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Selenium insertion into a cadmium–carbon bond; synthesis and structural characterisation of the loosely linked dimer $[\{\mathrm{Cd(SeC{\equiv}CPh)_2(tmen)}\}_2]$ (tmen = $\mathrm{Me_2NCH_2CH_2NMe_2}$)

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The heterogeneous reaction of elemental selenium with the monomeric complex $[\mathrm{Cd(C{\equiv}CPh)_2(tmen)}]$ (2:1 equivalents) produced the unusual loosely linked dimer $[\{\mathrm{Cd(SeC{\equiv}CPh)_2(tmen)}\}_2]$.

Recently, we have been interested in the synthesis of cadmium organometallic and metalloorganic complexes *via* the nucleophilic substitution of cadmium bis(trimethyl)silylamide by organic anions.[1-3] This approach, in contrast to transmetallation of the cadmium halides or the reactions of organic acids with diorganocadmium reagents, provides a general approach to homoleptic complexes $[\mathrm{CdR_2}]$. The syntheses of homoleptic complexes of Group 12 metals is far from trivial, for example, even desilylation of $[\mathrm{Ph_2PSiMe_3}]$ with $[\mathrm{CdCl_2}]$ gives the mixed-ligand complex $[\mathrm{Cd_4Cl_4(PPh_2)_4(PPr^n{}_3)_2}]$,[4] in which halide ions are incorporated into the adamantoid core. In contrast to the latter, we found that substitution of $[\mathrm{Cd\{N(SiMe_3)_2\}_2}]$ with $[\mathrm{Li(PPh_2)}]$ yields $[\mathrm{Li(thf)_4}]_2[\mathrm{Cd_4(PPh_2)_{10}}]$ (thf = tetrahydrofuran),[2] a complex which (it appears) cannot be prepared by any other method. A major goal in our current investigations is the extension of the 'silylamide route' to allow the preparation of complexes containing more diverse functionalities in the organic groups. However, owing to the lack of commercially available organic acids for selenium, we had so far been unable to extend this route to homoleptic cadmium organoselenides. We report here that the reactions of diorganocadmium complexes, formed by substitution of the metal silylamide, with solid selenium can be used as an effective one-pot synthesis of cadmium selenide compounds. This approach is exemplified by the *in situ* synthesis of the dimeric complex $[\{\mathrm{Cd(SeC{\equiv}CPh)_2(tmen)}\}_2]$ **1** (tmen = $\mathrm{Me_2NCH_2CH_2NMe_2}$) from the insertion reaction (1)

$$2[\mathrm{Cd(C{\equiv}CPh)_2(tmen)}] \xrightarrow[\text{toluene}]{4\mathrm{Se}} \underset{\mathbf{1}}{[\{\mathrm{Cd(SeC{\equiv}CPh)_2(tmen)}\}_2]} \quad (1)$$

of selenium metal with the diorganocadmium complex $[\mathrm{Cd(C{\equiv}CPh)_2(tmen)}]$.[1] The identity of complex **1** was confirmed by NMR and IR spectroscopy, elemental analysis and low-temperature X-ray crystallography.†

Although insertion of Se and Te into alkali-metal organometallics is well known,[6] surprisingly this simple approach has not been applied to the synthesis of cadmium selenide and telluride complexes. Previous studies have involved the reactions of the selenols [RSeH] or diselenides [RSeSeR] with an alkali metal or alkali-metal organometallic [LiR′] giving the alkali-metal selenides, which then react with cadmium halides. Alternatively, the acid–base reactions of selenols with $[\mathrm{Cd\{N(SiMe_3)_2\}_2}]$ has been employed.

A low-temperature X-ray study‡ shows that **1** exists as a loosely linked dimer in the solid state in which the Cd centres have identical highly distorted five-co-ordinate geometries [Se(1)–Cd(1) ··· Se(1a) 96.16(4), Se(1)–Cd(1)–Se(2) 115.50(4), Se(1a) ··· Cd(1)–Se(2) 76.22(4) and N(1)–Cd(1)–N(2) 78.2(2)°] (Fig. 1). The central $\mathrm{Cd_2Se_2}$ four-membered core forms a planar parallelogram with the *exo* Se–C≡C–Ph ligands adopting a *trans* geometry. The formulation of **1** as a loosely associated dimer is seen by an examination of the Cd–Se bonds within, and linking, the $[\mathrm{Cd(SeC{\equiv}CPh)_2(tmen)}]$ monomer units. Although a similar pattern of short, medium (intra-monomer) and long (inter-monomer) distances occurs in other dimeric cadmium selenides, *e.g.* 2.599(4) and 2.483(3) Å within the monomers and 2.693(3) Å linking them in $[\{\mathrm{Cd(SeC_6H_2Bu^t{}_3\text{-}2,4,6)_2}\}_2]$,[10] in **1** dimerisation has resulted in only a small elongation of the bridging Cd–Se bond within each monomer [Cd(1)–Se(1) 2.631(1) and Cd(1)–Se(2) 2.584(1) Å]. In addition, the Cd ··· Se bond lengths linking the monomer units are extremely long

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† A solution of phenylacetylene [0.54 $\mathrm{cm^3}$, 5.0 mmol in toluene (10 $\mathrm{cm^3}$)] was treated with $\mathrm{LiBu^n}$ (3.13 $\mathrm{cm^3}$, 2.5 mmol, 1.6 mol $\mathrm{dm^{-3}}$ in hexanes) at −78 °C and allowed to warm to room temperature, yielding a white precipitate. Then $[\mathrm{Cd\{N(SiMe_3)_2\}_2}]$[5] (1.0 $\mathrm{cm^3}$, 2.5 mmol) and tmen (0.38 $\mathrm{cm^3}$, 2.5 mmol) were added to the solution. Stirring at room temperature for 5 min produced a yellow solution, to which Se powder (0.395 g, 5 mmol) was added. The reaction mixture was stirred at 60 °C (12 h) to yield a red solution. The solution was filtered and reduced *in vacuo* to 5 $\mathrm{cm^3}$. The red oil was dissolved in the minimum amount of thf. Subsequent storage at −15 °C (48 h) yielded colourless, air-sensitive crystalline cuboids of **1** in 20% yield (first batch). Crystallisation from diethyl ether–toluene gave increased yields of **1** (45%), m.p. 129 °C (Found: C, 45.4; H, 4.0; N, 5.1. Calc. for $\mathrm{C_{44}H_{52}Cd_2N_4Se_4}$: C, 44.9; H, 4.4; N, 4.8%). IR (Nujol): $\tilde{\nu}_{max}/\mathrm{cm^{-1}}$ 3000–2800s (C–H str.), 2130w (C≡C str.), 1596w (C$\doteq$C str., Ph), 699 and 750s (C–H bend, Ph). ^{1}H NMR (25 °C, 250 MHz, [$^2\mathrm{H_8}$]thf): δ 7.00–6.65 (overlapping multiplets, 10 H, Ph), 2.03 (s, 4 H, tmen) and 1.88 (s, 12 H, tmen).

‡ Crystal data. $\mathrm{C_{44}H_{52}Cd_2N_4Se_4}$, M = 1177.08, monoclinic, space group $C2/c$, a = 26.990(7), b = 9.815(3), c = 17.539(5) Å, β = 97.82(5)°, U = 4603(2) Å^3, Z = 4, D_c = 1.699 Mg $\mathrm{m^{-3}}$, λ = 0.710 73 Å, T = 153(2) K, μ(Mo-Kα) = 4.121 $\mathrm{mm^{-1}}$. Data were collected on a Siemens-Stoe AED diffractometer using an oil-coated rapidly cooled crystal[7] of dimensions 0.5 × 0.4 × 0.3 mm mounted directly from solution by the θ–ω method ($8 \leqslant 2\theta \leqslant 45°$). The data were corrected for absorption by a semi-empirical method based upon ψ-scan data with a maximum and minimum transmission of 0.938 and 0.142, respectively. Of a total of 3118 reflections collected, 2997 were independent. The structure was solved by direct methods (SHELXTL PLUS[8]) and refined by full-matrix least squares on F^2 with $R1$ [$F > 4\sigma(F)$ (2686 reflections)] and $wR2$ (dall data) to 0.045 and 0.102, respectively (SHELXL 93[9]). Largest peak and hole in the final difference map, 1.062 and −0.975 e Å^{-3} respectively. The phenyl group attached to C(22) is disordered over two sites (50:50). Distance and ADP restraints were applied to the C atoms of both phenyl environments. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/90.

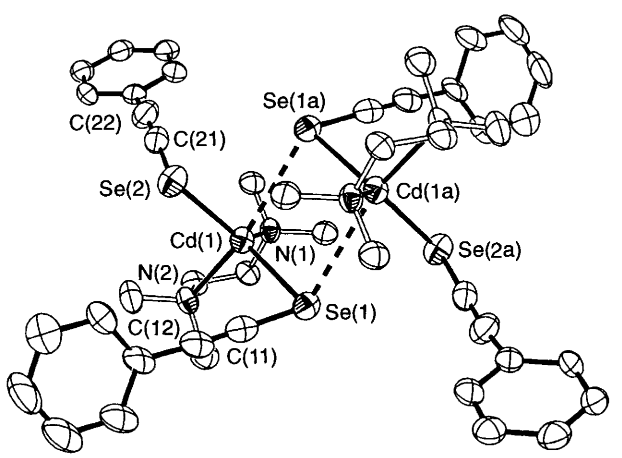

Fig. 1 Crystal structure of [{Cd(SeC≡CPh)$_2$(tmen)}$_2$] **1**. Hydrogen atoms have been omitted for clarity. A crystallographic centre of inversion relates the two monomer units. Selected bond lengths (Å) and angles (°): Cd(1)–Se(1) 2.631(1), Cd(1)–Se(2) 2.584(1), Cd(1) ··· Se(1a) 3.278(1), Se(1)–C(11) 1.851(7), Se(2)–C(21) 1.833(7), C(11)–C(12) 1.197(9), C(21)–C(22) 1.207(9); Se(1)–Cd(1) ··· Se(1a) 96.16(4), Se(1)–Cd(1)–Se(2) 115.50(4), Se(1a) ··· Cd(1)–Se(2) 76.22(4), N(1)–Cd(1)–N(2) 78.2(2), Cd(1)–Se(1)–C(11) 84.3(2), Cd(1)–Se(2)–C(21) 95.1(2)

[Cd(1) ··· Se(1a) 3.278(1) Å]. A further point, testifying to the weakness of the Cd ··· Se inter-monomer interactions, is the similarity of the terminal and bridging Se–C≡C–Ph groups within the monomer units of **1**. In both of these groups the Se–C and C≡C bond lengths are practically identical and there is also only a small difference in the Cd–Se–C angles occurring between the terminal and bridging Se–C≡C–Ph groups [Cd(1)–Se(1)–C(11) 84.3(2) and Cd(1)–Se(2)–C(21) 95.1(2)°].

The formation of a loosely associated dimer for complex **1** even in the presence of Lewis-base solvation by tmen is a consequence of the sterically undemanding Se–C≡C–Ph groups; the four-co-ordinate cadmium centres of a [Cd(SeC≡CPh)$_2$(tmen)] monomer not being completely co-ordinatively saturated. There are comparatively few examples of structurally characterised cadmium organoselenides. These include [NMe$_4$]$_2$[Cd$_4$Br$_4$(SePh)$_6$],[11] [NMe$_4$]$_2$[Cd(SePh)$_4$],[12] [NMe$_4$]$_2$[Cd$_4$(SePh)$_{10}$][13] and [{Cd(SeC$_6$H$_2$Bu$^t_3$-2,4,6)$_2$}$_2$].[10] Although there have been previous examples of monomeric complexes containing five-co-ordinate cadmium centres,[14] complex **1** is a rare example of a cadmium chalcogenide complex containing five-co-ordinate cadmium and a rare example of a 'loosely linked' dimer. The most closely related structure to **1** is that of the loosely linked dimer structure of [{Cd(Se$_2$CNEt$_2$)$_2$}$_2$] (Cd–Se 2.635 and 2.955 Å).[15]

Acknowledgements

We thank the EPSRC (M. A. B., K. L. V.), the Associated Octel Co. Ltd., Ellesmere Port (K. L. V.), the Royal Society (P. R. R., D. S. W.) and the EU (Fellowship for A. S.) for financial support.

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Received 16*th February* 1996; *Communication* 6/01144F