scheme 1

Complex **2** has an ion-separated structure (Fig. 2). The complex contains a tetraorganocadmiate dianion $[Cd(C_{12}H_8N)_4]^{2-}$ in which the four ligands are attached in a tetrahedral geometry around the cadmium centre [av. Cd–N 2.225 Å, av. N–Cd–N 109.5°]. Synthesis of such a Cd dianion, although structurally not unique,[9] contrasts with that of the neutral complex **1**.

Although $Cd[N(SiMe_3)_2]_2$ has been used as a metallating agent with weak acids, such as $HP(SiMe_3)_2$ in the synthesis of $Cd[P(SiMe_3)_2]_2$, the nucleophilic substitution of the $N(SiMe_3)_2$ ligands has not been reported.[10] The syntheses of **1** and **2** *via* the nucleophilic substitution reactions of $Cd[N(SiMe_3)_2]_2$[6] with organolithium compounds as described, highlight the potential of this method for the preparation of a large range of cadmium metallo-organic complexes. In contrast, the preparation of **1** using CdI_2 was unsuccessful, the only isolatable crystalline product formed being the alkali metal halide complex, $[LiI(tmeda)]_n$, rather than the desired species. During our studies with the reactions of other lithium organometallics with CdI_2, the preferential crystallisation of the alkali metal halide Lewis-base complex has proved to be a recurring problem. The halide-free synthesis described here successfully eliminates this problem since the byproduct, $LiN(SiMe_3)_2$, is extremely soluble in non-polar organic solvents and therefore will not crystallise in preference to the cadmium species.

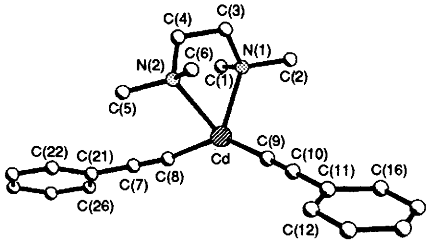

Fig. 1 Molecular structure of **1**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cd–C(8) 2.147(5), Cd–C(9) 2.134(5), Cd–N(1) 2.397(4), Cd–N(2) 2.510(4), C(7)–C(8) 1.209(7), C(9)–C(10) 1.207(7), C(8)–Cd–C(9) 142.8(2), N(1)–Cd–N(2) 76.16(14), C(7)–C(8)–Cd 164.5(4), C(10)–C(9)–Cd 175.4(4).

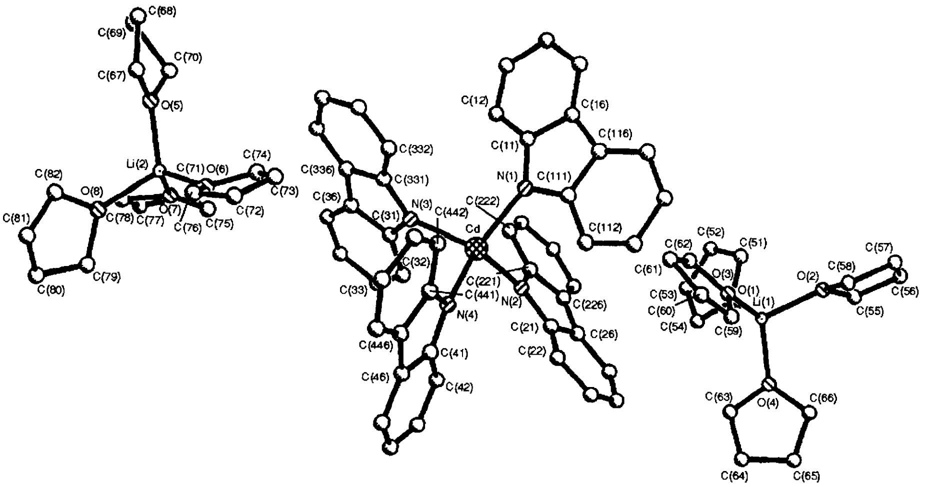

Fig. 2 Molecular structure of **2**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cd–N(1) 2.231(7), Cd–N(2) 2.226(7), Cd–N(3) 2.211(7) Å, Cd–N(4) 2.222(7), N(1)–Cd–N(2) 103.4(2), N(1)–Cd–N(3) 112.6(3), N(1)–Cd–N(4) 115.2(3), N(2)–Cd–N(3) 112.2(3), N(2)–Cd–N(4) 109.6(3), N(3)–Cd–N(4) 104.1(3).

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Footnotes

† A solution of phenylacetylene [0.27 ml, 2.5 mmol in toluene (10 ml)] was treated with Bu^{n}Li (1.56 ml, 2.5 mmol, 1.6 mol dm^{-3} in hexanes) at −78 °C and allowed to warm to room temp. yielding a white precipitate. Cd[N(SiMe$_3$)$_2$]$_2$ (1.0 ml, 2.5 mmol) and tmeda (0.38 ml, 2.5 mmol) were added, and stirring at room temp. for 5 min produced a yellow solution, which was reduced *in vacuo* to 5 ml. Subsequent storage at −15 °C for 48 h yielded colourless, air sensitive, crystalline cuboids of **1** in 65% yield (first batch): mp 154 °C; ^{1}H NMR (+25 °C, 250 MHz, 0.2 mol dm^{-3}, [^{2}H$_5$]pyridine): δ 7.77 (d, *J* 7 Hz), 7.31 (dd, *J* 7, 7 Hz) and 7.21 (dd, *J* 7, 7 Hz, 10 H, Ph), 2.36(s), 2.22(s, 16 H, tmeda); satisfactory elemental analyses (C, H, N) were obtained.

A solution of carbazole [1.67 g, 10.0 mmol in toluene (10 ml)] was reacted with Bu^{n}Li (6.25 ml, 10.0 mmol, 1.6 mol dm^{-3} in hexanes) at −78 °C and allowed to warm to room temp. yielding a cream precipitate. Cd[N(SiMe$_3$)$_2$]$_2$ (1.0 ml, 2.5 mmol), tmeda (0.76 ml, 5.0 mmol) and thf (10 ml) were added. Refluxing for 10 min followed by filtration produced an orange solution, which was reduced *in vacuo* to 10 ml. Subsequent storage at room temp. for 48 h yielded colourless, air-sensitive crystalline cuboids of **1** in 50% yield (first batch): decomp., to black solid above 175 °C; ^{1}H NMR (+25 °C, 250 MHz, 0.2 mol dm^{-3}, [^{2}H$_8$]thf): δ 8.05 (d, *J* 7 Hz), 7.43–7.09 (overlapping multiplets, 32 H, carbazole), 3.60 (m, 32 H, thf), 1.75 (m, 32 H, thf); satisfactory elemental analyses (C, H, N) were obtained.

‡ *Crystal data* for **1**: $C_{22}H_{26}CdN_2{\cdot}0.5C_6H_5Me$ M = 442.9, triclinic, space group $P\bar{1}$, a = 8.432(2), b = 9.600(2), c = 16.083(3) Å, α = 102.63(3), β = 98.68(3), γ = 108.29(3)°, V = 1171.8(4) Å^3, Z = 2, D_c = 1.255 Mg m^{-3}, λ = 0.71073 Å, T = 153(2) K, μ(Mo-Kα) = 0.939 mm^{-1}. Data was collected on a Siemens-Stoe AED diffractmeter using an oil-coated rapidly cooled crystal (T. Kottke and D. Stalke, *J. Appl. Crystallogr.*, 1993, **26**, 615) of dimensions 0.3 × 0.3 × 0.3 mm, mounted directly from solution, by the θ/ω method ($7 \leq 2\theta \leq 45°$). Of a total of 3166 reflections collected, 3039 were independent. The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares analysis on F^2 with $R1$ [$F > 4\sigma(F)$] and $wR2$ (all data) to 0.0295 and 0.0921, respectively (SHELXL-93, Göttingen, 1993). Largest peak and hole in the final difference map, 0.791 and −0.976 e Å^{-3} respectively. The complex crystallises with a disordered half molecule of toluene per formula unit in the lattice.

Crystal data for **2**: $C_{80}H_{96}CdLi_2N_4O_8$, M = 1367.89, triclinic, space group $P\bar{1}$, a = 12.723(3), b = 13.174(3), c = 24.337(5) Å, α = 89.79(3), β = 82.14(3), γ = 66.77(3)°, V = 3707.6(14) Å^3, Z = 2, D_c = 1.225 Mg m^{-3}, λ = 0.71073 Å, T = 153 K, μ(Mo-Kα) = 0.351 mm^{-1}. Data was collected on a Siemens-Stoe AED diffractometer using an oil-coated rapidly cooled crystal (T. Kottke and D. Stalke, *J. Appl. Crystallogr.*, 1993, **26**, 615) of dimensions 0.3 × 0.3 × 0.3 mm mounted directly from solution, by the θ/ω method ($7 \leq 2\theta \leq 45°$). Of a total of 9848 reflections collected, 9581 were independent. The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares analysis on F^2 with $R1$ [$F > 4\sigma(F)$] and $wR2$ (all data) to 0.0834 and 0.2303 respectively (SHELXL93, Göttingen 1993). Largest peak and hole in the final difference map, 3.182 and −0.911 e Å^{-3} respectively.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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