The β-dialdiminato ligand [{N(C$_6$H$_3$Pr$^i_2$-2,6)C(H)}$_2$CPh]$^-$: the conjugate acid and Li, Al, Ga and In derivatives†

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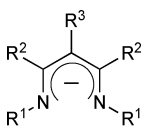
The synthesis of the following crystalline complexes is described: [Li(L)(thf)$_2$] (**2**), [Li(L)(tmeda)] (**3**), [MCl$_2$(L)] [M = Al (**4**), Ga (**5**)], [In(Cl)(L)(μ-Cl)$_2$Li(OEt$_2$)$_2$] (**6**), [In(Cl)(L){N(H)C$_6$H$_3$Pr$^i_2$-2,6}] (**7**), [In(L){N(H)C$_6$H$_3$Pr$^i_2$-2,6}$_2$] (**8**), [{In(Cl)(L)(μ-OH)}$_2$] (**10**), [L(Cl)In–In(Cl)(L)] (**11**) (the thf-solvate **11a**, the solvate-free **11b** and the hexane-solvate **11c**), [{In(Cl)L}$_2$(μ-S)] (**12**) and [InCl$_2$(L)(tmeda)] (**13**) ([L]$^-$ = [{N(C$_6$H$_3$Pr$^i_2$-2,6)C(H)}$_2$CPh]$^-$). From H(L) (**1**), *via* Li(L) in Et$_2$O and thf, tmeda, AlCl$_3$, GaCl$_3$ or InCl$_3$ there was obtained **2**, **3**, **4**, **5** or **6**, respectively in excellent yield. Compound **6** was the precursor for each of **7**–**11**, **13** and [{InCl$_3$(tmeda)$_2${μ-(OSnMe$_2$)$_2$}}] (**14**) by treatment with one (**7**) or two (**8**) equivalents of K[N(H)(C$_6$H$_3$Pr$^i_2$-2,6)], successively Li[N(SiMe$_3$)(C$_6$H$_3$Pr$^i_2$-2,6)] and moist air (**10**), Na in thf (**11a**), tmeda (**13**), or successively tmeda and Me$_3$SnSnMe$_3$ (**14**). Crystals of **11b** (with an equivalent of In) and **11c** were obtained from InCl or thermolysis of [In(Cl)(L){N(SiMe$_3$)(C$_6$H$_3$Pr$^i_2$-2,6)}] (**9**) {prepared *in situ* from **6** and Li[N(SiMe$_3$)(C$_6$H$_3$Pr$^i_2$-2,6)] in Et$_2$O}, respectively. Compound **12** was obtained from a thf solution of **11a** and sulfur. X-Ray data for crystalline **1**–**6**, **8**, **11a**, **11b**, **11c**, **12** and **14** are presented. The M(L) moiety in each (not the L-free **14**) has the monoanionic L ligated to the metal in the N,N′-chelating mode. The MN1C1C2C3N2 six-membered M(L) ring is π-delocalised and has the half-chair (**2**, **3** and **11**) or boat (**4**–**8**, **10** and **13**) conformation.

Introduction

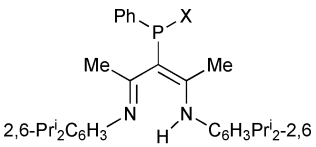
β-Diketiminates are widely used as spectator ligands; they are shown in **I** in their monoanionic N,N′-chelating, π-delocalised form. They bind strongly to metals, are readily tuneable (by means of changing the substituents R^1, R^2, R^3 in **I**) to provide a range of steric and electronic demands on the metal, and have a variety of ligand-to-metal binding modes. The ligands **I** are able to stabilise compounds not only in a low state of molecular aggregation, but also in a low metal oxidation state, as cations, and complexes containing metal-multiply-bonded-co-ligands. Many β-diketiminatometal complexes have a useful role as catalysts or biomolecular mimics. The topic has been reviewed.[1] Our studies in this field, initially with R^1 = SiMe$_3$, R^2 = Ph and R^3 = H, date back to 1994,[2] and our most recent publication is in ref. 3.



I

The majority of β-diketiminato ligands which have featured in the literature have been nitrogen analogues of acac$^-$: *i.e.*, **I** with R^2 = Me and R^3 = H, such as L^1 to L^5 with R^1 = C$_6$H$_3$Pr$^i_2$-2,6 (L^1), C$_6$H$_4$Me-4 (L^2), Me (L^3), Et (L^4) or Pr^i (L^5).

Some earlier studies had shown that β-diketiminato ligands were not invariably innocent spectators. Thus, there are examples that a β-methyl group in **I** (as in L^1–L^5) may be prone to deprotonation (*e.g.*, ref. 4); while a γ-H in H(L^1) was capable of undergoing a 1,3-prototropic shift, as in H(L^1) + PCl(Ph)X → **II** (X = Cl[5a] or Ph[5b]).These factors prompted us to focus on the β-dialdiminato



II

ligand L (*i.e.*, **I** with R^1 = C$_6$H$_3$Pr$^i_2$-2,6, R^2 = H and R^3 = Ph). It was first used by Tolman *et al.*, in the context of β-dialdiminatocopper(I)/O$_2$ reactivity, in order to provide less steric hindrance at the metal than its L^1 analogue.[6] It has recently been shown that crystalline [Tl(L)][7] and [Tl{(N(SiMe$_3$)C(Ph)$_2$CH)}],[7] like [Tl(L^1)][8] are monomers.

Results and discussion

The results and discussion is divided into three parts. The first deals with the structures of the crystalline β-dialdimine H[{N(C$_6$H$_3$Pr$^i_2$-2,6)C(H)}$_2$CPh] (**1**) [≡ H(L)], two of its lithium derivatives [Li(L)(thf)$_2$] (**2**) or [Li(L)(tmeda)] (**3**), and the synthesis and structures of the dichloro(β-dialdiminato)metallanes [MCl$_2$(L)] [M = Al (**4**) or Ga (**5**)]. The second is concerned with the synthesis and structure of the heterobimetallic (In^{III}/Li) compound [In(Cl)(L)(μ-Cl)$_2$Li(OEt$_2$)$_2$] (**6**) and six of its reactions leading to a range of β-dialdiminatoindium compounds: the In^{III} complexes **7**–**10**, **12** and

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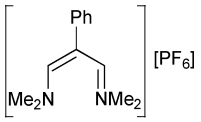
† Electronic supplementary information (ESI) available: Details of structural data for **11b** and **11c** and the molecular structures of **3** and **4**. See DOI: 10.1039/b607782j

13 and the binuclear In^{II} compound **11**, as well as the L-free In^{III} complex **14**. The final section describes the conformation of the M(L) fragment in nine of the crystalline complexes: **2–6**, **8** and **10–12**.

The crystalline compounds [H(L)] (1), [Li(L)(thf)$_2$] (2), [Li(L)(tmeda)] (3) and [MCl$_2$(L)] [M = Al (4), Ga (5)]

The β-dialdimine **1** was prepared by basic hydrolysis of the vinamidium pentafluorophosphate **III**,[9] yielding the β-dialdehyde PhC(H)(CH=O)$_2$, and treatment of the latter with 2,6-diisopropylaniline.[6]



III

Yellow, X-ray quality crystals of **1** were grown from hot diethyl ether. Its molecular structure is shown in Fig. 1 and selected geometrical parameters are listed in Table 1. The molecule lies on a two-fold axis with the NH-hydrogen atom disordered over two positions. While therefore the core NCCCN framework in **1** is π-delocalised, this is not the case for the crystalline β-diketimine H[{N(C$_6$H$_3$Pr$^i_2$-2,6)C(Me)}$_2$CH] since the pairs of N–C and C–C bond lengths in the equally planar NCCCN core are unequal: 1.313(4) or 1.358(4) Å and 1.434(4) and 1.362(4) Å, respectively.[10] The delocalisation in **1** does not extend to the γ-Ph group or the N-aryl groups, the dihedral angle between the C3-to-C4′ and the C1C2C1′ planes or the C7-to-C12 and the NC1C2 planes being 37.7 or 84.8°, respectively. The *ipso*-carbon atom of the γ-Ph group of **1** is coplanar with the NCCCN framework, and the *ipso*-carbon atoms of the aryl substituents at the nitrogen atoms are only 0.026 Å out of that plane.

Table 1 Selected bond lengths (Å) and angles (°) for **1**[a]

N–C1	1.314(2)	C1–N–C7	122.18(15)
N–C7	1.430(2)	N–C1–C2	124.41(16)
C1–C2	1.402(2)	C1–C2–C1′	120.9(2)
C2–C3	1.485(3)	N–C7–C12	119.56(17)
		N–C7–C8	118.56(16)

[a] Symmetry transformations to generate equivalents atoms: ′ $-x+1/2, -y+1/2, z$.

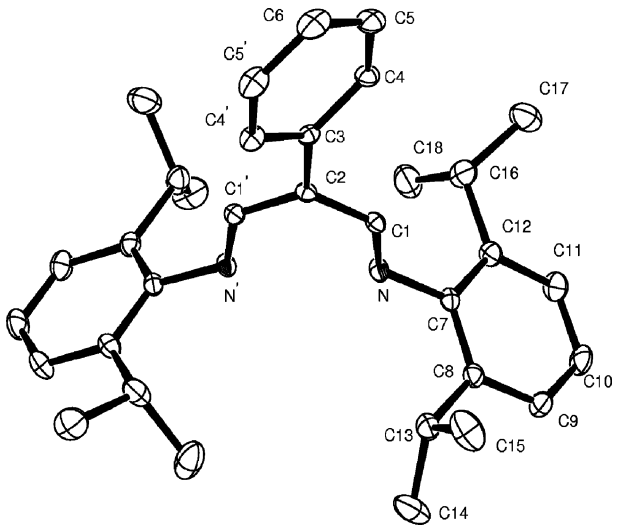
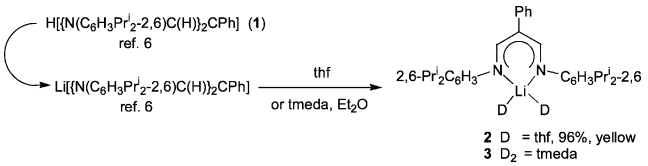
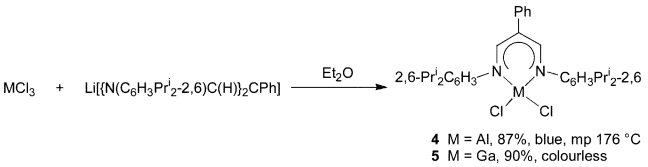


Fig. 1 The molecular structure of **1** (30% probability ellipsoids).

The yellow crystalline lithium β-dialdiminates **2** and **3** were obtained from a solution of Li(L)[6] and the appropriate neutral co-ligand, eqn (1). Likewise, Li(L) was the precursor for the Al (**4**) and Ga (**5**) dichloro(β-dialdiminate)s, eqn (2).



(1)



(2)

The molecular structure of **2** is illustrated in Fig. 2 (for **3**, see ESI†) and selected structural parameters for **2** and **3**, together with comparative data for [Li{(N(C$_6$H$_3$Pr$^i_2$-2,6)C(Me))$_2$CH}(OEt$_2$)$_2$] (**IV**),[10] are in Table 2.

Compounds **4** and **5** were characterised not only by their X-ray molecular structures but also by satisfactory C, H and N

Table 2 Selected bond lengths (Å) and angles (°) for **2**, **3** and [Li{(N(C$_6$H$_3$Pr$^i_2$-2,6)C(Me))$_2$CH}(OEt$_2$)$_2$] (**IV**)[10]

	2	**3**	**IV**[10]		**2**	**3**	**IV**[10]
Li–N1	1.995(3)	2.067(3)	1.912(4)	C1–C2	1.419(3)	1.408(2)	1.402(3)
Li–N2	1.986(4)	2.005(3)	1.917(4)	C2–C3	1.410(3)	1.410(2)	1.402(3)
N1–C1	1.307(2)	1.314(2)	1.324(3)	C2–C4	1.481(3)	1.482(2)	
N2–C3	1.308(2)	1.311(2)	1.325(3)	Li–O1	1.920(4)		1.911(4)
N1–C10	1.431(2)	1.429(2)	1.402(3)	Li–O2	2.003(4)		1.911(4)
N2–C22	1.425(2)	1.432(2)	1.402(3)	Li–N3		2.125(3)	
				Li–N4		2.240(3)	
N1–Li–N2	94.76(15)	94.72(12)	99.9(2)	N1–C1–C2	128.02(17)	128.53(14)	124.3(2)
Li–N1–C1	114.52(15)	115.85(13)	120.9(2)	N2–C3–C2	126.66(17)	127.85(14)	123.2(2)
Li–N2–C3	115.15(16)	117.37(13)	122.0(2)	C1–C2–C4	116.83(16)	118.18(18)	
C1–C2–C3	123.02(7)	124.53(14)	129.5(2)	C3–C2–C4	120.02(17)	116.94(13)	

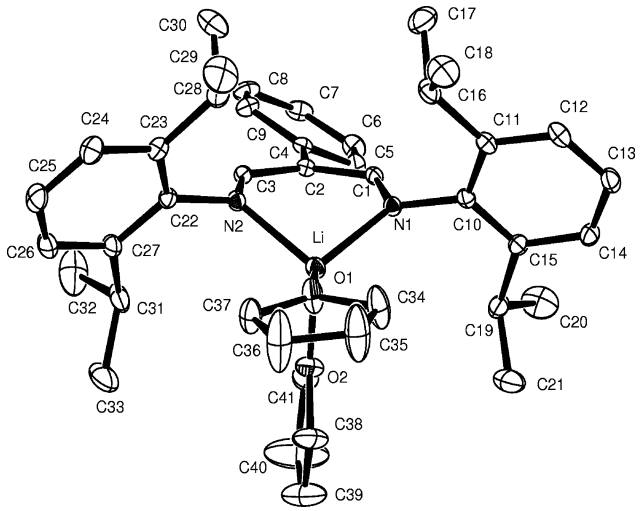


Fig. 2 The molecular structure of **2** (30% probability ellipsoids).

microanalyses and ^{1}H, ^{13}C and ^{27}Al (for **4**) NMR spectra in C_6D_6. The EI-mass spectrum of **4** showed an intense parent molecular ion. Crystalline **4** and **5** are isomorphous. Hence the molecular structure of just one of them (**5**) is shown in Fig. 3 (that of **4** is in the ESI†). Selected geometric parameters for both are listed in Table 3. The bonds within the N1C1C2C3N2 core are

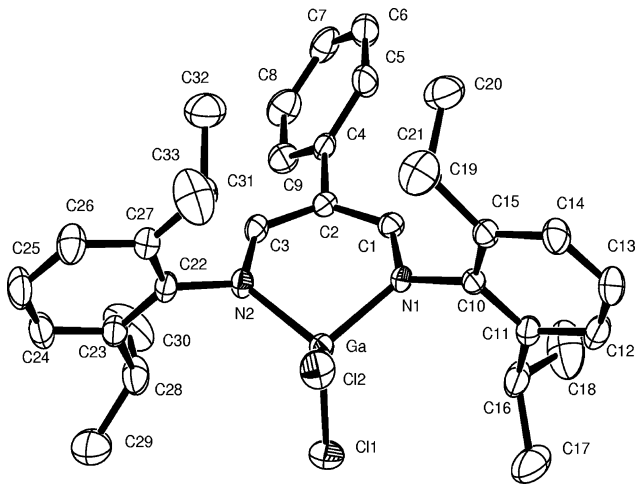


Fig. 3 The molecular structure of **5** (50% probability ellipsoids).

significantly π-delocalised, since each of the N1–C1/N2–C3 and the C1–C2/C2–C3 pairs are essentially identical and intermediate between being single and double. The conformation of this core and its substituents at N1, N2 and C2 is considered later, together with corresponding data for **2**, **3** and In derivatives.

Several β-diketiminatoaluminium dichlorides and their gallium analogues have been reported, including $[MCl_2\{(N(R)(Me))_2CH\}]$ {M = Al and R = C_6H_4Me-4,[11a] $C_6H_3Pr^i_2$-2,6 (**Va**),[11b] Me,[11c] Et,[11c] Pr^i;[11c] and M = Ga with R = $C_6H_3Pr^i_2$-2,6 (**Vb**)[11b]}. The structural data for **Va** and **Vb** are similar to those for **4** and **5**, respectively, *e.g.*, the endocyclic Al–N, N–C and C–C bond lengths for **Va** are 1.884(2), 1.345(4) and 1.400(5) Å, respectively, and the N1–Al–N2, Al–N–C, N–C–C and C–C–C bond angles are 99.4(1), 119.7, 121.8(10) and 127.7(1)°, respectively.[11b]

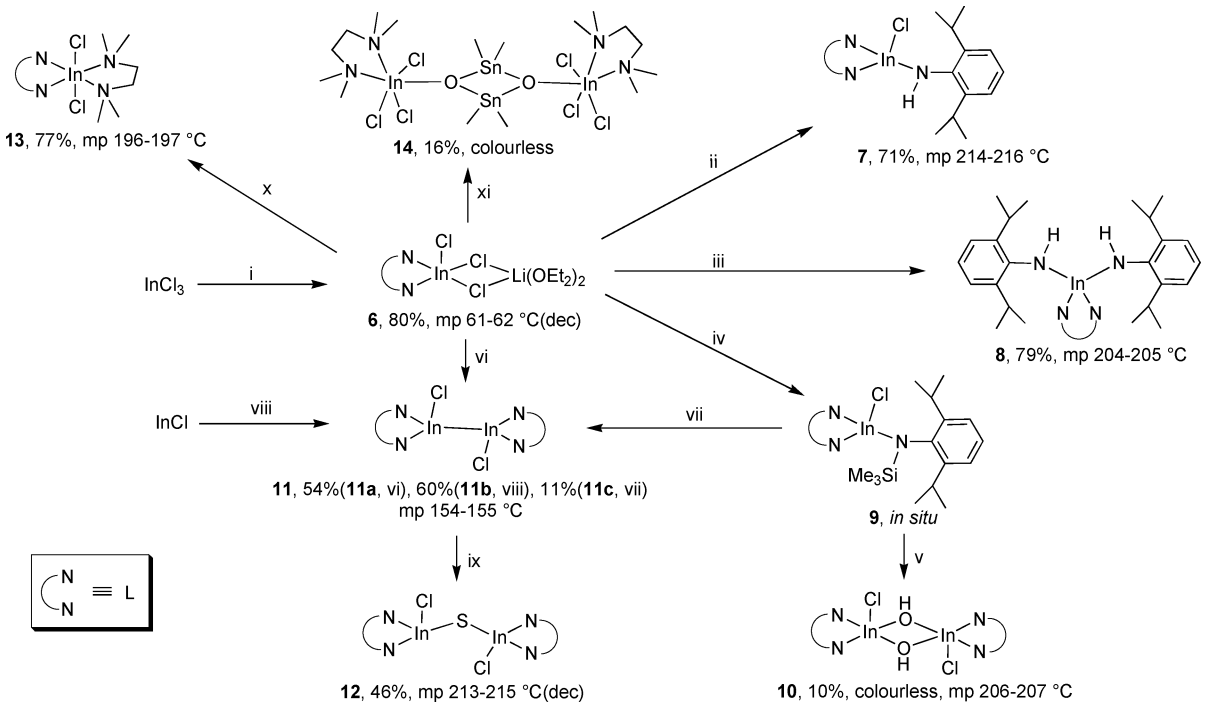
Synthesis, structures and reactions of selected β-dialdiminatoindium compounds and of an L-free In^{III} complex

A series of new, yellow [except for the colourless compound **10**] β-dialdiminatoindium(III) compounds **6–10**, **12** and **13**, as well as the yellow dinuclear $[L(Cl)In^{II}–In^{II}(Cl)L]$ (**11**) and the colourless L-free complex **14**, have been prepared as shown in Scheme 1. Apart from **7**, **9** and **11**, each was obtained in X-ray-quality crystalline form and was structurally characterised. Except for **9** (which was only obtained *in situ*), **10** (isolated in small yield) and the L-free **14**, each gave satisfactory microanalytical (C, H, N) and NMR spectral solution data. Aside from **9**, each of **6–13** showed a parent ion or near daughter fragment in its EI-mass spectrum.

Treatment of indium(III) chloride with Li(L), prepared *in situ* from the β-dialdimine H(L) (**1**) and $LiBu^n$, gave (i in Scheme 1) the key heterobimetallic (In/Li) complex **6** in high yield. Complex **6** was the precursor to each of the complexes **7–11**, **13** and **14** and indirectly (*via* **11**) to **12**. Thus, **6** with the appropriate alkali metal amide gave **7**, **8** or **9** (ii, iii or iv, respectively in Scheme 1); and **9** in moist air afforded (v in Scheme 1) **10**. Reduction of **6**, using sodium, gave (vi in Scheme 1), **11** in reasonable yield as the 1:1 thf adduct **11a**. Solvent-free crystals **11b** were isolated (vii in Scheme 1) in low yield by thermal In–N homolysis of **9**, while the hexane-solvate crystals **11c** were obtained (viii in Scheme 1) in good yield, together with metallic indium, from indium(I) chloride and Na(L). Oxidation of **11** with sulfur furnished (ix in Scheme 1) the bis[indium(III)] sulfide **12**. Chloride bridge-splitting of **6** by tmeda afforded (x in Scheme 1) the mononuclear In(III) dichloride **13**. Attempted reduction of **6** by hexamethylditin failed,

Table 3 Selected bond lengths (Å) and angles (°) for **4** and **5**

	4 M = Al	**5** M = Ga		**4** M = Al	**5** M = Ga
M–N1	1.8808(14)	1.924(2)	C1–C2	1.398(2)	1.396(4)
M–N2	1.8801(13)	1.923(2)	C2–C3	1.395(2)	1.399(4)
N1–C1	1.329(2)	1.327(3)	M–Cl1	2.1195(6)	2.1644(8)
N2–C3	1.330(2)	1.325(3)	M–Cl2	2.1143(7)	2.1544(7)
N1–C10	1.4597(19)	1.455(3)	C2–C4	1.488(2)	1.492(4)
N2–C22	1.4579(19)	1.458(3)			
N1–M–N2	96.91(6)	97.26(9)	N1–C1–C2	126.03(15)	126.8(2)
M–N1–C1	121.59(10)	120.48(17)	N2–C3–C2	127.28(14)	127.9(2)
M–N2–C3	120.64(10)	119.75(17)	N1–M–Cl1	112.37(5)	112.28(7)
C1–C2–C3	122.07(14)	123.1(2)	N1–M–Cl2	112.16(5)	112.14(7)
M–N1–C10	122.41(10)	121.18(16)			

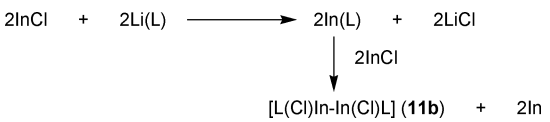


Scheme 1 Preparation of the β-dialdiminatoindium compounds **6–13** [L = η^2-{N(C$_6$H$_3$Pr$^i_2$-2,6)C(H)}$_2$CPh] and the InCl$_3$ complex **14**. *Reagents and conditions*: i, Li(L), Et$_2$O, 25 °C; ii, K[N(H)(C$_6$H$_3$Pr$^i_2$-2,6)], Et$_2$O, 25 °C; iii, 2 K[N(H)(C$_6$H$_3$Pr$^i_2$-2,6)], Et$_2$O, 25 °C; iv, Li[N(SiMe$_3$)(C$_6$H$_3$Pr$^i_2$-2,6)], Et$_2$O, 25 °C; v, moist air; vi, Na, Et$_2$O, then thf; vii, PhMe, 100 °C; viii, Na(L), thf, then InCl, 25 °C; x, tmeda, Et$_2$O; xi, tmeda, Et$_2$O, then (SnMe$_3$)$_2$, thf, 50 °C.

the isolated very low yield product was the cyclodistannoxane-bridged bis[trichloroindium(III)] complex **14** (xi in Scheme 1). Although the mechanism of its formation remains obscure, its structure may be of some interest.

It is noteworthy that compound **6** has an In^{III}(μ-Cl)$_2$Li core, a structural feature, which is very rare in β-diketiminatometal(III) chemistry. There are only few X-ray-characterised β-diketiminato complexes having an M^{III}(μ-Cl)$_2$Li core, mainly with a less bulky substituents on the nitrogen atoms.[12] Furthermore, as evident from Scheme 1, **6** is a valuable substrate for a range of β-dialdiminatoindium compounds.

The indium(III) amides **7**, **8** and **9** and the bridged sulfide **12** are of interest since, we believe, there are no β-diketiminatoindium amides or a sulfide in the literature. However, each of the (μ-OH)$_2$-bridged di[indium(III)] compound **10** and the di[indium(II)] complex **11** has a single precedent. Thus, Stender and Power showed that treatment of indium(I) chloride with Li(L^1) gave not only indium metal but also the crystalline compounds [L^1(Cl)In–In(Cl)L^1] (16%) and [{In(Cl)(L^1)(μ-OH)}$_2$] (15%) [L^1 = {N(C$_6$H$_3$Pr$^i_2$-2,6)C(Me)}$_2$CH].[13] The latter was presumably (like **10**) formed by inadvertent hydrolysis. This L^1 reaction parallels that of viii in Scheme 1, in which the formation of **11b** and indium metal, each in good yield, supports the view that the course of the reaction may have followed the pathway shown in Scheme 2.



Scheme 2 Proposed reaction pathway for reaction viii of Scheme 1.

The preparation of **11**, as the crystalline **11b** (vi in Scheme 1) by reduction of [InCl$_2$(L)(tmeda)] (**13**) with metallic sodium, contrasts with the report that In(L^1)X$_2$ (X = Cl or I) with Na or K gave indium metal and H(L^1).[13] There is circumstantial support for the notion that In(L) was an intermediate, since Hill and Hitchcock have shown that the crystalline indium(I) β-diketiminate In(L^1) was obtained from InI, K[N(SiMe$_3$)$_2$] and H(L^1).[8] Using this procedure, but with less sterically hindered β-diketiminato ligands [L^6]$^-$ and [L^7]$^-$ Hill *et al.* obtained the X-ray-characterised compounds [(L^6)InIn(L^6)] and [{(L^7)(I)In}$_2${(μ-L^7)In}$_4$] [L^6 = {N(C$_6$H$_2$Me$_3$-2,4,6)C(Me)}$_2$CH, L^7 = {N(C$_6$H$_3$Me$_2$-3,5)C(Me)$_2$}CH].[14]

Although a bis[β-diketiminatoindium(III)] sulfide is presently unknown, an oxygen analogue [{In(Cl)(L^2)}$_2$(μ-O)] is well documented, [L^2 = {N(C$_6$H$_4$Me-4)C(Me)}$_2$CH].[15] Several β-diketiminatoindium(III) halides, related to **13**, are known, including [InCl$_2$(L^1)],[11b] [InI$_2$(L^1)],[11b] and [InI$_2$(L^2)].[15] Whereas cyclodistannoxanes are rare and require sterically demanding substituents at the tin(IV) atoms, as in [Sn{CH(SiMe$_3$)$_2$}(μ-O)]$_2$,[16] there are examples of complexes in which a much less bulky analogue acts as an O,O′-bridging ligand, as in [{SnBu$^t_2$(Cl)$_2$}$_2${μ-(SnMe$_2$(μ′-O))$_2$}][17a] and [{SnCl$_2$(Me)$_2$}$_2${μ-(SnMe$_2$(μ′-O))$_2$}].[17b]

Selected molecular structural data for compounds **6**, **8**, **10**, **11a**, **12** and **14** are shown in Tables 4–9, respectively, with ORTEP representations shown in the corresponding Fig. 4–9. Such data on **11b** and **11c**, solvates of **11**, are provided in the ESI.† As for compounds **2–5**, conformational aspects of the In(L) fragment of each of **6**, **8**, **10**, **11a** and **12** are summarised in Table 10 and are discussed in the next section of the "results and discussion" portion of this paper, together with a consideration of the geometric parameters for the In(L) moieties.

Table 4 Selected bond lengths (Å) and angles (°) for **6**

In–N1	2.187(2)	C2–C4	1.501(3)
In–N2	2.218(2)	In–Cl1	2.4481(7)
N1–C1	1.330(3)	In–Cl2	2.3782(7)
N2–C3	1.314(3)	In–Cl3	2.4982(8)
N1–C10	1.438(3)	Li–Cl1	2.385(5)
N2–C22	1.436(3)	Li–Cl3	2.361(5)
C1–C2	1.390(4)	Li–O1	1.928(5)
C2–C3	1.408(4)	Li–O2	1.931(5)
N1–In–N2	83.67(8)	N1–In–Cl3	88.82(6)
In–N1–C1	120.02(18)	Cl2–In–Cl3	100.15(3)
In–N2–C3	123.70(15)	Cl2–In–Cl1	105.38(3)
C1–C2–C3	123.2(2)	In–Cl1–Li	90.56(12)
In–N1–C10	123.70(15)	In–Cl3–Li	89.92(13)
N1–C1–C2	129.1(2)	Cl1–Li–Cl3	86.69(6)
N2–C3–C2	127.5(2)	Cl1–Li–O1	108.2(2)
N1–In–Cl1	146.01(6)	Cl1–Li–O2	113.6(2)
N1–In–Cl2	108.61(6)	O1–Li–O2	116.1(3)

Table 5 Selected bond lengths (Å) and angles (°) for **8**

In–N1	2.166(2)	In–N3	2.081(2)
In–N2	2.150(2)	In–N4	2.078(2)
N1–C1	1.319(3)	N3–C34	1.400(3)
N2–C3	1.325(3)	N4–C46	1.408(3)
N1–C10	1.448(3)	C2–C3	1.396(4)
N2–C22	1.446(3)	C2–C4	1.405(4)
C1–C2	1.405(4)		
N1–In–N2	87.10(7)	N1–In–N3	107.12(9)
In–N1–C1	121.70(17)	N1–In–N4	112.84(8)
In–N2–C3	122.85(17)	N2–In–N3	123.96(9)
C1–C2–C3	123.9(2)	N2–In–N4	103.22(9)
In–N1–C10	120.11(15)	N3–In–N4	118.47(10)
N1–C1–C2	128.7(2)	In–N3–C34	132.16(18)
N2–C3–C2	128.1(2)	In–N4–C46	119.05(17)
In–N2–C22	118.55(15)	C3–N2–C22	118.1(2)
C1–N1–C10	118.2(2)	C3–C2–C4	119.3(2)
C1–C2–C4	116.4(2)		

Table 6 Selected bond lengths (Å) and angles (°) for **10**[a]

In–N1	2.1857(15)	In–Cl	2.3653(5)
In–N2	2.1512(15)	In–O1	2.0954(13)
N1–C1	1.318(2)	In–O1′	2.1523(13)
N2–C3	1.330(2)	C1–C2	1.403(2)
N1–C10	1.449(2)	C2–C3	1.399(3)
N2–C22	1.447(2)		
N1–In–N2	86.34(6)	N1–C1–C2	128.12(17)
In–N1–C1	123.45(12)	N2–C3–C2	128.33(17)
In–N2–C3	123.44(12)	C1–C2–C4	117.54(16)
C1–C2–C3	124.11(11)	C3–C2–C4	117.80(16)
In–N1–C10	120.16(11)	N1–In–Cl	106.43(4)
In–N2–C22	121.22(11)	N2–In–Cl	110.19(4)
C1–N1–C10	116.37(15)	N1–In–O1′	153.35(6)
C3–N2–C22	115.15(15)	N2–In–O1′	90.25(5)
O1–In–O1′	72.61(6)	In–O1–In′	107.39(6)
N1–In–O1	93.68(5)	N2–In–O1	140.69(6)
O1–In–Cl	107.46(4)	O1′–In–Cl	99.55(4)

[a] Symmetry transformations to generate equivalents atoms: ′ $-x, -y, -z$.

The molecular structure of $[In(Cl)(L)(\mu\text{-}Cl)_2Li(OEt_2)_2]$ (**6**) (Fig. 4 and Table 4) has the five-coordinate distorted square pyramidal (the terminal Cl2 atom is quasi-axial) In atom and the four-coordinate distorted Li atom as part of the buckled four-membered InCl1LiCl3 ring; this has a fold angle of 22.81(12)° through the Cl1–Cl3 vector. The In–Cl1(or Cl3) bridge bonds are *ca.* 0.2 Å longer than the terminal In–Cl2 bond.

Table 7 Selected bond lengths (Å) and angles (°) for **11a**[a]

In–N1	2.164(2)	C1–C2	1.393(4)
In–N2	2.159(2)	C2–C3	1.402(4)
N1–C1	1.321(4)	C2–C4	1.494(4)
N2–C3	1.320(3)	In–Cl	2.4009(7)
N1–C10	1.450(3)	In–In′	2.7575(4)
N2–C22	1.444(3)		
N1–In–N2	87.55(8)	N1–In–Cl	103.01(6)
In–N1–C1	121.11(18)	N2–In–Cl	98.85(6)
In–N2–C3	121.00(18)	N1–In–In′	123.23(6)
C1–C2–C3	123.9(3)	N2–In–In′	124.44(6)
In–N1–C10	124.24(17)	C1–C2–C4	118.5(2)
In–N2–C22	122.32(17)	C3–C2–C4	116.9(2)
N1–C1–C2	129.0(3)	Cl–In–In′	114.31(2)
N2–C3–C2	128.6(3)		

[a] Symmetry transformations to generate equivalents atoms: ′ $-x + 1, -y, -z$.

Table 8 Selected bond lengths (Å) and angles (°) for **12**

In1–N1	2.147(2)	In2–N3	2.140(2)
In1–N2	2.142(2)	In2–N4	2.145(2)
N1–C1	1.313(4)	N3–C34	1.317(4)
N2–C3	1.320(4)	N4–C36	1.322(4)
N1–C10	1.450(4)	N3–C43	1.446(4)
N2–C22	1.447(4)	N4–C55	1.434(4)
C1–C2	1.403(4)	C34–C35	1.408(4)
C2–C3	1.402(4)	C35–C36	1.406(4)
C2–C4	1.493(4)	C35–C37	1.494(4)
In1–Cl1	2.3454(8)	In2–Cl2	2.3540(9)
In1–S	2.3691(8)	In2–S	2.3640(8)
N1–In1–N2	87.50(9)	N3–In2–N4	88.31(9)
In1–N1–C1	122.95(19)	In2–N3–C34	120.5(2)
In1–N2–C3	122.9(2)	In2–N4–C36	121.83(19)
In1–S–In2	100.47(3)	N3–C34–C35	129.4(3)
N1–C1–C2	128.3(3)	N4–C36–C35	127.6(3)
N2–C3–C2	128.4(3)	C34–C35–C36	123.9(3)
C1–C2–C3	124.0(3)	In2–N3–C43	120.27(18)
In1–N1–C10	118.01(18)	In2–N4–C55	119.01(18)
In1–N2–C22	119.28(18)	N3–In2–Cl2	105.69(7)
N1–In1–Cl1	110.59(7)	N4–In2–Cl2	111.51(7)
N2–In1–Cl1	109.08(7)	N3–In2–S	126.22(7)
N1–In1–S	110.48(7)	N4–In2–S	104.43(7)
N2–In1–S	120.60(7)	Cl2–In2–S	116.54(3)
Cl1–In1–S	115.16(3)	C34–C35–C37	117.9(3)
C1–C2–C4	117.3(3)	C36–C35–C37	118.0(3)
C3–C2–C4	118.4(3)		

The molecular structure of $[In(L)\{N(H)(C_6H_3Pr^i_2\text{-}2,6)\}_2]$ (**8**) (Fig. 5 and Table 5) has the four-coordinate distorted tetrahedral In atom as part of an InN4 core. The bonds to the amido ligands, In–N3(or N4) are almost 0.1 Å shorter than those to the β-dialdiminato ligand, In–N1(or N2). The three widest angles subtended at the In atom decrease in the sequence N2–In–N3 > N3–In–N4 > N1–In–N4. The angle In–N–C subtended at N3 is very much wider than that at N4.

The molecular structure of the centrosymmetric $[\{In(Cl)(L)(\mu\text{-}OH)\}_2]$ (**10**) (Fig. 6 and Table 6) has the five-coordinate distorted square pyramidal (the terminal Cl or Cl′ atom is quasi-axial) In and In′ atoms at the centre of a spiro junction, the InO1In′O1′ rhomboid being its core. The In–Cl distance is closely similar to the terminal In–Cl (In–Cl2) in **6**. Likewise, each of the geometric

Table 9 Selected bond lengths (Å) and angles (°) for **14**

In1–N1	2.315(7)	In2–N3	2.331(7)
In1–N2	2.381(6)	In2–N4	2.359(6)
In1–Cl1	2.450(2)	In2–Cl4	2.4520(19)
In1–Cl2	2.522(2)	In2–Cl5	2.524(2)
In1–Cl3	2.548(2)	In2–Cl6	2.535(2)
In1–O1	2.104(5)	In2–O2	2.111(5)
Sn1–O1	2.048(5)	Sn2–O1	2.040(5)
Sn1–O2	2.044(5)	Sn2–O2	2.049(5)
N1–In1–N2	77.7(2)	N3–In2–N4	77.5(2)
In1–O1–Sn1	124.9(2)	In2–O2–Sn1	126.2(2)
Cl1–In1–Cl2	91.78(8)	In2–O2–Sn2	125.0(2)
Cl1–In1–Cl3	91.56(8)	Cl4–Sn2–Cl5	101.43(13)
Cl2–In1–Cl3	166.70(8)	Cl4–Sn2–Cl6	90.14(7)
Cl1–In1–O1	101.85(13)	Cl6–Sn2–Cl5	169.04(8)
Cl2–In1–O1	83.64(15)	Cl4–In2–O2	84.31(15)
Cl3–In1–O1	83.08(15)	Cl5–In2–O2	84.31(15)
O1–Sn1–O2	77.9(2)	Cl6–In2–O2	84.78(15)
Sn1–O1–Sn2	101.0(2)	O1–Sn2–O2	77.9(2)
O1–In1–N1	167.4(2)	Sn1–O2–Sn2	100.9(2)
Cl1–In1–N2	168.38(17)		

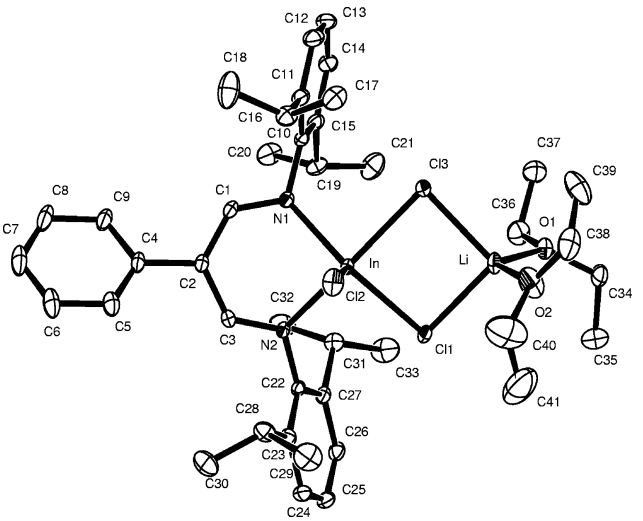


Fig. 4 The molecular structure of **6** (30% probability ellipsoids).

parameters of **10** and of [{In(Cl)(L^1)(μ-OH)}$_2$][L^1 = {N(C$_6$H$_3$Pr$^i_2$-2,6)C(Me)}$_2$CH],[13] excluding the substituents at the β- and γ-positions of the L$^-$ or [L^1]$^-$ ligand, are markedly similar.

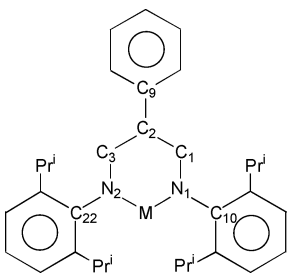
The molecular structure of the centrosymmetric binuclear In(II) compound [L(Cl)In–In(Cl)L] (**11a**) has the four-coordinate distorted tetrahedral In and In′ atoms joined by the In–In′ bond. The widest angles subtended at the In atom are N1(or N2)–In–In′ and the narrowest is the chelating ligand's bite angle N1–In–N2. The In^{II}–Cl bond of **11a** is longer than the In^{III}–Cl bond of **10**. Each of the geometric parameters of **11a** is essentially identical to those of **11b** and **11c** (see ESI†) and also similar, excluding the substituents at the β- and γ-positions of the L$^-$ or [L^1]$^-$ ligand, to those of [L^1(Cl)In–In′(Cl)L^1];[13] *e.g.*, the In–In′ distance in the latter is 2.8342(7) Å.

The molecular structure of the binuclear In(III) sulfide [{In(Cl)L}$_2$(μ-S)] (**12**) (Fig. 8 and Table 8) has the four-coordinate distorted tetrahedral In1 and In2 atoms bridged by a sulfide. The six angles subtended at In1 (or In2) range from 87.5° (or 88.3°) to 120.6° (or 126.2°), with an average of 109° (or 108.8°); hence it is concluded that each of the formally In(III) lone pairs is implicated in π-bonding. The In–Cl distances in **12** are *ca.* 0.015 Å shorter than in **10**. The geometric parameters at the sulfur atom of **12** may be compared with those in [{In(CH(SiMe$_3$)$_2$)$_2$(μ-S)}$_2$].[18] In the latter, the sulfur atom was disordered between two positions, with the angle In1–S–In2 112.4(1) and 116.8(2)° and the distances In1–S 2.419(3) and 2.356(4) Å and In2–S 2.433(3) and 2.376(4) Å.

The molecular structure of the cyclobis(dimethylstannoxane)-bridged bis(trichloroindium) complex [{InCl$_3$(tmeda)}$_2${μ-(OSnMe$_2$)$_2$}] (**14**) (Fig. 9 and Table 9) has the six-coordinate

Table 10 Conformation of the β-dialdiminatometal fragment of crystalline **2–6**, **8**, **10**, **11a** and **12**

Compound	No.	*a*/Å	*b*/Å	*c*/Å	*d*/Å	*e*/°	*f*/°	*g*/°
[Li(L)(thf)$_2$]	**2**	0.073	0.808	−0.197	−0.357	26.6	81.0	83.0
[Li(L)(tmeda)]	**3**	−0.084	−0.662	0.365	0.205	40.0	79.3	61.6
[Al(L)Cl$_2$]	**4**	0.103	0.399	−0.373	−0.372	46.9	86.5	87.6
[Ga(L)Cl$_2$]	**5**	0.111	0.369	−0.396	−0.377	47.5	87.5	87.1
[In(Cl)(L)(μ-Cl)$_2$Li(OEt$_2$)$_2$]	**6**	−0.122	−0.834	0.331	0.267	40.3	74.3	85.4
[In(L){N(H)(C$_6$H$_3$Pr$^i_2$-2,6)}$_2$]	**8**	0.153	0.537	−0.547	−0.374	40.4	71.4	89.6
[{In(Cl)(L)(μ-OH)}$_2$]	**10**	0.069	0.535	−0.283	−0.368	40.0	89.0	89.9
		−0.145	−0.616	0.385	0.416	39.3	78.9	88.5
[L(Cl)In–In(Cl)L]	**11a**	−0.091	−0.626	0.391	0.379	44.8	85.4	83.4
		−0.085	−0.487	0.307	0.377	39.5	87.8	88.2
[{In(Cl)L}$_2$(μ-S)]	**12**	−0.114	−0.487	0.376	0.270	39.0	88.8	78.5
		−0.117	−0.592	0.214	0.450	39.6	80.4	74.8



N1C1C3N2 coplanar; atoms out of plane (Å) C2, *a*; M, *b*; C22, *c*; C10, *d*
Dihedral angles (°): C4 to C9/C1C2C3, *e*; C22 to C27/MN2C3, *f*; C10 to C15/MN1C1, *g*

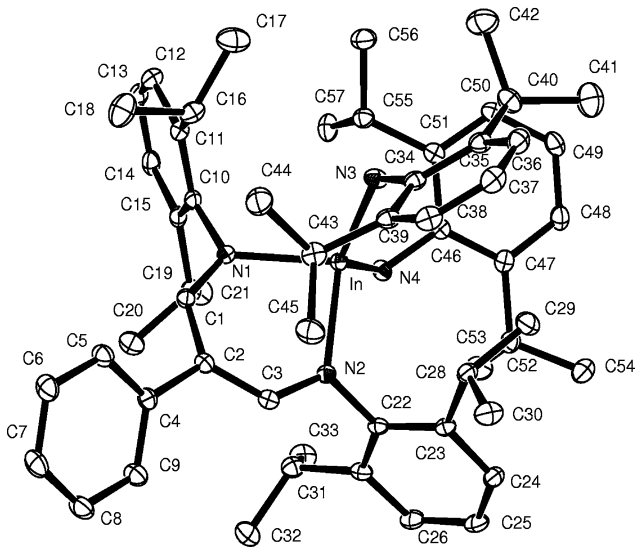
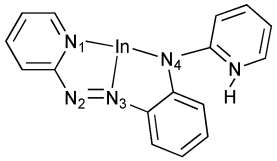
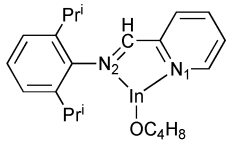


Fig. 5 The molecular structure of **8** (30% probability ellipsoids).

distorted octahedral In1 and In2 atoms bridged through the O1 and O2 atoms of the cyclodistannoxane. At In1, the atoms N1, N2 and Cl2 are mutually transoid with respect to the O1, Cl1 and Cl3 atoms, respectively; and for In2, the corresponding *trans*-pairs are N3/O2, N4/Cl4 and Cl5/Cl6. The In–Cl bond *trans* to an N atom is *ca.* 0.07 Å shorter than that *trans* to a Cl atom, while the In–N bond *trans* to an O atom is *ca.* 0.08 Å shorter than to a Cl atom. The coordination environment at each In atom of **14** may be compared to that in $InCl_3(HX)$] [In(HX) = **VI**, with the atoms N4/N1, N3/Cl2 and Cl1/Cl3 mutually *trans*],[19] [$InCl_3(Y)$] [In(Y) = **VII**, with the atoms N1/Cl2, N2/Cl3 and Cl1/O mutually *trans*],[20] and [*mer*-$InCl_3(py)_3$] (**VIII**)[21a] or its 4-EtC_5H_4N analogue.[21b] For [$InCl_3(HX)$] the In–Cl distances are 2.5775(7), 2.3876(7) and 2.4968(7) for Cl1, Cl2 and Cl3, respectively, and In–N3 2.577(9) Å;[19] for [$InCl_3(Y)$], the In–Cl1, In–Cl2, In–Cl3, In–O, In–N1 and In–N2 distances are 2.4381(13), 2.4103(13), 2.4405(13), 2.396(3), 2.306(4) and 2.348(4) Å, respectively;[20] and for [*mer*-$InCl_3(py)_3$], the In–Cl1, In–Cl2, In–N1 and In–N2 distances are 2.471(8), 2.476(2), 2.377(21) and 2.302(7) Å, respectively.[21a] The geometric parameters of the Sn1O1Sn2O2 ring of the coordinated cyclodistannoxane of **14** may be compared with those in [{$SnCl_2(Me)_2$}$_2${μ-($SnMe_2$(μ′-O))$_2$}] [having Sn–O 2.062(3) Å, O–Sn–O′ 74.2(3)° and Sn–O–Sn′ 105.8(3)°,[17b]] and [{$SnMe_2$(nap)}$_2$O]$_2$, having a mean Sn–O distance of 2.099 Å and a mean O–Sn–O′ angle of 76.8° (nap = (*S*)-(+)-6-methoxy-α-methyl-2-naphthaleneaceto anion).[22]



VI



VII

The geometric parameters of the M(L) fragment in 2–6, 8 and 10–12

The conformation of the M(L) fragment in **2–6**, **10**, **11a** and **12** is summarised in Table 10. In each of these crystalline complexes, the α-(N1 and N2) and γ-(C1 and C2) atoms are essentially coplanar. The MN1C1C2C3N2 six-membered ring is then either of the half-chair or boat conformation; the former is found in **2** and **3** (M = Li) and **11a** (M = In) with M (*b* in Table 10) out of the N1C1C2C3N2 near-plane, and the latter with $b > a$ (C2 in Table 10) and both out of the N1C1C3N2 plane. The aryl substituents at N1 and N2 (*c* and *d*, respectively in Table 10) are *cis* to one another but *trans* to C2 and M. The dihedral angle (*e* in Table 10) between the phenyl ring at C2 and the C1C2C3 plane is 43.5 ± 4.5° for each except **2** (*e* = 26.6°). The aryl substituents at N1 and N2 tend towards orthogonality with respect to the MN1C1 and MN2C3 planes, respectively (*g* and *f* in Table 10); with **3** and **12** being exceptions for *g*, and **8** and **6** for *f*.

The endocyclic bond lengths in the MN1C1C3C2N2 ring reveal that in each of the crystalline complexes **2–6**, **8** and **10–12** there is π-delocalisation, as evident from the almost identical bond lengths in each of the M–N1/M–N2, N1–C1/N2–C3 and C1–C2/C2–C3

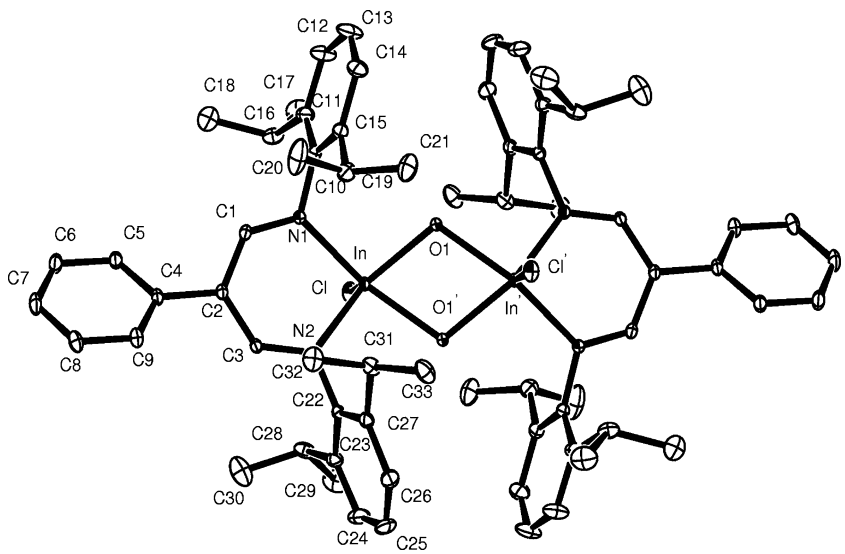


Fig. 6 The molecular structure of **10** (30% probability ellipsoids).

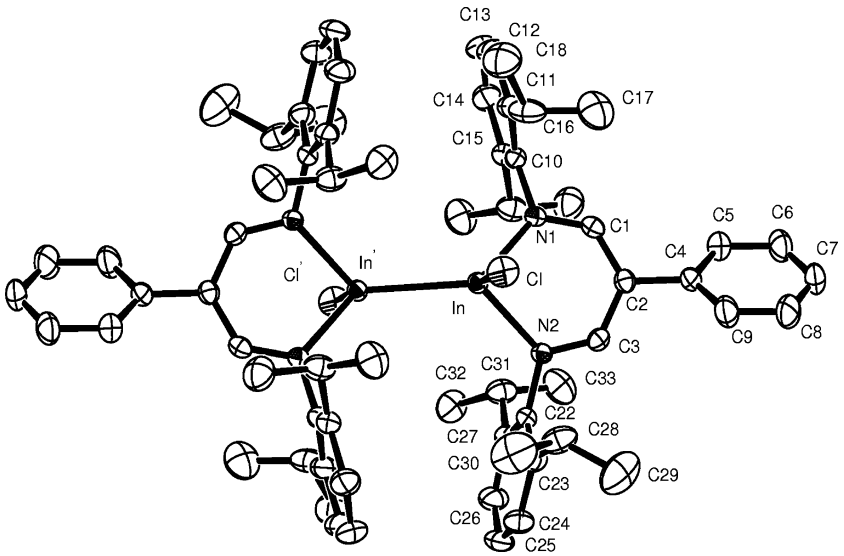


Fig. 7 The molecular structure of **11a** (50% probability ellipsoids).

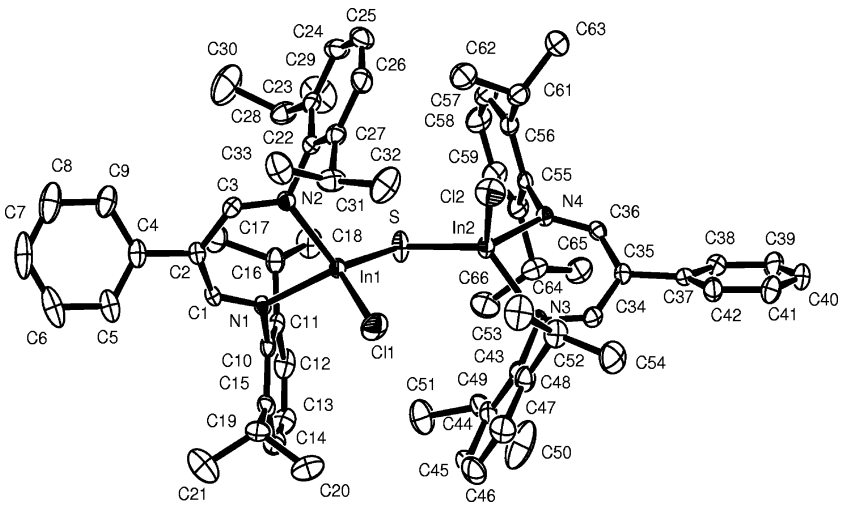


Fig. 8 The molecular structure of **12** (50% probability ellipsoids).

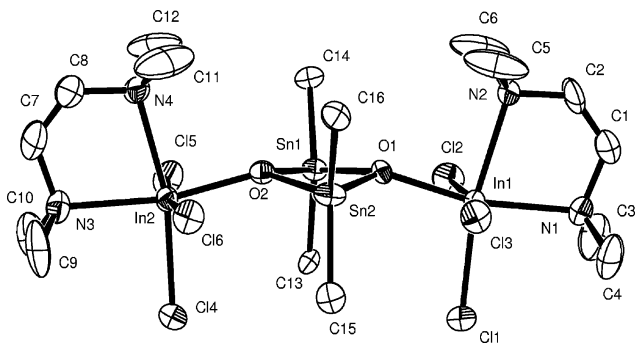


Fig. 9 The molecular structure of **14** (50% probability ellipsoids).

pairs; the latter two pairs shown distances intermediate between single and double bonds. Likewise, the bond angles in each of the pairs M–N1–C1/M–N2–C3 and N1–C1–C2/N2–C3–C2 are closely similar.

Comparison between the ligated $[\{N(C_6H_3Pr^i_2\text{-}2,6)C(H)\}_2\text{-}CPh]^-$ (≡ L^-) and $[\{N(C_6H_3Pr^i_2\text{-}2,6)C(Me)\}_2CH]^-$ [≡ $(L^1)^-$] is available for the pairs of metal complexes **2/IV** (Li), **4/Va** (Al), **5/Vb** (Ga), **10**/$[\{In(Cl)(L^1)(\mu\text{-}OH)\}_2]$,[13] and **11a**/$[L^1(Cl)In\text{–}In(Cl)L^1]$.[13] Each of the $M(L^1)$ complexes has the MN1C1C2C3N2 ring in the half-chair conformation with M 0.525 Å (Al), 0.507 Å (Ga), 0.800 and 0.895 Å (In hydroxide) and 0.626 Å (In^{II}_2 complex) out of the N1C1C2C3N2 plane. The aryl substituents at N1 and N2 of the $M(L^1)$ complexes are almost orthogonal to the N1MN2 plane. The endocyclic bond lengths in these M(L) and $M(L^1)$ complexes are similar, except for the M–N bonds which are longer in the former. The endocyclic bond angles, however, are significantly different: that subtended at M, N and C2 is wider for $M(L^1)$ than M(L) complexes, whereas the reverse order is found for that at C1 and C3.

In conclusion, we report the synthesis, characterisation and structures of eleven crystalline metal complexes of the ligand $[\{N(C_6H_3Pr^i_2\text{-}2,6)C(H)\}_2CPh]^-$ (≡ L^-) **2–8** and **10–12** in which M = Li (**2**, **3**), Al (**4**), Ga (**5**), In^{III} (**6–8**, **10**, **12** and **13**)

and In^{II} (**11**). Elemental (C, H, N) analysis (**4**, **6–8** and **11–13**), EI-MS (**4**, **6–8** and **10–13**), ^{27}Al (**4**) and ^{1}H and ^{13}C solution NMR spectral data (**2–8** and **11–13**) are presented. The X-ray molecular structures of crystalline H(L) (**1**), **2–6**, **8** and **10–13** show endocyclic π-delocalisation; that of $[\{InCl_3(tmeda)\}_2\{\mu\text{-}(OSnMe_2)_2\}]$ (**14**) is also described. The endocyclic MN1C1C2C3N2 six-membered M(L) ring has either the half-chair (**2**, **3** and **11a**) or boat (**4–8**, **10** and **13**) conformation, with M out of the N1C1C3N2 plane for each and C2 also out of this plane for the boat (the deviation from the plane being greater for M than C2). The data for the M(L) and the $M[\{N(C_6H_3Pr^i_2\text{-}2,6)C(Me)\}_2CH]$ [≡ M(L^1)] ring are compared for the isoleptic L^1 analogues of **2**, **4**, **5**, **10** and **11**, in which the major differences are the endocyclic bond angles subtended at M, N1, N2 and C2 [wider for M(L^1) than M(L)] and the reverse for those at C1 and C3.

Experimental

General remarks

All manipulations were performed under argon using standard Schlenk techniques. Benzene, diethyl ether, thf and hexane were dried using sodium-potassium alloy and stored over a sodium mirror under argon. Deuterated solvents (C_6D_6, C_7D_8, C_4D_8O and $CDCl_3$) were freeze/thaw degassed and stored over dried 4 Å molecular sieves under an argon atmosphere. $H[\{N(C_6H_3Pr^i_2\text{-}2,6)C(H)\}_2CPh]$ [≡ H(L)] (**1**),[6] Li(L),[6] and $HN(C_6H_3Pr^i_2\text{-}2,6)(SiMe_3)$[23] were synthesised by published procedures. The NMR spectra were recorded on a Bruker DPX 300 (300.1 MHz for ^{1}H, 75.5 MHz for ^{13}C and 116.6 MHz for ^{7}Li) or AMX 500 (130.31 MHz for ^{27}Al) instruments and referenced externally (^{7}Li, using LiCl; ^{27}Al, using aqueous $Al(OH)_3$ with a D_2O lock), or internally (^{1}H and ^{13}C) to the residual solvent resonances. Unless otherwise stated, all NMR spectra were measured at 293 K and other than ^{1}H were proton-decoupled. Electron impact mass spectra were taken from solid samples using a Kratos MS 80 RF instrument. Melting points were taken in sealed capillaries and are uncorrected. Elemental analyses were determined by Medac Ltd., Brunel University (analyses for complexes **2** and **3** were not carried out due to their high sensitivity to air and moisture).

Preparations

[Li(L)(thf)$_2$] (2). A solution of n-butyllithium in hexane (3.42 cm^3, 6.0 mmol) was added to a stirred solution of H(L) (2.56 g, 6.0 mmol) in thf (20 cm^3) at 0 °C. After 1 h at *ca.* 25 °C, volatiles were removed *in vacuo* and hexane (15 cm^3) was added. Cooling at −25 °C yielded yellow crystals of **2** (3.71 g, 96%). ^{1}H NMR (C_6D_6): δ 8.09 (s, 2 H, NC*H*); 7.50 (m, 2 H), 7.17 (m, 8 H), 7.00 (m, 1 H) (aryl); 3.49 [sp, 4 H, C*H*Me$_2$, $^{3}J(^{1}H\text{–}^{1}H) = 7.02$], 3.27 (t, 8 H, C$H_2$O), 1.22 [d, 24 H, CH(C$H_3$)$_2$, $^{3}J(^{1}H\text{–}^{1}H) = 6.90$ Hz], 1.17 (q, 8 H, CH_2CH$_2$O); ^{13}C NMR (C_6D_6): δ 161.8 (N*C*H); 152.8, 145.7, 141.8, 129.1, 126.8, 126.0, 123.3 (aryl); 104.7 (*C*Ph), 68.45 (*C*H$_2$O), 28.8 (*C*H$_2$CH$_2$O); 25.7, 25.1, 24.0 (Pr^i).

Li(L)(tmeda) (3). This was obtained in high yield from **2** and tmeda. ^{1}H NMR (C_6D_6): δ 8.20 (s, 2 H, NC*H*), 7.62 [d, 2 H, $J(^{1}H\text{–}^{1}H) = 7.7$], 7.34–7.28 (m, 8 H), 7.12 [t, 1 H, $J(^{1}H\text{–}^{1}H) = 7.3$] (aryl); 3.61 [sp, 4 H, C*H*Me$_2$, $^{3}J(^{1}H\text{–}^{1}H) = 6.7$], 1.89 (s, 16 H, tmeda), 1.38 [d, 24 H, CH(CH_3)$_2$, $^{3}J(^{1}H\text{–}^{1}H) = 6.7$ Hz]; ^{13}C NMR (C_6D_6): δ 162.4 (N*C*H); 153.8, 145.8, 141.4, 128.7, 125.5, 123.7, 123.4, 122.7 (aryl); 103.2 (*C*Ph), 57.1 (tmeda); 28.4, 26.2, 23.3 (Pr^i).

[Al(L)Cl$_2$] (4). Li(L) (0.41 g, 0.76 mmol) was added to $AlCl_3$ (0.10 g, 0.76 mmol) in diethyl ether at 0 °C. The mixture was stirred at *ca.* 25 °C for *ca.* 12 h, then filtered. Volatiles were removed *in vacuo* from the filtrate. The residue was extracted with pentane. The extract was stored at −25 °C, yielding blue crystals of 4 (0.39 g, 87%) (Found: C, 70.6; H, 7.64; N, 4.77. $C_{33}H_{41}AlCl_2N$ requires C, 70.3; H, 7.33; N, 4.97%), mp 176 °C. ^{1}H NMR (C_6D_6): δ 7.83 (s, 2 H, NC*H*), 7.54–7.00 (m, 11 H, aryl), 3.67 [sp, 4 H, C*H*Me$_2$, $3J(1H\text{–}1H) = 7.02$], 1.43 [d, 12 H, CH(CH_3), $^{3}J(^{1}H\text{–}^{1}H) = 7.02$], 1.11 [d, 12 H, CH(C$H_3$), $^{3}J(^{1}H\text{–}^{1}H) = 6.55$ Hz]; ^{13}C NMR (C_6D_6): δ 165.5 (N*C*H); 144.6, 141.4, 137.9, 129.4, 128.7, 126.7, 124.7 (aryl); 109.2 (*C*Ph); 25.6, 23.5, 23.3 (Pr^i); ^{27}Al NMR (C_6D_6): δ 100.55; MS (**M** denotes the parent) *m*/*z* (% and assignment): 562 (100, **M**$^+$), 527 (7, [**M** − Cl]$^+$).

Ga(L)Cl$_2$ (5). Similarly, from of Li(L) (0.64 g, 1.2 mmol) and $GaCl_3$ (0.21 g, 1.2 mmol) colourless crystals of **5** (0.69 g, 90%) were obtained. ^{1}H NMR (C_6D_6): δ 7.82 (s, 2 H, NC*H*), 7.25–7.00 (m, 11 H, aryl), 3.68 [sp, 4 H, C*H*Me$_2$, $^{3}J(^{1}H\text{–}^{1}H) = 6.83$], 1.47 [d, 12 H, CH(C$H_3$), $^{3}J(^{1}H\text{–}^{1}H) = 6.83$], 1.09 [d, 12 H, CH(C$H_3$), $^{3}J(^{1}H\text{–}^{1}H) = 6.83$ Hz]; ^{13}C NMR (C_6D_6): δ 164.5 (N*C*H); 144.6, 138.4, 129.3, 128.8, 126.6, 126.5, 124.6 (aryl); 107.6(*C*Ph); 25.8, 25.5, 23.5, 23.3 (Pr^i).

[In(Cl)(L)(μ-Cl)$_2$Li(OEt$_2$)$_2$] (6). A solution of *n*-butyllithium in hexane (2.5 cm^3, 4.00 mmol) was added dropwise with stirring to a solution of H(L) (**1**) (1.52 g, 3.26 mmol) in diethyl ether (20 cm^3) at 0 °C. Stirring was continued for *ca.* 2 h at *ca.* 25 °C, then the solution was added dropwise to a suspension of $InCl_3$ (0.73 g, 3.30 mmol) in diethyl ether (20 cm^3). The mixture was set aside for *ca.* 48 h and then filtered. Concentration of the filtrate *in vacuo* yielded yellow crystals of **6** (2.19 g, 80%) (Found: C, 58.75; H, 6.98; N, 3.18. $C_{41}H_{61}Cl_3InLiN_2O_2$ requires C, 58.5; H, 7.30; N, 3.33%), mp 61–62 °C (decomp.). ^{1}H NMR (C_6D_6): δ 7.75 (s, 2 H, NC*H*), 7.13–7.00 (m, 11 H, aryl), 3.68 [sp, 4 H, C*H*Me$_2$, $^{3}J(^{1}H\text{–}^{1}H) = 6.7$], 3.26 [q, 8 H, OC$H_2$, $^{3}J(^{1}H\text{–}^{1}H) = 7.0$], 1.38 [d, 12 H, CH(C$H_3$), $^{3}J(^{1}H\text{–}^{1}H) = 6.7$], 1.12 [t, 12 H, OCH$_2CH_3$, $^{3}J(^{1}H\text{–}^{1}H) = 7.0$], 1.04 [d, 12 H, CH(C$H_3$), $^{3}J(^{1}H\text{–}^{1}H) = 6.7$ Hz]; ^{13}C NMR (C_6D_6): δ 166.2 (N*C*H); 143.7, 139.8, 129.3, 128.4, 127.0, 126.4, 124.6 (aryl); 106.8 (*C*Ph); 65.9 (O*C*H$_2$); 29.0, 25.6, 23.3 (Pr^i); 15.5 (OCH$_2$*C*H$_3$). MS (**M** denotes the parent) *m*/*z* (% and assignment): 650 (83, [**M** − LiCl − 2Et$_2$O]$^+$).

[In(Cl)(L){N(H)(C$_6$H$_3$Pr$^i_2$-2,6)}] (7). A solution of **6** (1.10 g, 1.31 mmol) in diethyl ether (20 cm^3) was added to a stirred suspension of K[N(H)(C$_6$H$_3$Pr$^i_2$-2,6)] (0.28 g, 1.30 mmol) in Et$_2$O (20 cm^3) at *ca.* 25 °C. The mixture was set aside for 24 h with stirring, then filtered. The yellow filtrate was concentrated to yield yellow microcrystals of 7 (0.73 g, 71%) (Found: C, 68.2; H, 7.67; N, 5.04. $C_{45}H_{59}ClInN_3$ requires C, 68.2; H, 7.51; N, 5.30%), mp 214–216 °C. ^{1}H NMR (C_6D_6): δ 7.80 (s, 2 H, NC*H*), 7.16–6.91 (m, 14 H, aryl), 3.78 (sp, 2 H, C*H*Me$_2$), 3.48 (sp, 2 H, C*H*Me$_2$), 3.05 (s, 1 H, N*H*), 2.35 (sp, 2 H, C*H*Me$_2$), 1.42 (d, 6 H, CHCH_3), 1.31 (d, 6 H, CHCH_3), 1.07 (d, 12 H, CHCH_3), 0.95 (d, 12 H, CHCH_3); ^{13}C NMR (C_6D_6): δ 165.5 (N*C*H); 145.0, 144.1, 143.0, 137.9, 129.2, 127.9, 126.8, 126.1, 125.4, 123.9, 123.0, 120.2 (aryl); 106.8 (*C*Ph); 29.6, 28.8, 28.4, 25.9, 25.7, 24.0, 23.8, 22.5 (Pr^i). MS

(**M** denotes the parent) *m*/*z* (% and assignment): 791 (21, $\mathbf{M}^+$), 756 (12, [**M** − Cl]$^+$), 615 (92, [**M** − N(H)($C_6H_3Pr^i_2$-2,6)]$^+$).

[In(L){N(H)($C_6H_3Pr^i_2$-2,6)}$_2$] (8). K[N(H)($C_6H_3Pr^i_2$-2,6)] (0.72 g, 3.34 mmol) was added to a stirred solution of **6** (1.43 g, 1.70 mmol) at *ca.* 25 °C. The mixture was set aside for *ca.* 12 h with stirring, then filtered. The bright yellow filtrate was concentrated to afford yellow crystals of **8** (1.26 g, 79%) (Found: C, 73.6; H, 8.89; N, 5.62. $C_{57}H_{77}InN_4$ requires C, 73.4; H, 8.32; N, 6.00%), mp 204–205 °C. ^{1}H NMR (C_6D_6): δ 7.79 (s, 2 H, NC*H*), 7.27–7.00 (m, 15 H, aryl), 6.86 (t, 2 H, aryl); 3.41 (sp, 4 H, C*H*Me$_2$), 3.14 (br, 2 H, N*H*), 1.16–1.00 (m, 48 H, CHC*H*$_3$); ^{13}C NMR (C_6D_6): δ 164.8 (N*C*H); 147.4, 145.4, 143.9, 140.8, 137.3, 129.3, 129.1, 126.2, 126.1, 125.8, 124.7, 124.6, 123.0, 118.9 (aryl); 106.9(*C*Ph); 28.8, 28.4, 26.4, 24.4, 23.2 (Pr^i). MS (**M** denotes the parent) *m*/*z* (% and assignment): 933 (4.0, $\mathbf{M}^+$), 757 (58, [**M** − {N(H)($C_6H_3Pr^i_2$-2,6)}]$^+$), 580 (51, [**M** − 2{N(H)($C_6H_3Pr^i_2$-2,6)}]$^+$).

[{In(Cl)(L)(μ-OH)}$_2$] (10). A solution of Li[N($SiMe_3$)($C_6H_3Pr^i_2$-2,6)] was prepared *in situ* by the addition of a 1.6 *M* solution of LiBu^n in hexane (1.6 cm^3) to HN($SiMe_3$)($C_6H_3Pr^i_2$-2,6) (0.42 g, 1.68 mmol) in Et_2O (20 cm^3) at *ca.* 25 °C. The solution was set aside for *ca.* 2 h, whereafter **6** (1.35 g, 1.60 mmol) was added. A colourless precipitate was formed instantly; the mixture was stirred for *ca.* 12 h, then filtered. The yellow filtrate was concentrated to *ca.* 10 cm^3 in the open laboratory. Cooling to −27 °C yielded yellow microcrystals, which upon recrystallisation from thf/Et_2O afforded colourless crystals of **10** (0.11 g, 10%), mp 206–207 °C, which were insoluble in a wide selection of aprotic solvents. MS (**M** denotes the parent) *m*/*z* (% and assignment): 1266 (0.1, [**M** − thf]$^+$), 1247 (0.2, [**M** − thf − H_3O]$^+$), 1212 (0.2, [**M** − thf − H_3O − Cl]$^+$), 651 (35, [(**M** − thf)/2 + H_3O]$^+$), 581 (27, [(**M** − thf)/2 + H_2O − Cl]$^+$).

[L(Cl)In–In(Cl)L] (11). (a) A solution of **6** (2.44 g, 2.90 mmol) in Et_2O (50 cm^3) was introduced into a Schlenk tube containing a sodium mirror (180 mg, 7.83 mmol) at *ca.* 25 °C. A grey precipitate was instantly formed. The mixture was set aside for *ca.* 48 h, then filtered. The yellow filtrate afforded a yellow precipitate (0.13 g), which was filtered off. Volatiles were removed from the filtrate *in vacuo* and the residue was extracted into thf. The extract was cooled at −15 °C to afford crystals of **11a** (0.68 g, 54%) (Found: C, 64.0; H, 6.92; N, 4.55. $C_{66}H_{82}Cl_2In_2N_4$ requires C, 64.35; H, 6.71; N, 4.55%), mp 161–162 °C (decomp). ^{1}H NMR ($CDCl_3$): δ 7.78 (s, 4 H, NC*H*), 7.65 (s, 4 H, NC*H*), 7.36–7.20 (m, 18 H, aryl), 3.44 (m, 8 H, C*H*Me$_2$), 1.44 (d, 24 H, CHC*H*$_3$), 1.28 (d, 24 H, CHC*H*$_3$); ^{13}C NMR ($CDCl_3$): δ 166.0 (N*C*H); 144.6, 143.7, 142.1, 129.2, 128.2, 126.2, 124.4, 123.5 (aryl); 106.7(*C*Ph); 28.9, 25.9, 23.2 (Pr^i). MS (**M** denotes the parent) *m*/*z* (% and assignment): 650 (46, [InLCl_2]$^+$), 615 (13, [**M**/2]$^+$), 580 (35, [InL]$^+$).

(b) The mother liquor from the preparation of **10** was concentrated yielding a yellow powder (1.02 g). This was heated in toluene (50 cm^3) at 100 °C for 24 h and then filtered. The filtrate was concentrated and hexane (20 cm^3) was added, affording the hexane 1:1 adduct of **11** (0.12 g, 11%) (Found: C, 65.8; H, 7.64; N, 4.46. $C_{72}H_{98}Cl_2In_2N_4$ requires C, 65.6; H, 7.36; N, 4.25%), mp 218–219 °C. ^{1}H NMR (C_6D_6): δ 7.76 (s, 4 H, NC*H*), 7.22–6.96 (m, 22 H, aryl); 3.74 (sp, 8 H, C*H*Me$_2$), 1.44 (d, 12 H, CHC*H*$_3$), 1.28 (d, 12 H, CHC*H*$_3$), 1.18 (d, 12 H, CHC*H*$_3$), 1.03 (d, 12 H, CHC*H*$_3$); ^{13}C NMR (C_6D_6): δ 166.9 (N*C*H); 146.9, 146.7, 145.4, 142.4, 140.7, 129.3, 127.2, 124.9, 124.1, 124.0 (aryl); 105.9 (*C*Ph); 29.4, 29.2, 27.3, 26.4, 26.0, 24.8, 24.0, 23.1, 22.9 (Pr^i).

(c) A solution of Na(L) (2.19 g, 4.48 mmol) in thf (40 cm^3) was added to a suspension of InCl (0.74 g, 4.92 mmol) in thf (20 cm^3) at *ca.* 25 °C. There was an immediate colour change from orange to light yellow, accompanied by the formation of a grey precipitate. The mixture was set aside for *ca.* 12 h, whereafter a further portion of InCl (0.32 g) was added (because a bright silver-coloured deposit of In was observed). After *ca.* 48 h at *ca.* 25 °C, the mixture was filtered. The filtrate upon concentration *in vacuo* and cooling at −27 °C furnished yellow crystals of the 1 : 1 thf adduct of **11** (1.74 g, 60%) (Found: C, 64.4; H, 7.09; N, 4.18. $C_{70}H_{90}Cl_2In_2N_4O$ requires C, 64.5; H, 6.96; N, 4.30%), mp 154–155 °C. ^{1}H NMR (C_4D_8O): δ 7.61 (s, 4 H, NC*H*), 7.11–6.99 (m, 22 H, aryl), 3.53 (m, 8 H, C*H*Me$_2$), 1.29 (d, 12 H, CHC*H*$_3$), 1.08–1.00 (m, 24 H, CHC*H*$_3$); ^{13}C NMR (C_4D_8O): δ 166.9 (N*C*H), 166.5 (N*C*H); 156.4, 147.2, 146.5, 146.0, 144.6, 144.2, 143.6, 142.9, 142.3, 141.3, 129.4, 129.2, 127.9, 127.7, 127.3, 127.0, 126.9, 126.7, 126.1, 125.7, 124.3, 124.1, 123.8 (aryl); 107.3, 106.6, 105.9 (*C*Ph); 29.4, 29.3, 29.1, 26.3, 23.9, 23.2 (Pr^i).

[{In(Cl)L}$_2$(μ-S)] (12). A solution of **11** (1.43 g, 1.10 mmol) in thf (20 cm^3) was added to a solution of sulfur (80.2 mg, 2.50 mmol) in thf (10 cm^3) at *ca.* 25 °C. The mixture was stirred for *ca.* 48 h, then filtered. The filtrate was concentrated *in vacuo* and Et_2O (15 cm^3) was added, yielding yellow crystals of **12** (0.64 g, 46%) (Found: 62.4; H, 6.58; N, 4.26. $C_{66}H_{82}Cl_2In_2N_4S$ requires C, 62.7; H, 6.54; N, 4.19%), mp 213–215 °C (decomp.). ^{1}H NMR (C_4D_8O): δ 7.65 (s, 4 H, NC*H*), 7.07–6.86 (m, 22 H, aryl), 3.46 (m, 4 H, C*H*Me$_2$), 1.31 (m, 12 H, CHC*H*$_3$), 1.05–0.99 (m, 36 H, CHC*H*$_3$); ^{13}C NMR (C_4D_8O): δ 165.4 (N*C*H); 144.9, 144.1, 143.2, 141.0, 126.8, 125.8, 124.6, 123.6 (aryl); 105.8 (*C*Ph); 29.5, 28.4, 26.0, 25.9, 23.8, 22.6 (Pr^i). MS (**M** denotes the parent) *m*/*z* (% and assignment): 1264 (21, $\mathbf{M}^+$), 1225 (10), 797 (15), 650 (32), 465 (100, L$^+$).

[$InCl_2$(L)(tmeda)] (13). Tmeda (0.18 cm^3) was added dropwise to a solution of **6** (1.35 g, 1.60 mmol) in Et_2O (30 cm^3) at *ca.* 25 °C. The mixture was stirred for *ca.* 12 h, then filtered. The pale yellow precipitate was washed with Et_2O, then crystallised from thf at −27 °C, furnishing pale microcrystals of **13** (0.72 g, 77%) (Found: C, 60.8; H, 7.70; N, 7.09. $C_{39}H_{57}Cl_2InN_4$ requires C, 61.0; H, 7.48; N, 7.30%), mp 196–197 °C. ^{1}H NMR (C_4D_8O): δ 7.68 (s, 2 H, NC*H*), 7.22–7.01 (m, 11 H, aryl), 3.48 (sp, 4 H, C*H*Me$_2$), 2.24 (s, 4 H, NCH_2), 2.11 (s, 12 H, N*Me*$_2$), 1.26 (d, 12 H, CHC*H*$_3$), 1.10 (d, 12 H, CHC*H*$_3$); ^{13}C NMR (C_4D_8O): δ 166.6 (N*C*H), 156.5 (N*C*H); 144.7, 142.4, 129.3, 127.4, 127.0, 124.3, 123.9 (aryl); 106.5 (*C*Ph); 58.7, 46.4 (tmeda); 29.3, 25.9, 23.4 (Pr^i). MS (**M** denotes the parent) *m*/*z* (% and assignment): 650 (89, [**M** − tmeda]$^+$), 615 (8, [M − tmeda − Cl]$^+$).

[{$InCl_3$(tmeda)}$_2$(μ-OSn(Me_2)OSnMe_2})] (14). Tmeda (0.15 cm^3) was added to a solution of **6** (0.84 g, 1.00 mmol) in Et_2O (20 cm^3) at *ca.* 25 °C. After *ca.* 2 h, the mixture was filtered. The yellow precipitate was washed with Et_2O (2 × 10 cm^3) and dissolved in thf (20 cm^3). Hexamethylditin (0.21 cm^3, 1.01 mmol) was added. The mixture was heated with stirring at 50 °C for

Table 11 Crystal and refinement data for **1–6**, **8**, **10–12** and **14**

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**8**
Empirical formula	$C_{33}H_{42}N_2$	$C_{41}H_{57}LiN_2O_2$	$C_{39}H_{57}LiN_4$	$C_{33}H_{41}AlCl_2N_2$	$C_{33}H_{41}Cl_2GaN_2$	$C_{41}H_{61}Cl_3InLiN_2O_2$	$C_{57}H_{77}InN_4$
M_r	466.69	616.83	588.83	563.56	606.30	842.03	933.05
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Trigonal	Orthorhombic
Space group	*Pccn* (no. 56)	*Pbca* (no. 61)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P3_2$ (no. 145)	*Pbca* (no. 61)
a/Å	11.2223(2)	18.8630(2)	10.2941(2)	10.0584(1)	10.0613(1)	17.7096(2)	12.1201(2)
b/Å	13.0825(3)	19.5833(2)	18.5693(3)	11.9404(1)	11.9025(2)	17.7096(2)	22.6524(3)
c/Å	19.4125(4)	20.7986(2)	19.6964(4)	26.9485(3)	27.0265(5)	12.2877(1)	37.2258(4)
α/°	90	90	90	90	90	90	90
β/°	90	90	100.636(1)	98.394(1)	98.114(1)	90	90
γ/°	90	90	90	90	90	120	90
V/Å^3	2850.06(10)	7683.00(14)	3700.36(12)	3201.88(5)	3204.15(9)	3337.48(6)	10220.3(2)
Z	4	8	4	4	4	3	8
μ/mm^{-1}	0.06	0.06	0.06	0.25	1.05	0.74	0.50
Unique reflections, R_{int}	2504, 0.096	6731, 0.070	6471, 0.067	5581, 0.055	5604, 0.073	8192, 0.041	8929, 0.073
Reflections with $I > 2\sigma(I)$	2020	5411	5094	4826	4320	7941	6952
Final R indices [$I > 2\sigma(I)$], $R1$, $wR2$	0.058, 0.133	0.063, 0.156	0.049, 0.115	0.036, 0.086	0.039, 0.072	0.024, 0.055	0.033, 0.077
R indices (all data) $R1$, $wR2$	0.075, 0.142	0.080, 0.169	0.068, 0.127	0.044, 0.091	0.064, 0.079	0.026, 0.056	0.051, 0.086

Table 11 (*Contd.*)

Compound	**10**	**11a**	**11b**	**11c**	**12**	**14**
Empirical formula	$C_{66}H_{84}Cl_2In_2N_4O_2{\cdot}C_4H_8O$	$C_{66}H_{82}Cl_2In_2N_4{\cdot}C_4H_8O$	$C_{66}H_{82}Cl_2In_2N_4$	$C_{66}H_{82}Cl_2In_2N_4{\cdot}C_6H_{14}$	$C_{66}H_{82}Cl_2In_2N_4S$	$C_{16}H_{44}Cl_6In_2N_4O_2Sn_2{\cdot}1.5C_4H_8O$
M_r	1338.02	1304.00	1231.90	1318.07	1263.96	1112.43
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Tetragonal
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$I4_1/a$ (no. 88)
a/Å	14.3394(2)	13.9262(3)	12.3372(5)	13.3062(2)	18.6868(2)	23.5091(9)
b/Å	14.4401(2)	14.4149(2)	12.3604(6)	13.9612(2)	12.9207(2)	23.5091(9)
c/Å	17.9795(3)	17.9008(4)	12.9731(4)	18.5787(2)	26.4950(4)	28.5786(6)
α/°	83.201(1)	83.762(1)	92.242(2)	90	90	90
β/°	70.719(1)	72.690(1)	118.216(2)	95.975(1)	101.491(1)	90
γ/°	71.788(1)	72.979(1)	111.648(2)	90	90	90
V/Å^3	3337.55(9)	3279.55(11)	1564.23(11)	3432.62(8)	6268.90(15)	15794.8(9)
Z	2	2	1	2	4	16
μ/mm^{-1}	0.82	0.83	0.86	0.79	0.90	2.84
Unique reflections, R_{int}	15237, 0.034	11549, 0.043	4345, 0.056	7826, 0.034	11596, 0.056	6811, 0.109
Reflections with $I > 2\sigma(I)$	13503	9867	3773	6811	9635	4602
Final R indices [$I > 2\sigma(I)$], $R1$, $wR2$	0.026, 0.064	0.032, 0.071	0.037, 0.082	0.032, 0.087	0.036, 0.074	0.050, 0.079
R indices (all data) $R1$, $wR2$	0.031, 0.068	0.042, 0.076	0.047, 0.087	0.039, 0.095	0.050, 0.079	0.096, 0.091

12 h, then filtered. Concentration of the filtrate and cooling at −25 °C afforded colourless crystals of **14** (0.09 g, 16%), which was characterised solely by X-ray diffraction.

X-Ray crystallographic study

Diffraction data for compounds **1–6**, **8**, **10**, **11a**, **11b**, **11c**, **12** and **14** were collected at 173(2) K on an Enraf-Nonius Kappa-CCD diffractometer using monochromated Mo-Kα radiation, $\lambda =$ 0.71073 Å. Crystals were directly mounted on the diffractometer under a stream of cold nitrogen gas. The hydrogen atoms of the μ-OH groups of **10** were located on a difference map and refined. Absorption corrections were not applied for **1–5**, but for the remaining structures were corrected by MULTISCAN. The structures were refined on all F^2 using SHELXL 97.[24] Further details are given in Table 11.

CCDC reference numbers 609658–609670

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b607782j

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