

A halide-free route to Groups 12 and 13 organometallic and metalloorganic complexes

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Nucleophilic substitution of the bis(trimethylsilyl)amido groups of $[M\{N(SiMe_3)_2\}_2]$ ($M = Zn$ or Cd) and $[In\{N(SiMe_3)_2\}_3]$ was found to be a halide-free and homogeneous approach to organometallic and metalloorganic complexes. The breadth of this new synthetic approach is illustrated by the formation of $[Cd(SCPh_3)_2(tmen)]$ **1** ($tmen = Me_2NCH_2CH_2NMe_2$), $[(PhC\equiv C)_4Zn\{Li(tmen)\}_2]$ **2** and $[Li(thf)_4][In(C\equiv CPh)_4]$ **3** ($thf =$ tetrahydrofuran) from nucleophilic substitution reactions utilising $[M\{N(SiMe_3)_2\}_2]$ ($M = Zn$ or Cd) and $[In\{N(SiMe_3)_2\}_3]$, the outcome of which is dependent upon the Lewis bases and nucleophiles employed and the metal centres concerned. The crystal structures of complexes **1–3** have been determined.

Previously we reported that nucleophilic substitution of $[Cd\{N(SiMe_3)_2\}_2]$ **1** with organometallic and metalloorganic lithium compounds is an efficient synthetic strategy to cadmium organometallic and metalloorganic complexes.² Significantly, this new synthetic approach avoids the preferential crystallisation of Lewis-base donor complexes of the alkali-metal halides, produced as the by-product in nucleophilic substitution reactions using cadmium halides as precursors. Thus, using $[Cd\{N(SiMe_3)_2\}_2]$ as the precursor we were able to synthesise and characterise structurally $[Cd(C\equiv CPh)_2\cdot tmen]$ ($tmen = Me_2NCH_2CH_2NMe_2$), the first example of a cadmium acetylide, and $[Li(thf)_4]_2[Cd(NC_{12}H_8)_4]$ ($thf =$ tetrahydrofuran, $NC_{12}H_8 =$ carbazoyl), containing the first example of an amidocadmium dianion. From the outcome of these two reactions we proposed that the major influences on the nature of the products formed were the nucleophilicity of the nucleophiles and the nature of the Lewis-base donor employed.

Here we report the further investigation of nucleophilic substitution of bis(trimethylsilyl)amidometal derivatives as a general halide-free strategy to Groups 12 and 13 organometallic and metalloorganic complexes and the syntheses and structures of $[Cd(SCPh_3)_2(tmen)]$ **1**, $[(PhC\equiv C)_4Zn\{Li(tmen)\}_2]$ **2**, and $[Li(thf)_4][In(C\equiv CPh)_4]$ **3**. The syntheses and structures of the latter, together with those of $[Cd(C\equiv CPh)_2(tmen)]$ **4** and $[Li(thf)_4]_2[Cd(NC_{12}H_8)_4]$ **5**, not only illustrate the breadth of this synthetic approach but also that the outcome of the nucleophilic substitution reactions is highly dependent upon the character of the metal.

Results and Discussion

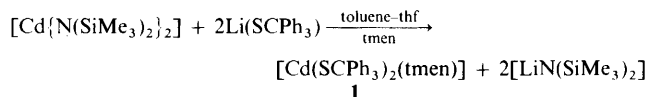
Since all the materials involved are air- and/or moisture-sensitive, all the synthetic work reported here was performed under dry O_2 -free argon using standard inert-atmosphere techniques.³ The metal bis(trimethylsilyl)amide precursors $[M\{N(SiMe_3)_2\}_2]$ ($M = Cd$ or Zn)¹ and $[In\{N(SiMe_3)_2\}_3]$ ⁴ were prepared using the literature methods by the stoichiometric reactions of the appropriate metal halides with $[LiN(SiMe_3)_2]$ in Et_2O .

Despite the ultimate differences in the stoichiometries of the products, $[Cd(SCPh_3)_2(tmen)]$ **1** and $[(PhC\equiv C)_4Zn\{Li(tmen)\}_2]$ **2** were both prepared in good yields by the 1:2 reactions of $[M\{N(SiMe_3)_2\}_2]$ ($M = Cd$ or Zn) with $Li(SCPh_3)$ and $Li(C\equiv CPh)$, respectively, using only 1 equivalent

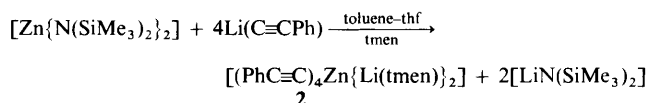
of $tmen$ in thf -toluene. In addition, $[Li(thf)_4][In(C\equiv CPh)_4]$ **3** is obtained from the reaction of $[In\{N(SiMe_3)_2\}_3]$ with $Li(C\equiv CPh)$ in thf -toluene irrespective of the stoichiometry of the reagents. These observations are similar to those which were made previously in the syntheses of $[Cd(C\equiv CPh)_2(tmen)]$ **4** and $[Li(thf)_4]_2[Cd(NC_{12}H_8)_4]$ **5**,² and illustrate that the outcome of the individual reactions is dictated by the thermodynamic stability of the product as opposed to the stoichiometry of the reagents supplied. Additionally, the empirical formulae of **1–3**, obtained from spectroscopic and elemental analyses, provided an initial indication that the interplay between Lewis-base solvation of the metal centres present and the radii of the Groups 12 and 13 metals is an important influence on the structures of these complexes.

Crystal structures of complexes **1–3** were determined at low temperature (153 K). Selected bond lengths and angles are given in Tables 1–3 for **1–3**, respectively.

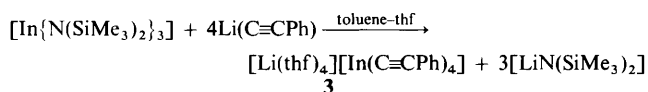
The structure of complex **1** shows it to be a monomeric neutral species $[Cd(SCPh_3)_2(tmen)]$ (Fig. 1). The outcome of the nucleophilic substitution reaction of $Li(SCPh_3)$ with $[Cd\{N(SiMe_3)_2\}_2]$ is therefore similar to that observed previously in the synthesis of $[Cd(C\equiv CPh)_2(tmen)]$ **4**. The cadmium centre of **1** has a highly distorted pseudo-tetrahedral geometry [range of angles about Cd $78.0(3)$ – $155.43(12)^\circ$]. It is bonded almost symmetrically to the S atoms of the Ph_3CS^- ligands with $Cd-S$ bond lengths which are similar to those occurring in $[Cd(SC_6H_2Pr^{1-2,4,6})_2(py)_2]$ ⁵ ($py =$ pyridine) (2.417 \AA ; cf. average 2.44 \AA in **1**). The cisoid orientation of the



Scheme 1



Scheme 2



Scheme 3

Ph₃CS groups of **1**, which point (downwards) away from the NMe groups of the co-ordinated tmen, presumably arises for steric reasons. However, the steric congestion between them which this cisoid orientation imparts gives rise to the very irregular cadmium co-ordination geometry and in particular to a very obtuse S–Cd–S angle [155.4(1)°]. However, distortion of the valence angles may, in addition, be explained in electronic terms. In the structurally analogous compound [Zn(NC₅H₆)₂(py)₂]⁶ the angle spanned by the normally bonded (amide) N atoms is 123° whilst the datively bonded (pyridine) atoms span an angle of 98°. This is explained in terms of the valence shell electron pair repulsion (VSEPR) model. The Zn–N (amide) bonds are normal Lewis electron-pair bonds whilst the Zn–N (pyridine) bonds are dative. The electron pairs in the dative bonds are proposed to be primarily localised on the donor N atoms and should, according to the VSEPR model, have little steric requirement at the zinc centre. It is also noteworthy that in **1** the bidentate tmen has associated restraints upon the bite angle within the chelate ring. Structurally characterised cadmium sulfides are comparatively numerous; these include [Cd(SC₆H₂Bu^t₃)₂]₂,⁷ [NBuⁿ₄][Cd(SC₆H₂Prⁱ₃)₃]⁸ and [NEt₄][NEt₃H][Cd₄(SPh)₄(μ-SPh)₆].⁹

The crystal structure of complex **2** shows it to be the unusual ion-paired [(PhC≡C)₄Zn{Li(tmen)}₂] (Fig. 2). Despite the poor quality of the X-ray data for **2**, which resulted from its crystallisation as face-sharing octahedra, the basic structure of the complex has been unequivocally determined. The complex, which is the first structurally characterised zinc acetylide, is constructed from the association of a pseudo-tetrahedral

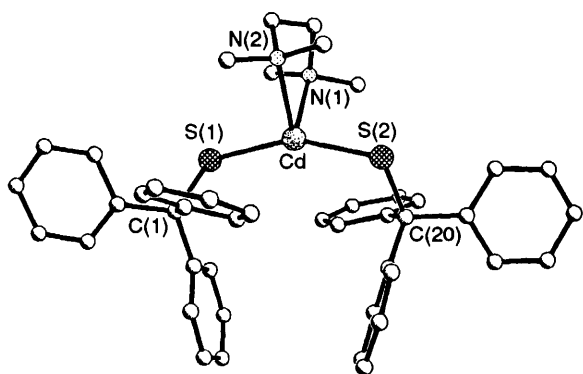


Fig. 1 Molecular structure of complex **1**. Hydrogen atoms have been omitted for clarity

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**

Cd–S(1)	2.433(3)	Cd–N(1)	2.429(10)
Cd–S(2)	2.440(3)	Cd–N(2)	2.392(10)
S(1)–Cd–S(2)	155.43(12)	N(1)–Cd–S(2)	104.6(2)
N(1)–Cd–N(2)	78.0(3)	N(2)–Cd–S(1)	101.8(3)
N(1)–Cd–S(1)	95.4(2)	N(2)–Cd–S(2)	96.3(3)

Table 2 Selected bond lengths (Å) and angles (°) for complex **2**

Zn–C(10,20) (average)	2.05	Li–C(11,21) (average)	2.74
C(10,20)–C(11,21) (average)	1.20	Li–C _{centroid} (average)	2.46
Zn–Li	2.67	Li–N (average)	2.09
Li–C(10,20) (average)	2.22		
C(10)–Zn–C(20)	102.9(5)	C(11,21)–C(10,11)–Zn (average)	175.5
C(10)–Zn–C(20 ^b)	115.5(5)	Zn–C(10,20)–Li (average)	77.4
C(10 ^b)–Zn–C(20)	115.5(5)	C(10,20)–C(11,21)–C(12,22) (average)	175
C(10 ^b)–Zn–C(20 ^b)	102.9(5)	N(1)–Li–N(2)	89.9(8)
C(10)–Zn–C(10 ^b)	115.4(10)	C≡C _{centroid} –Li–C≡C _{centroid} (average)	116.3
C(20)–Zn–C(20 ^b)	104.6(9)		

Symmetry relation: **1** – *x*, –*y*, *z*.

[Zn(C≡CPh)₄][–] anion (average C–Zn–C 109.5°) with two [Li(tmen)]⁺ cation units *via* acetylide–lithium π interactions. Although the Zn is bonded equivalently to all four PhC≡C[–] groups (average 2.05 Å), the effect of the symmetrical interaction of a pair of acetylide groups with each of the Li⁺ cations [C(10,20)⋯Li average 2.22 Å, C(11,21)⋯Li average 2.74 Å] is to introduce marked angle distortions at the Zn [C–Zn–C range 102.9(5)–115.5(5)°]. However, the interactions of the pairs of PhC≡C[–] ligands with their respective lithium centres does not induce any major distortions from linearity in the attachment of the acetylenic groups to Zn [average C_β≡C_α–Zn 175°].

Although agostic C⋯Li bonding is responsible for the cation–anion association in [Li₂(ZnMe₄)]¹⁰ and [Zn{(CH₂)_n}]₂·2Li(tmen)^{11,12} (*n* = 4 or 5), the acetylenic⋯lithium π interactions of complex **2** are unprecedented for anion complexes of post-transition metals. However, acetylenic (–C≡C–) and cumulenyl [(–C=C–)_n] π bonding to Li is now well known in organolithium compounds and there are also several structurally characterised transition-metal alkene complexes in which C⋯Li bonding provides the means for cation–anion association.^{13,14} The nature of these interactions is probably best described as an electrostatic (ion–dipole) rather than a covalent interaction.

The structure of complex **3** (Fig. 3) shows it to be an ion-separated species [Li(thf)₄][In(C≡CPh)₄] containing a tetraorganotin monoanion and thf-solvated lithium cation. The In–C (average 2.159 Å) and C≡C (average 1.200 Å) bonds within the anion are highly uniform and are shorter than those observed in polymeric [InMe₂(C≡CMe)]_∞ (In–C 2.193, C≡C 1.212 Å),¹⁵ the only other structurally characterised indium acetylide. Despite the ion-separated nature of the [In(C≡CPh)₄][–] anion, there are nonetheless considerable variations in the C–In–C angles [range 105.2(2)–112.7(2)°]. Comparison of the bond lengths and angles within the PhC≡C

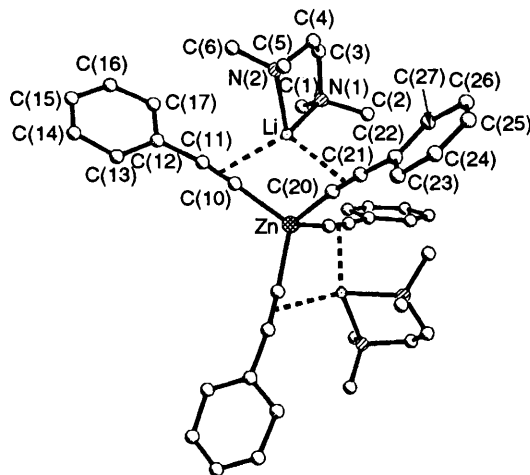


Fig. 2 Molecular structure of complex **2**. Hydrogen atoms have been omitted for clarity

groups of 3 with those in 2 and 4 indicates that there is little difference in the electronic character of these groups in all three complexes, within the error of the X-ray experiments. This testifies to the fact that the acetylide–lithium interactions of 2 are weak and electrostatic.

The varied outcomes of the nucleophilic substitution reactions witnessed in the structures of complexes 1–3 and of the previously reported 4 and 5 arise from the influences of the nature of the Lewis-base donor ligands and of the nucleophiles employed in their syntheses. In addition, the Groups 12 and 13

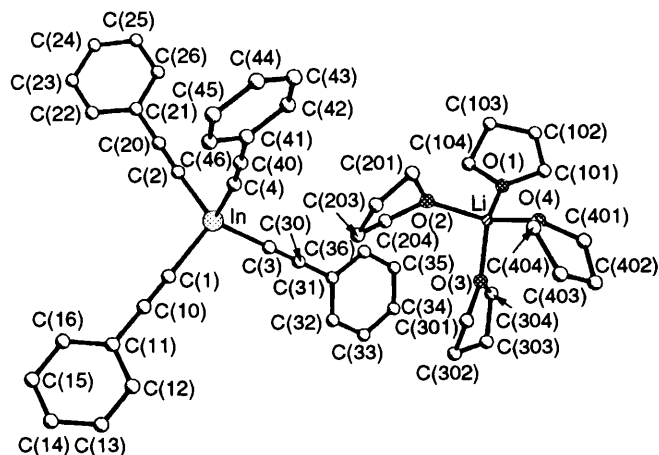


Fig. 3 Molecular structure of complex 3. Hydrogen atoms have been omitted for clarity

Table 3 Selected bond lengths (Å) and angles (°) for complex 3

In–C(1)	2.155(6)	C(1)–C(10)	1.204(8)
In–C(2)	2.156(6)	C(2)–C(20)	1.202(8)
In–C(3)	2.165(6)	C(3)–C(30)	1.200(8)
In–C(4)	2.161(6)	C(4)–C(40)	1.194(8)
C(1)–In–C(2)	112.7(2)	In–C(2)–C(20)	171.4(5)
C(1)–In–C(3)	109.6(2)	In–C(3)–C(30)	179.0(5)
C(1)–In–C(4)	106.5(2)	In–C(4)–C(40)	171.2(5)
C(2)–In–C(3)	110.6(2)	C(1)–C(10)–C(11)	179.2(6)
C(2)–In–C(4)	105.2(2)	C(2)–C(20)–C(21)	178.9(6)
C(3)–In–C(4)	112.2(2)	C(3)–C(30)–C(31)	179.7(6)
In–C(1)–C(10)	172.2(5)	C(4)–C(40)–C(41)	176.9(6)

Table 4 Details of the structure refinements and data collection for complexes 1–3*

	1	2	3
Empirical formula	C ₄₄ H ₄₆ CdN ₂ S ₂	C ₄₄ H ₅₂ Li ₂ N ₄ Zn	C ₄₈ H ₄₈ InLiO ₄
<i>M</i>	779.35	716.15	810.62
Crystal system	Orthorhombic	Tetragonal	Triclinic
Space group	<i>Pbca</i>	<i>I4₁</i>	<i>P2₁/n</i>
Crystal size/mm	0.5 × 0.5 × 0.4	0.3 × 0.3 × 0.2	0.4 × 0.4 × 0.3
<i>a</i> /Å	17.768(7)	16.327(2)	11.812(2)
<i>b</i> /Å	19.529(8)	16.327(2)	22.684(5)
<i>c</i> /Å	21.984(9)	16.081(3)	16.072(3)
α /°	—	—	102.63(3)
β /°	—	—	98.68(3)
γ /°	—	—	108.29(3)
<i>U</i> /Å ³	7628(5)	4281.5(14)	4286.7(11)
<i>Z</i>	8	4	4
μ /mm ⁻¹	0.715	0.605	0.593
θ range/°	4.02–22.54	3.05–22.50	3.52–22.50
Maximum, minimum transmission	0.652, 0.431	No correction	No correction
Reflections collected	5798	1795	5814
Independent reflections	4973	1672	5587
<i>R</i> 1, <i>wR</i> 2 [<i>F</i> > 2 σ (<i>F</i>)]	0.079, 0.144	0.072, 0.168	0.532, 0.145
(all data)	0.154, 0.196	0.101, 0.1872	0.063, 0.165
Peak, hole in final electron-density map/e Å ⁻³	1.059, –1.414	0.457, –0.309	1.097, –0.788
Absolute structure parameter	—	0.49(5)	—

* Data in common: *T* = 153(2) K, λ = 0.710 73 Å, $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$, $w = 1 / [\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2) / 3$.¹⁷

metals present also have a major influence on the outcome. This is seen in a comparison of the structures [(PhC≡C)₄Zn{Li(tmen)}₂] 2 and [Cd(C≡CPh)₂(tmen)] 4 which are prepared using the same 1 : 2 : 1 stoichiometry of [M{N(SiMe₃)₂}₂] (M = Zn or Cd), Li(C≡CPh) and tmen, respectively. Presumably the main reason for the formation of a [Zn(C≡CPh)₄]²⁻ anion in 2, as opposed to a tmen chelated complex similar to 4, partly stems from the difference in ionic radii of Zn and Cd (1.25 and 1.41 Å).¹⁶ Thus complexation of Zn²⁺ by four acetylides may be sterically more favourable than by two acetylides and a tmen. The emergence of steric crowding and of subsequent distortion of the metal geometry is clearly seen in the structure of [Cd(SCPh₃)₂(tmen)] 1, where the more sterically demanding Ph₃CS is attached to Cd. Evidently the formation of ion-separated complexes containing metal-centred anions for [Li(thf)₄][In(C≡CPh)₄] 3 and [Li(thf)₄]₂[Cd(NC₁₂H₈)₄] 5 is dictated by lattice-energy considerations and by the favourable co-ordination of tetrahydrofuran to the hard Li⁺ cation.

Experimental

Synthetic techniques

All compounds were prepared under dry O₂-free argon using standard inert-atmosphere techniques.³ Syntheses were carried out in Schlenk tubes on a vacuum line and dry samples for analytical, IR and NMR work were handled using a glove-box (Faircrest shell, with internal Belle Technology recirculator). The complexes [Cd{N(SiMe₃)₂}₂]¹ and [In{N(SiMe₃)₂}₃]⁴ were synthesised as described in the literature. The NH(SiMe₃)₂ used in the syntheses of the latter, and tmen, were dried over molecular sieve (13 ×). However, all other chemicals were used as supplied without any further purification. Solvents were freshly distilled over sodium–benzophenone prior to use. Elemental compositions (C, H, N) were determined using a Perkin-Elmer 240 elemental analyser, the samples being sealed in air-tight aluminium boats in the glove-box prior to analysis. Infrared spectra (as Nujol mulls) of samples prepared in the glove-box were recorded on a Perkin-Elmer FT-IR spectrophotometer. The NMR samples were sealed in air-tight NMR tubes (Wilmad, 528PP) in the glove-box and were run on a Bruker WH250 spectrometer; ¹H NMR spectra were referenced using the solvent peaks as the internal standard.

Table 5 Atomic coordinates ($\times 10^4$) for complex 1

Atom	x	y	z	Atom	x	y	z
Cd	7 865(1)	777(1)	4 129(1)	C(26)	9 750(8)	2 408(7)	3 910(6)
S(1)	6 955(2)	649(2)	3 310(1)	C(27)	9 132(7)	2 564(7)	5 271(5)
S(2)	8 888(2)	1 331(2)	4 682(2)	C(28)	9 292(7)	2 177(7)	5 790(5)
C(1)	7 326(6)	919(6)	2 558(5)	C(29)	9 603(7)	2 482(9)	6 294(6)
C(2)	6 835(7)	551(6)	2 081(5)	C(30)	9 740(8)	3 153(8)	6 318(7)
C(3)	6 738(7)	-165(7)	2 138(5)	C(31)	9 585(8)	3 556(8)	5 811(7)
C(4)	6 311(8)	-512(7)	1 727(5)	C(32)	9 294(7)	3 269(7)	5 294(6)
C(5)	5 922(7)	-171(8)	1 267(6)	C(33)	7 875(7)	2 382(6)	4 786(5)
C(6)	6 009(8)	532(7)	1 221(6)	C(34)	7 543(7)	2 570(7)	5 355(5)
C(7)	6 438(6)	876(7)	1 627(5)	C(35)	6 779(7)	2 616(7)	5 418(7)
C(8)	8 170(7)	716(7)	2 490(5)	C(36)	6 300(7)	2 500(7)	4 925(6)
C(9)	8 688(7)	1 069(6)	2 855(5)	C(37)	6 615(7)	2 336(7)	4 375(6)
C(10)	9 447(8)	889(8)	2 835(6)	C(38)	7 372(7)	2 280(7)	4 303(6)
C(11)	9 698(9)	407(7)	2 434(7)	C(39)	6 273(9)	186(13)	4 721(9)
C(12)	9 191(8)	69(8)	2 076(6)	C(40)	7 037(12)	793(11)	5 450(8)
C(13)	8 431(7)	238(6)	2 088(5)	N(1)	7 049(6)	320(5)	4 917(4)
C(14)	7 249(7)	1 715(6)	2 467(5)	C(41)	7 448(10)	-327(8)	5 113(7)
C(15)	6 651(7)	2 060(7)	2 749(5)	C(42)	7 718(9)	-718(9)	4 565(8)
C(16)	6 578(8)	2 752(7)	2 660(6)	N(2)	8 327(6)	-368(5)	4 236(4)
C(17)	7 046(10)	3 113(8)	2 292(6)	C(43)	8 484(15)	-698(13)	3 631(7)
C(18)	7 604(9)	2 763(7)	1 994(6)	C(44)	9 051(9)	-374(11)	4 564(10)
C(19)	7 731(8)	2 076(7)	2 089(5)	C(39')	6 246(15)	529(23)	4 770(19)
C(20)	8 712(6)	2 262(6)	4 705(5)	C(40')	7 225(23)	556(22)	5 523(12)
C(21)	9 038(7)	2 607(6)	4 125(5)	C(41')	7 129(14)	-425(11)	4 825(18)
C(22)	8 698(8)	3 146(7)	3 835(6)	C(42')	7 919(16)	-651(16)	4 785(13)
C(23)	9 021(10)	3 471(8)	3 352(7)	C(43')	8 067(21)	-765(19)	3 687(11)
C(24)	9 720(8)	3 280(8)	3 142(6)	C(44')	9 139(11)	-449(25)	4 301(20)
C(25)	10 068(9)	2 746(8)	3 431(6)				

[Cd(SCPh)₂(tmen)] 1. *n*-Butyllithium (3.25 cm³, 1.6 mol dm⁻³ in hexanes, 5.0 mmol) was added to a solution of Ph₃CSH (1.38 g, 5 mmol) in toluene (10 cm³) at 0 °C. When the lithiation was complete, [Cd{N(SiMe₃)₂}₂] (1.0 cm³, 2.5 mmol), tmen (0.38 cm³, 2.5 mmol) and thf (5 cm³) were added and the reaction mixture stirred at room temperature (5 min). The resulting orange solution was reduced *in vacuo* to ca. 10 cm³ and storage at room temperature (48 h) gave colourless needles of complex 1 in 56% yield (1.09 g, first batch): m.p. 205 °C; IR (Nujol), $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 3040w (C–H str., Ph), 1591s (C=C str., Ph) and 700s, 740s (C–H bend, Ph); ¹H NMR (+25 °C, 250 MHz, [²H₈]toluene), δ 7.74 (d), 7.12 (t), 7.03 (dd) (20 H, Ph), 2.10 (s, 8 H, CH₂ of tmen) and 1.60 (s, 12 H, NMe₂ of tmen) (Found: C, 66.7; H, 5.8; N, 3.6. Calc.: C, 67.8; H, 5.9; N, 3.6%).

[(PhC≡C)₄Zn{Li(tmen)}₂] 2. *n*-Butyllithium (3.25 cm³, 1.6 mol dm⁻³ in hexanes, 5.0 mmol) was added to a solution of PhC≡CH (0.54 cm³, 5 mmol) in toluene (10 cm³). When the lithiation was complete, [Zn{N(SiMe₃)₂}₂] (1.0 cm³, 2.5 mmol) and tmen (0.39 cm³, 2.5 mmol) were added and the reaction mixture was brought to reflux (5 min). The resulting orange solution was reduced *in vacuo* to ca. 7 cm³ and storage at room temperature (48 h) gave colourless octahedra of complex 2 in 48% yield (0.43 g, first batch): m.p. 200–205 °C to red oil; IR (Nujol), $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 3053w (C–H str., Ph), 2082w (C≡C str.), 1595s, 1570s, 1484s (C=C str., Ph), 693s, 757s (C–H bend, Ph); ¹H NMR (+25 °C, 250 MHz, [²H₈]toluene), δ 7.40–7.00 (overlapping multiplets, 20 H, Ph), 2.30 (s, 8 H, CH₂ of tmen) and 2.14 (s, 24 H, NMe₂ of tmen) (Found: C, 73.0; H, 7.6; N, 7.6. Calc.: C, 73.9; H, 7.5; N, 7.8%).

[Li(thf)₄][In(C≡CPh)₄] 3. *n*-Butyllithium (6.25 cm³, 1.6 mol dm⁻³ in hexanes, 10 mmol) was added to a solution of PhC≡CH (1.08 cm³, 10 mmol) in toluene (15 cm³) at 0 °C. A white precipitate was formed on warming to room temperature. The complex [In{N(SiMe₃)₂}₃] (1.49 g, 2.5 mmol) and thf (10 cm³) were added and the mixture was brought to reflux (15 min), producing a yellow solution. This was reduced *in vacuo* to ca. 18 cm³ and subsequent storage at room temperature (72 h) yielded colourless cuboids of complex 3 in 55% yield (1.11 g, first

Table 6 Atomic coordinates ($\times 10^4$) for complex 2

Atom	x	y	z
Zn	-20 000	-20 000	-18 926(2)
C(10)	-19 705(7)	-18 986(9)	-19 603(11)
C(11)	-19 550(8)	-18 437(9)	-20 020(11)
C(12)	-19 322(9)	-17 801(10)	-20 639(13)
C(13)	-19 674(9)	-17 796(10)	-21 438(11)
C(14)	-19 447(12)	-17 159(11)	-21 999(13)
C(15)	-18 911(12)	-16 584(16)	-21 808(19)
C(16)	-18 556(14)	-16 608(14)	-21 047(20)
C(17)	-18 783(8)	-17 198(9)	-20 435(12)
C(20)	-20 904(9)	-19 577(8)	-18 142(10)
C(21)	-21 480(9)	-19 396(7)	-17 673(9)
C(22)	-22 172(10)	-19 240(9)	-17 136(10)
C(23)	-22 946(11)	-19 422(13)	-17 358(12)
C(24)	-23 612(13)	-19 215(21)	-16 815(17)
C(25)	-23 521(15)	-18 923(17)	-16 103(21)
C(26)	-22 760(15)	-18 744(13)	-15 838(14)
C(27)	-22 065(11)	-18 905(12)	-16 378(14)
Li	-20 206(11)	-18 446(11)	-18 450(13)
N(1)	-19 355(6)	-18 167(6)	-17 513(7)
N(2)	-20 714(7)	-17 283(7)	-18 327(8)
C(1)	-18 503(8)	-18 218(9)	-17 759(12)
C(2)	-19 461(9)	-18 692(10)	-16 798(10)
C(3)	-19 562(9)	-17 306(9)	-17 289(11)
C(4)	-20 393(12)	-17 064(12)	-17 471(14)
C(5)	-21 561(9)	-17 234(10)	-18 307(13)
C(6)	-20 369(14)	-16 687(15)	-18 877(17)

batch): m.p. 138 °C; IR(Nujol), $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 3043w (C–H str., Ph), 1597s (C=C str., Ph), 698s, 747s (C–H bend, Ph); ¹H NMR (+25 °C, 250 MHz, [²H₈]toluene), δ 7.42–7.00 (overlapping multiplets, 20 H, Ph), 3.59 (m, 16 H, thf) and 1.42 (m, 16 H, thf) (Found: C, 68.3; H, 6.3. Calc.: C, 71.0; H, 6.0%).

X-Ray crystallography

X-Ray-quality crystals were mounted under argon directly from solution using an oil-coating method in which the crystal was protected in a drop of perfluorocarbon oil (Riedel-de Haën) which solidifies and thus holds the crystal static in the beam at low temperatures.¹⁷ Data were collected by the θ - ω method on a Stoe-Siemens AED diffractometer equipped with

Table 7 Atomic coordinates ($\times 10^4$) for complex 3

Atom	x	y	z	Atom	x	y	z
In	321(1)	1011(1)	2680(1)	C(41)	447(5)	-911(2)	3913(4)
C(1)	956(5)	847(3)	1493(4)	C(42)	497(6)	-1056(3)	4763(4)
C(10)	1344(5)	689(3)	867(4)	C(43)	503(6)	-1640(3)	5015(4)
C(11)	1797(5)	495(3)	107(4)	C(44)	447(6)	-2090(3)	4433(4)
C(12)	2970(6)	403(3)	97(5)	C(45)	388(6)	-1957(3)	3591(4)
C(13)	3397(7)	215(3)	-629(5)	C(46)	387(5)	-1370(3)	3335(4)
C(14)	2669(7)	119(3)	-1347(5)	Li	4325(9)	1206(5)	7047(6)
C(15)	1531(6)	199(3)	-1341(4)	O(1)	3586(4)	1725(2)	7746(3)
C(16)	1082(5)	381(3)	-623(4)	C(101)	3868(8)	1841(4)	8614(5)
C(2)	-1462(5)	1239(3)	2551(4)	C(102)	2790(10)	2059(6)	8928(8)
C(20)	-2480(5)	1289(3)	2505(4)	C(103)	1888(8)	1999(5)	8261(6)
C(21)	-3705(5)	1360(3)	2439(4)	C(104)	2475(7)	1967(4)	7486(6)
C(22)	-4349(5)	1379(3)	1664(4)	O(2)	5282(4)	1701(2)	6439(3)
C(23)	-5527(6)	1455(3)	1611(5)	C(201)	2784(6)	225(3)	6166(5)
C(24)	-6058(7)	1503(3)	2326(5)	C(202)	3010(8)	27(4)	5293(6)
C(25)	-5451(6)	1475(3)	3087(5)	C(203)	3035(8)	582(4)	4806(5)
C(26)	-4268(5)	1405(3)	3156(4)	C(204)	2894(7)	1071(3)	5417(5)
C(3)	1324(5)	1699(3)	3340(4)	O(3)	3241(4)	817(2)	6225(3)
C(30)	1871(5)	2086(3)	3698(4)	C(301)	5962(7)	1517(4)	5806(5)
C(31)	2524(5)	2548(3)	4120(4)	C(302)	6257(8)	2065(4)	5377(6)
C(32)	3336(5)	2857(3)	3720(4)	C(303)	6353(7)	2510(4)	6065(5)
C(33)	3970(6)	3308(3)	4134(4)	C(304)	5470(7)	2321(4)	6598(5)
C(34)	3807(6)	3455(3)	4942(4)	C(4)	5313(3)	674(2)	7707(3)
C(35)	3012(6)	3146(3)	5349(5)	C(401)	6281(7)	876(4)	8235(5)
C(36)	2371(6)	2702(3)	4944(4)	C(402)	7329(7)	601(3)	7917(5)
C(4)	433(5)	186(3)	3353(4)	C(403)	6860(7)	94(4)	7371(5)
C(40)	436(5)	-304(3)	3626(4)	C(404)	5617(7)	106(4)	7414(5)

an Oxford Cryostream cooling system. In the case of complex 1, data were corrected for absorption using a semiempirical method based upon ψ -scan data. The structures were solved by direct methods (SHELXTL PLUS)¹⁸ and refined by full-matrix least squares on F^2 (SHELXL 93).¹⁹ Details of the structural refinements of all the complexes are described in Table 4 and Tables 5–7 give the atomic coordinates.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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