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Ketiminate-Supported LiCl Cages and Group 13 Complexes

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The coordination preferences of the ketiminato ligands L^1H, {[RN(H)(C(Me))$_2$C(Me)=O], R = 2,6-diisopropylphenyl (Dipp) or 2,6-dimethylphenyl (Dmp)} and L^2H {[RN(H)C(Me)-CHC(Me)=O], R = $C_2H_4NEt_2$} with group 13 elements were investigated. The expected *N*,*O*-chelated products [DmpL^{1}BF$_2$] (**1**), [L^{2}Al(Me)Cl] (**2A** and **2B**), and [L^{2}InMe$_2$] (**6**), were obtained from reactions with BF_3·OEt_2, $AlMe_2Cl$ and $InMe_3$ respectively, but the reaction of DippL^1 with $GaCl_3$ afforded a metal-halide, neutral ligand adduct, [GaCl$_3$·DippL^{1}H] (**3**). More interestingly the reactions of DippL^1 with $InMe_3$, formed in situ from $InCl_3$ and MeLi, led to the isolation of two ketiminate-supported LiCl cages [InMe$_2$Li$_7$Cl$_5$(DippL^{1-})$_2$(DippL^1)(THF)$_3$] (**4**) and [Li$_5$(Cl)-(DippL^1)$_4$]·2PhMe (**5**). The lithium cage **4** features reaction of $InMe_3$ with one backbone methyl group from each of two DippL^1 ligands, to afford a tetraalkylindate moiety in the framework of two doubly deprotonated ligands (L$^-$).

Introduction

β-Diketiminate ligands (Figure 1, **A**) constitute one of the most important and investigated class of ligands in recent years and have been employed in the formation of complexes from all parts of the periodic table.[1] Relative to their β-diketiminato counterparts, the related ketiminato ligands (**B** and **C**, Figure 1) have seen less attention, a surprising fact in light of the many attractive features shared by the two related ligand classes.[2] We were interested in exploring the general coordination chemistry of the more bulky, bidentate ArL^1 (**B**) (Ar = Dipp = 2,6-diisopropylphenyl or Dmp = 2,6-dimethylphenyl) and the more flexible, tridentate L^2 (**C**) (Figure 1), with group 13 elements.

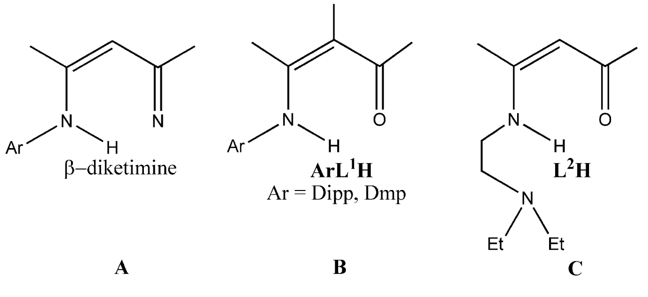


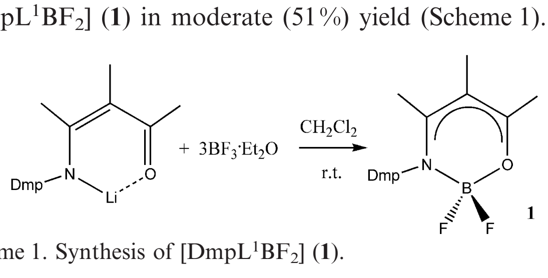
Figure 1. Structures of β-diketiminato and ketiminato ligands ArL^1 and L^2.

Group 13 elements have proven useful in a wide array of applications.[3] For example, BF$_2$-chelate products of organic ligands have been exploited for their photoelectric properties, their use as laser dyes and molecular probes.[4] Aluminum complexes continue to be an important presence in the field of catalysis[5–7] due to their strong Lewis acidity and low cost.[6] Of particular interest has been the partial hydrolysis reactions of aryl- and alkylaluminum compounds,[8–12] with the goal of mimicking methylalumoxane (MAO). MAO is an extremely potent cocatalyst in polymerization processes,[10] but at present lacks structural characterization.[11] Roesky and co-workers have used β-diketiminate ligands to fine-tune the steric and electronic properties of the partial hydrolysis products by inhibiting unpredictable aggregation and providing electronic relief to the Lewis-acidic Al center by chelation.[9,13] Analogous work with ketiminate ligands has not been reported. Furthermore, gallium- and indium-containing complexes with a variety of ligands have been resourceful precursors to industrially significant thin films such as Ga_2O_3 and In_2O_3.[14,15] Herein we report the coordination preferences and reactivity of the ketiminato ligands, L^1 and L^2 with selective group 13 halides and alkyl compounds.

Results and Discussion

Discussion of [DmpL^{1}BF$_2$] (1)

Treatment of DmpL^{1}Li with a threefold excess of boron trifluoride–diethyl ether in dichloromethane at room temperature yields air-stable, colorless crystalline needles of [DmpL^{1}BF$_2$] (**1**) in moderate (51%) yield (Scheme 1). The



Scheme 1. Synthesis of [DmpL^{1}BF$_2$] (**1**).

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1:1 and 1:2 reactions were also performed and the reaction monitored by ^{11}B NMR spectroscopy. Both of these reactions result in the formation of **1**, but from these reactions a crystalline product could not be obtained. Therefore, a threefold excess of boron trifluoride–diethyl ether was found to optimize the isolation of **1**.

BF_2-chelate products are typically prepared by reaction of BF_3 with the neutral ligand in the presence of a base.[16] The HF elimination method was recently employed by Gardinier et al.,[17] in their extensive survey of β-diketonate, β-ketoiminato and β-diiminate BF_2 complexes. This study found that the electronic properties of boron difluoride complexes were greatly influenced by the nitrogen and carbon substituents of the chelate ring. Incidentally, **1** can also be prepared by salt metathesis as has been documented for the synthesis of β-diketiminato boron dihalides.[18]

Figure 2 displays the X-ray structure of one of two crystallographically independent molecules of **1**. Due to the similarity in metrical parameters of the two molecules, only the molecule shown in Figure 2 will be discussed. Complex **1** exhibits tetrahedral geometry around the boron center, with angles between 108.87(16)–110.47(16)°. The B–N distance of 1.563(2) Å is slightly longer than a normal B–N single bond (ca. 1.52 Å), and the B–O distance of 1.445(3) Å is slightly shorter than a normal B–O single bond (B–O ≈ 1.48 Å).[19] Although the intermediate bond lengths of the ligand backbone indicate π-delocalization, they are consistent with the prominence of resonance form **B**, which contains a B–N dative bond (Figure 3), which is in agreement to previously reported related examples.[17] The B–N and B–O bond lengths of **1** show good agreement with those of other conjugated, six-membered ring (NC_3O)-BF_2 chelate complexes [B–N: 1.543(6)–1.560(8) Å; B–O: 1.446(5)–1.459(3) Å].[17,20] As was observed in the β-ketoiminato BF_2 complexes reported by Gardinier, the ^{11}B and ^{19}F NMR resonances are indicative of a symmetric tetrahedral coordinated boron center supported by a planar chelate ring.[17]

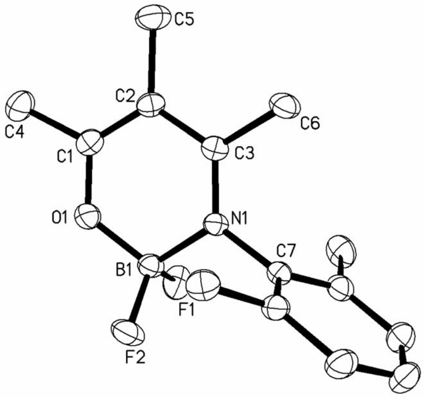


Figure 2. Molecular structure of **1**. Thermal ellipsoids drawn at 30% probability. Hydrogen atoms omitted for clarity. Select bond lengths [Å] and angles [°]: B(1)–F(1) 1.374(3), B(1)–F(2) 1.392(3), B(1)–O(1) 1.445(3), C(1)–O(1) 1.328(2), N(1)–C(3) 1.318(2), C(1)–C(2) 1.358(3), C(2)–C(3) 1.424(3), C(3)–N(1)–B(1) 121.81(15), F(1)–B(1)–F(2) 109.30(17).

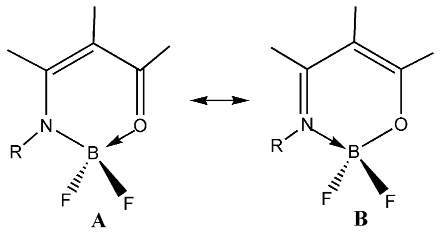
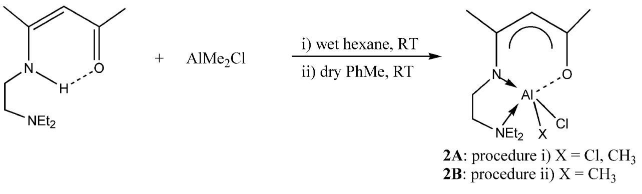


Figure 3. Resonance structures **A** and **B** of **1**.

Discussion of [L^{2}Al(Me)Cl] (2A and 2B)

In view of the successful formation of aluminum hydroxo and oxo aluminum products with β-diketiminates[13,21] and with our continued interest in aluminum oxide and hydroxide complexes, we wished to use DippL^{1}H and L^{2}H to examine the effect of partial hydrolysis on the reaction products of $AlMe_2Cl$ (Scheme 2). Thus, $AlMe_2Cl$ was treated with neutral L^{2}H at ambient temperature. With the intent of introducing trace moisture into the reaction mixture to obtain a partial hydrolysis product, the reaction was performed under N_2 but not under strictly anhydrous conditions. Therefore, the Schlenk flask was not flame-dried prior to the reaction and the reaction was carried out in un-dried hexane. The addition of $AlMe_2Cl$ to L^2 resulted in the immediate formation of a bright yellow precipitate. Following workup in toluene (directly from the bottle) large colorless crystals of **2A** were obtained.



Scheme 2. Synthesis of complex [L^{2}Al(Me)Cl] (**2**).

Examination of the crystals by single-crystal X-ray diffraction revealed that no deliberate introduction of oxygen into the final product had occurred. Instead, the CH_4-elimination product **2A**, [L^{2}Al(Me)Cl], was formed in low yield (Figure 4). The Al-methyl carbon exists at mixed occupancy with a chlorine atom (C: ca. 70%, Cl: ca. 30%). This disorder is possibly due to the fact that that $(Me_2AlCl)_2$ can disproportionate to form $AlMe_3$ and $MeAlCl_2$ in the presence of a base,[22] but could also be due to the reaction conditions. The carbon and chlorine atoms sharing this position have bond lengths of Al(1)–C(6) 2.023(6) Å and Al(1)–Cl(1) 2.079(4) Å. The latter is significantly shorter than the other Al(1)–Cl(2) bond length of 2.1964(8) Å in **2A**, but this difference is attributable to the disorder at that position. To ascertain whether the mixed occupancy in **2A** was due to the reaction conditions employed, the reaction was repeated under strictly anhydrous conditions (Scheme 2, procedure ii)). The toluene solution was concentrated, filtered, and stored at room temperature to again afford large colorless crystalline blocks. Solid state analysis revealed that the product was identical to **2A**, but with the

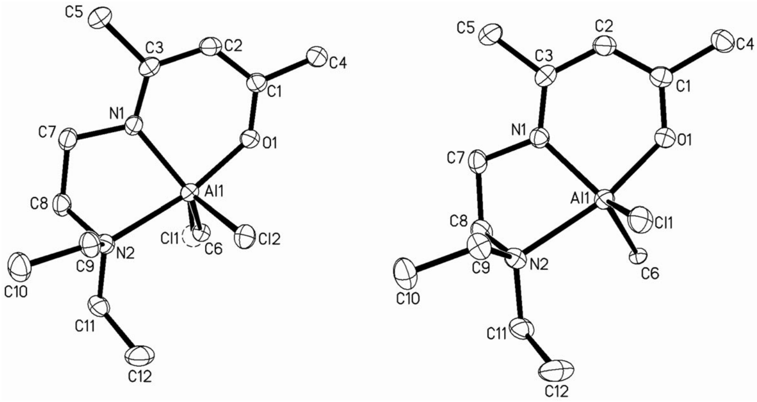


Figure 4. Molecular structures of **2A** (left) and **2B** (right). Thermal ellipsoids drawn at 30% probability. Hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: **2A**: Al(1)–O(1) 1.8560(15), Al(1)–N(1) 1.9498(17), Al(1)–N(2) 2.2374(17), Al(1)–C(6) 2.023(6), Al(1)–Cl(1) 2.079(4), Al(1)–Cl(2) 2.1964(8), O(1)–Al(1)–N(1) 89.92(7), O(1)–Al(1)–C(6) 91.63(18), O(1)–Al(1)–N(2) 168.63(7), N(1)–Al(1)–N(2) 79.15(7), N(1)–Al(1)–C(6) 125.60(16), N(1)–Al(1)–Cl(2) 14.61(6), C(6)–Al(1)–Cl(2) 112.66(15); **2B**: Al(1)–O(1) 1.859(2), Al(1)–N(1) 1.950(2), Al(1)–N(2) 2.252(2), Al(1)–C(6) 2.020(2), Al(1)–Cl(1) 2.190(11), O(1)–Al(1)–N(1) 89.59(9), O(1)–Al(1)–C(6) 94.90(10), O(1)–Al(1)–N(2) 168.07(10), N(1)–Al(1)–N(2) 79.03(9), N(1)–Al(1)–C(6) 124.48(11), N(1)–Al(1)–Cl(1) 120.64(9), C(6)–Al(1)–Cl(1) 114.44(8).

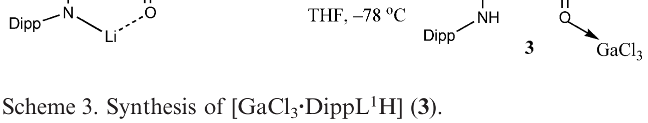
methyl carbon at full occupancy, **2B** (Figure 4). It is noteworthy to mention that our attempts to partially hydrolyze complex **2** through addition of one equivalent of water to the reaction mixture using procedure (ii), Scheme 2, resulted in the formation of a mixture of products that were not crystalline. Further attempts at the deliberate hydrolysis of ketiminate-Al complexes were not pursued.

In both **2A** and **2B**, the pentacoordinate aluminum center exists in a trigonal bipyramidal environment.[23] The N(1)–Al(1) bond lengths in both complexes [**2A**: 1.9498(17), **2B**: 1.950(2) Å] are expectedly shorter than the N(2)–Al(1) dative bonds [**2A**: 2.2374(17), **2B**: 2.252(2) Å]. The Al(1)–C(6) bond lengths of **2A** [2.023(6) Å] and **2B** [2.020(2) Å] are almost identical and are somewhat longer than other *N*,*O*-chelated Al–C(methyl) bond lengths [1.932(7)–1.9857(11) Å].[23] ^{1}H NMR confirmed the assignment of a methyl carbon in the solid-state structures, with peaks corresponding to the Al–methyl at –0.68 ppm in each spectrum, which is in the normal range for *N*,*O*-chelated Al–CH_3 protons (–0.7 to –1.11 ppm).[24,25]

Aluminum complexes of aryl-substituted ketiminate ligands have been reported,[6,7,25,26] so synthesis of a novel aluminum-ArL^1 complex was not pursued. However, the structure of **2** can be compared to previously reported Dipp-substituted ketiminate aluminum complexes. For example, Huang and co-workers have synthesized several bis(ketiminate)AlX complexes [ketiminate = MeC(O)-CHC(Me)NHAr, Ar = Dipp; X = H, OCOH, SCHS, OCH = NPh].[6] The authors were unable to isolate any mono-ketiminate products, even with an excess of the aluminum precursor.[6] Similar inability to isolate the mono-ketiminate product was observed in the synthesis of bis-(ketiminate)AlCl [ketiminate = MeC(O)CHC(Me)NHAr, Ar = *p*-C_6H_4F].[7] The isolation of bis products in the previously reported cases highlights the inability of aryl-substituted bidentate ketiminate ligands to stabilize the metal center from further ligand attack, despite their steric bulk. Therefore, the isolation of **2** suggests the superior ability of tridentate L^2 to protect the metal center from further ligand attack, thus forming the mono-ligated products. Although it might appear intuitive that any tridentate ligand would be more likely to form mono-ligated products over a similar bidentate ligand, the formation of mono-ketiminate Al complexes does not necessarily extend to other tridentate ketiminate ligands. For example, the tridentate ketimine ligand $SC_6H_4N=C(Me)CH_2C(O)Me$ acts only as a bidentate chelating agent upon reaction with Al(O*i*Pr)$_3$, forming tris{$SC_6H_4N=C(Me)CH_2C(O)Me$}Al which features only *N*,*S* contacts with the Al center and no Al–O interactions.[27]

Synthesis and Discussion of [GaCl$_3$·DippL^{1}H] (3)

A stoichiometric quantity of *n*BuLi was added to DippL^{1}H in THF at –78 °C and, after allowing the reaction mixture to warm to room temperature, the lithiation reaction was stirred overnight (Scheme 3). At this time, the solution of DippL^{1}Li was added to a THF solution of GaCl$_3$ at –78 °C. Instead of loss of LiCl, and formation of [DippL^{1}GaCl$_2$], [DippL^{1}H-GaCl$_3$] (**3**), a ligand–metal halide adduct was isolated as colorless crystals (Figure 5). Preferential formation of the neutral-ligand adduct of main-group halides over salt metathesis with L^1 has been previously observed by us in the isolation of [SbCl$_3$·DippL^{1}H] and [SnCl$_2$·DippL^{1}H] adducts,[28] and



Scheme 3. Synthesis of [GaCl$_3$·DippL^{1}H] (**3**).

Lappert and co-workers in the isolation of a related complex, β-dialdiminium pentachlorotellurate–diethyl ether.[29] In the former cases (Sb, Sn) the lithiations were not performed in situ, as the lithiation leading to **3** had been, eliminating this as the cause for lack of salt displacement. In the case of Sb, the analogous reaction of L^2Li with $SbCl_3$ successfully displaced LiCl, and $[L^2SbCl_2]$ prevailed.[28a] Although the inclusion of moisture into the reaction cannot be eliminated, given the repeated isolation of **3** and other neutral ligand adducts, coupled with the observation that an acidic gas is evolved on addition of solvent to $GaCl_3$, it is more likely that HCl is the source of protonation. Furthermore, given the fairly low yield (20%) of crystalline material that was isolated, we believe **3** to be the minor product of the reaction, with the major product, L^1GaCl_2, formed from LiCl displacement. ^1H NMR spectroscopic data on the crude reaction product reveals a mixture of products, therefore it is possible that both products form but **3** is isolated because it preferentially crystallizes. The comparison reaction of $DippL^1H$ with $GaCl_3$ was performed, but surprisingly **3** could not be isolated, instead an oily product was obtained. Pertinent to the formation of **3** is the equivalent reaction of L^2Li with $GaCl_3$,[28b] which resulted in loss of LiCl to form L^2GaCl_2. These findings are likely due to the increased stabilization of the metal center by the pendant arm nitrogen of tridentate L^2. The π-bonding tendencies of aryl-substituted ketiminato ligands is reportedly lower than that of diaryl-substituted β-diketiminates;[30] therefore, the electron-donor ability of bidentate ArL^1H, is presumably insufficient to form the stable chelation products with these particular metals, instead favoring adducts.

One of the two crystallographically independent molecules of $[GaCl_3 \cdot DippL^1H]$ is shown in Figure 5. Despite all of the angles in the unit cell being equal to 90.00°, the data could not be solved and refined in an orthorhombic crystal system, instead, converging in the monoclinic space group $P2_1/c$. The hydrogen atom on the nitrogen atom [N(2)], of one $DippL^1H$ molecule in the asymmetric unit was located using the electron-density difference map and freely refined, but could not be located on the nitrogen atom [N(1)] in the remaining molecule. Nevertheless, the existence of the NH hydrogen is detectable in the proton NMR spectrum at δ = 13.01 ppm and as an N–H stretch at 3285 cm^{-1} in the infrared spectrum. The bond lengths and angles of **3** are unexceptional.

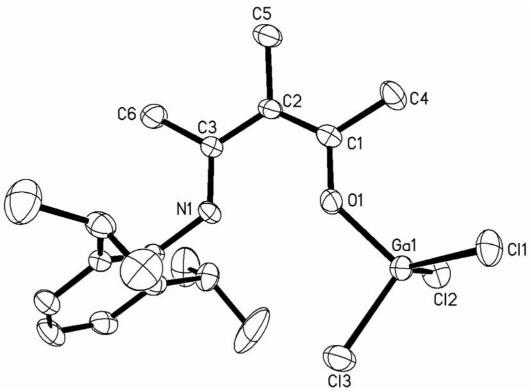


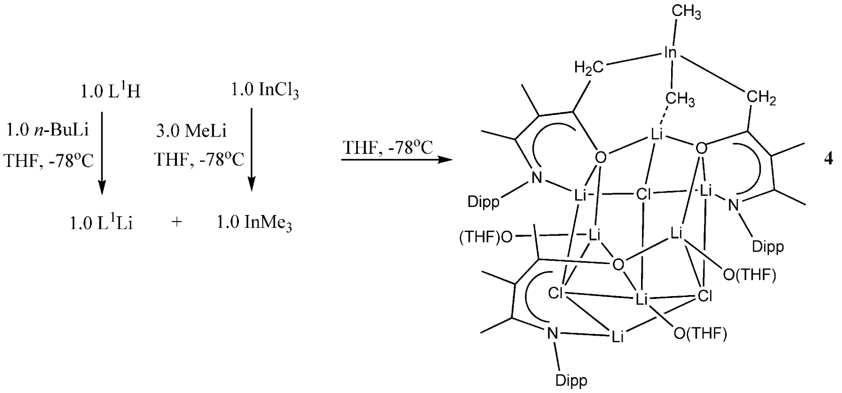
Figure 5. Molecular structure of **3**. Thermal ellipsoids drawn at 30% probability. Hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Ga(1)–O(1) 1.864(5), O(1)–C(1) 1.308(8), C(1)–C(2) 1.386(10), C(2)–C(3) 1.424(9), N(1)–C(3) 1.333(9), O(1)–Ga(1)–Cl(1) 113.13(18), O(1)–Ga(1)–Cl(2) 107.38(1), O(1)–Ga(1)–Cl(3) 98.05(16).

Discussion of $[InMe_2Li_7Cl_5(DippL^{1-})_2(DippL^1)(THF)_3]$ (4)

There has been recent interest in generating lithium chloride cages as they sometimes bear close resemblance to the structure of the parent ionic lattice of LiCl.[31] These cages or clusters often exhibit properties different from the parent ionic compound such as lower melting points and solubility in organic solvents.[31] Previously reported reactions involving $InMe_3$ (freshly prepared from $InCl_3$ and MeLi) and a lithiated ligand have been utilized as a synthetic pathway to heterobimetallic $InCH_3$-containing LiCl cages or clusters.[32]

The reaction of in situ generated $DippL^1Li$ and $InMe_3$, the latter freshly prepared from $InCl_3$ and 3 equiv. of MeLi afforded extremely air-sensitive, large colorless crystals of **4** in 25% yield (Scheme 4).

X-ray structural analysis reveals that complex **4** is a highly unusual heterobimetallic LiCl cage supported by



Scheme 4. Synthesis of complex **4**.

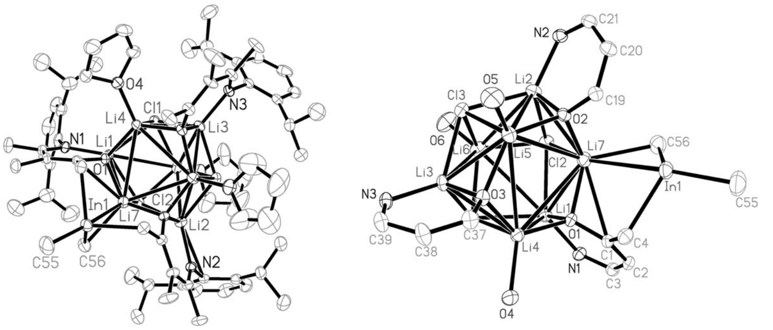


Figure 6. Molecular structure of **4**, on the left is the full molecule, on the right hand side the Dipp groups and carbon atoms from the backbone have been omitted for clarity. Thermal ellipsoids drawn at 30% probability. Hydrogen atoms omitted for clarity.

three deprotonated ketiminate ligands, three THF molecules, and most intriguingly, an $In(CH_3)_2(CH_2)_2$ moiety (Figure 6). Key bond lengths and angles are recorded in Table 1. The $[Li_7O_3Cl_3]$ core is comprised of seven tetrahedrally-bonded lithium cations, three tetrahedrally-bonded ketiminate oxygen atoms bonded to three lithiums each, and 3 interstitial, μ_4-Cl atoms. These core atoms make up nine fused four-membered rings of two different compositions, capped with one six-membered ring. All nine four-membered rings have two lithium cations occupying opposite corners, with the other two corners being occupied by 2 chlorine atoms in three of the rings, and an oxygen atom and a chlorine atom in six of the rings. The six-membered Li–O heterocycle capping the core of the cage consists of alternating lithium and oxygen atoms.

Table 1. Selected bond lengths [Å] and angles [°] of $[InMe_2Li_7Cl_5(DippL^{1-})_2(DippL^1)(THF)_3]$ (**4**).

In(1)–C(4)	2.294(5)	Li(6)–O(6)	1.862(9)
In(1)–C(55)	2.172(6)	Li(7)–O(2)	1.937(8)
In(1)–C(56)	2.207(6)	Li(7)–C(1)	2.792(9)
Li(1)–O(1)	1.869(8)	Li(7)–Cl(2)	2.387(8)
Li(2)–O(2)	1.849(8)	Cl(1)–Li(1)	2.447(8)
Li(3)–O(3)	1.875(8)	Cl(1)–Li(3)	2.381(8)
Li(4)–O(4)	1.901(9)	Cl(1)–Li(4)	2.492(8)
Li(1)–N(1)	1.933(8)	Cl(1)–Li(6)	2.343(9)
Li(2)–N(2)	1.920(9)	Cl(2)–Li(1)	2.446(8)
Li(3)–N(3)	1.921(8)	Cl(2)–Li(2)	2.449(8)
Li(4)–O(4)	1.901(9)	Cl(2)–Li(6)	2.295(9)
Li(5)–O(5)	1.917(9)		
C(22)–In(1)–C(5)	99.48(18)	O(2)–Li(5)–O(3)	128.4(4)
C(4)–In(1)–C(55)	109.5(2)	Li(5)–O(2)–Li(7)	111.3(4)
C(4)–In(1)–C(56)	106.5(2)	Li(1)–Cl(2)–Li(6)	82.5(3)
C(22)–In(1)–C(55)	117.8(2)	Li(1)–Cl(2)–Li(7)	69.5(3)
C(22)–In(1)–C(56)	105.83(19)	Li(2)–Cl(2)–Li(6)	77.6(3)
C(55)–In(1)–C(56)	116.0(3)	Li(2)–Cl(2)–Li(7)	67.0(3)
O(1)–Li(7)–O(2)	126.1(5)	Li(1)–Cl(1)–Li(6)	81.5(3)
O(1)–Li(4)–O(3)	126.7(4)	Li(2)–Cl(3)–Li(6)	77.5(3)
Li(4)–O(3)–Li(5)	109.8(3)		

Four-coordinate chloride anions surrounded by four lithium atoms are common[33] and the geometry around Cl^- varies significantly, ranging from tetrahedral[33a–33d] to seesaw[33e–33j] arrangements, depending on cluster size and ligand sterics. In several cases,[33k–33l] including the three Cl^- anions in **4**, each chloride anion is best described geometrically as occupying the apex of a square pyramid. The Li–Cl–Li_{cis} angles around these chlorides in **4** are [°] Cl(1): Li(1)–Cl(1)–Li(4) 68.0(2), Li(1)–Cl(1)–Li(6) 81.5(3), Li(3)–Cl(1)–Li(4) 69.1(2), Li(3)–Cl(1)–Li(6) 76.6(3); Cl(2): Li(1)–Cl(2)–Li(6) 82.5(3), Li(1)–Cl(2)–Li(7) 69.5(3), Li(2)–Cl(2)–Li(6) 77.6(3), Li(2)–Cl(2)–Li(7) 67.0(3); Cl(3): Li(2)–Cl(3)–Li(5) 70.8(3), Li(2)–Cl(3)–Li(6) 77.5(3), Li(3)–Cl(3)–Li(5) 71.1(3), Li(3)–Cl(3)–Li(6) 76.5(3).

The most unusual feature of **4** is the additional cage support provided by the tetraalkylindate moiety. From our previous work on selenium and tellurium halides with β-diketiminate ligands,[28c,28d] it was observed that reaction with a backbone methyl group occurred, leading to the formation of a ligand–CH_2–M (M = Se, Te) fragment. Similarly, complex **4** contains a ligand–$InCH_2$ moiety but also includes an additional ligand–CH_2–(In) fragment from a second molecule of L^1. Although the complicated structure implies a less straightforward mechanism than the imine–enamine tautomerization observed with β-diketiminate Se and Te complexes,[28c,28d] this portion of the complex was ostensibly formed by the consecutive reactions of $InMe_3$ with the enamine form of two ketiminate ligands with the loss of 1 equiv. of CH_4. The indium atom retains two of the methyl groups, one of which is terminal [C(55)] and the other bridging [C(56)], the latter occupying the fourth coordination site of a core lithium atom [Li(7)–C(56) distance: 2.40(1) Å]. Bridging methyl groups are well known[34] and have been observed in indium compounds[35] as well as in $Li–CH_3$(bridging) interactions.[36] The bridging methyl carbon atom distance of 2.207(6) Å to the indium center is expectedly longer than that of the terminal methyl carbon of **4** [2.172(6) Å] and of other $InCH_3$ compounds [2.139(5)–2.211(5) Å].[37] The In–CH_2 distances in **4** [2.287(5), 2.294(5) Å] are longer than those of other In–CH_2 [2.130(3)–2.193(2) Å] compounds due to the greater steric demands of $DippL^1$.[38] Both the In–CH_2 and In–CH_3 groups are detectable in the NMR spectra (^1H NMR: CH_3 0.30 ppm, CH_2 0.37 ppm. ^{13}C NMR: CH_3 –8.4 ppm, CH_2 –3.1 ppm).

Each of the two indium-bound ligands is also *N*,*O*-chelated with a lithium cation, making each ligand formally dianionic ($DippL^{1-}$). Dianionic ketiminate and β-diketiminate ligands are far less common but have been documented.[39] The third ketiminate ligand at the base of the complex makes no indium contacts and is monoanionic, exhibiting only the typical *N*,*O*-chelation to a lithium cation. For charge balance the +10 cationic charge from the seven Li^+ cations and one In^{3+} atom balance the ten negative charges from the three chlorides, one monoanionic ketiminate ligands, two dianionic ketiminate ligands, and two CH_3 groups on the indium center.

Discussion of $[Li_5(Cl)(DippL^1)_4]\cdot 2PhMe$ (5)

To investigate whether another cage with increased indium content could be synthesized, the same reaction in THF was performed using two equivalents of in situ-generated $InMe_3$ [Scheme 5, procedure (i)]. Upon workup of the THF reaction mixture in toluene and storage at –30 °C, large colorless crystals of a second ketiminate-supported LiCl cage **5** were formed in 79% yield (Figure 7). Complex **5** was reproducibly obtained when the 1:1 reaction was repeated, but in diethyl ether rather than THF [Scheme 5, procedure (ii)]. Attempts were made at generating analogous cages using $GaMe_3$ under the same conditions, but no crystalline material could be isolated from these reactions.

X-ray structural determination shows that **5** exhibits several distinctions from **4**. No indium is contained in the final product, and the $[Li_5O_4Cl]$ core is supported by four ketiminate ligands and no THF molecules. Four of the five lithium cations in the core of this cage are in a tetrahedral coordination environment, with the fifth, Li(5), featuring square pyramidal geometry.

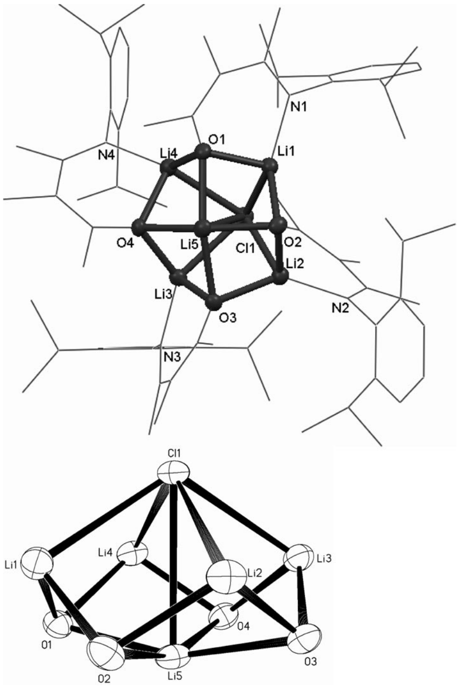
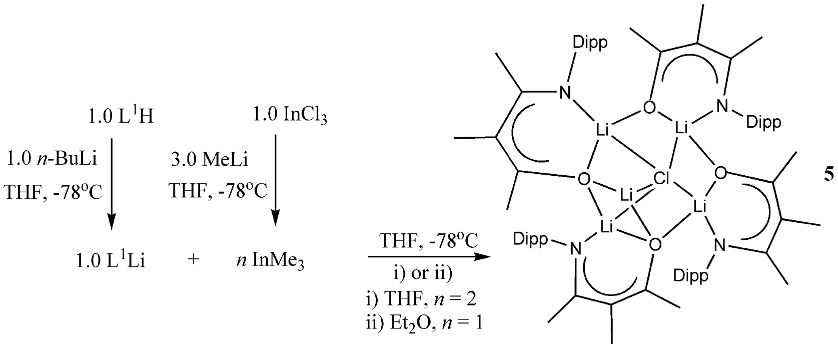


Figure 7. X-ray structure of 5 (full structure, left; cone-shaped core, right). Ketiminate ligands shown with wire frames in full structure, and core shown with ellipsoids drawn at 30% probability. Hydrogen atoms omitted for clarity.



Scheme 5. Synthesis of complex **5**.

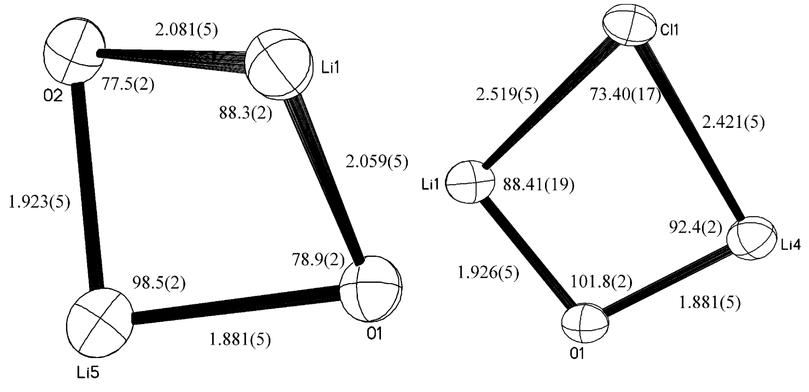


Figure 8. Representative "rectangle" (left) and kite (right) making up the core of **5** (bond lengths given in Å, angles in °).

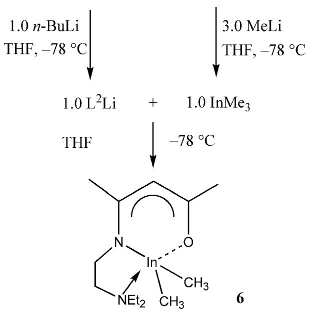
This geometry is less common for lithium atoms,[40] but examples include lithium bis(methoxycarbony1)phosphanide-1,2-dimethoxyethane,[40a] bis(l,2-dimethoxyethan-*O,O′*)-bis(THF-*O*){μ-1,2,4-triphospholo[1,2-*a*]-1,2,4-triphosphol-1,3,5,7-tetraonato(2–)-O^1,O^7:O^3,O^5} dilithium,[40b] $Li_2V_6O_{13}$,[40c] and $Li[B(C_2O_4)_2]$.[40d] Like **4**, the listed examples have oxygen atoms occupying the basal positions of the square pyramid at average distances to the lithium atom (ca. 2.039–2.294 Å) similar to that of **5** (ca. 2.072 Å). The core can be described as roughly cone-shaped (Figure 7), with the square pyramidal Li^+ occupying the center of the base and a μ_5-Cl capping the cone. The lithium–oxygen–chloride core is comprised of eight fused four-membered rings of two types. The first type are Li–O–Li–O rectangles, the second, Li–O–Li–Cl kites (Figure 8). Select bond lengths and angles are listed in Table 2.

Table 2. Selected bond lengths [Å] and angles [°] of $[Li_5(Cl)(DippL^1)_4]\cdot 2PhMe$ (**5**).

Li(1)–O(1)	1.881(5)	Li(4)–N(4)	1.984(5)
Li(1)–O(2)	1.923(5)	Li(1)–Cl(1)	2.421(5)
Li(2)–O(2)	1.868(5)	Li(2)–Cl(1)	2.524(5)
Li(2)–O(3)	1.922(5)	Li(3)–Cl(1)	2.463(5)
Li(3)–O(3)	1.874(5)	Li(4)–Cl(1)	2.519(5)
Li(3)–O(4)	1.919(5)	Li(5)–O(1)	2.059(5)
Li(4)–O(4)	1.877(5)	Li(5)–O(2)	2.081(5)
Li(4)–O(1)	1.926(5)	Li(5)–O(3)	2.077(5)
Li(1)–N(1)	1.967(5)	Li(5)–O(4)	2.069(5)
Li(2)–N(2)	1.985(6)	Li(5)–Cl(1)	2.742(4)
Li(3)–N(3)	1.968(5)		
O(1)–Li(1)–N(1)	92.8(2)	O(1)–Li(5)–Cl(1)	79.95(15)
O(2)–Li(2)–N(2)	92.9(2)	O(2)–Li(5)–Cl(1)	79.66(15)
O(3)–Li(3)–N(3)	93.8(2)	O(3)–Li(5)–Cl(1)	78.62(15)
O(4)–Li(4)–N(4)	93.5(2)	O(4)–Li(5)–Cl(1)	79.99(16)
O(1)–Li(5)–O(2)	88.2(2)	Li(1)–Cl(1)–Li(2)	73.23(17)
O(2)–Li(5)–O(3)	88.5(2)	Li(2)–Cl(1)–Li(3)	74.50(16)
O(3)–Li(5)–O(4)	88.1(2)	Li(3)–Cl(1)–Li(4)	72.97(16)
O(4)–Li(5)–O(1)	87.6(2)	Li(4)–Cl(1)–Li(1)	73.40(17)

Discussion of $[L^2InMe_2]$ (6)

Having identified a synthetic route to LiCl cages, we performed the analogous reaction as that employed for the formation of **4** to determine whether L^2 would support similar cages. Thus, in situ-generated L^2Li was treated with $InMe_3$ in THF. Following reaction work-up, colorless crystals of $[L^2InMe_2]$ (**6**) the CH_4 elimination product were isolated (Scheme 6).



Scheme 6. Synthesis of **6**.

The elimination of methane for the formation of **6** is in contrast to that observed in the reaction with $DippL^1H$ under the same conditions, which resulted in the cage complex **4**, rather than $[DippL^1InMe_2]$ (the analogous complex to **6**). This occurrence is consistent with our comparison of ArL^1 and L^2 with aluminum, specifically the exploitation of the tridentate functionality of L^2 to form three contacts with the metal. Again we observe the formation of a mono-ketiminate product **6** when employing tridentate L^2 and the inability of bidentate ArL^1 to stabilize such a mono-ligated product. Thus, in the case of **6**, the availability of the neutral ligand in solution to react with $InMe_3$ and eliminate methane, forming three ligand contacts with the indium center, is the primary driving force. The deliberate synthesis of **6** by reaction of L^2H and $InMe_3$ was performed and afforded **6** in higher yield.

Although complex **6** (Figure 9) was not the targeted L^2-supported LiCl cage, it is desirable in its own right due to its structural similarity to the previously reported complex $[InMe_2(\text{ketiminate})]$ {ketiminate = $O{=}C(CF_3)CH_2C(CF_3){=}NCH_2CH_2NMe_2$} with CF_3 substituents in place of the backbone methyls[41] which was shown to be a useful precursor in the chemical vapor deposition of indium oxide thin films. In spite of the extreme air and moisture sensitivity of $InMe_3$, $[L^2InMe_2]$ is relatively stable upon exposure to ambient air, as determined by a unit cell check of the crystals after exposure to air for 1 h. Complex **6** has fairly low thermal stability melting cleanly between 88–91 °C, but attempts at sublimation were unsuccessful. The bond lengths and angles of **6** compare well with that of the CF_3-substituted complex, $[InMe_2(\text{ketiminate})]$ {ketiminate = $O{=}C(CF_3)CH_2C(CF_3){=}NCH_2CH_2NMe_2$}, with expected variations around the indium center attributed to the electron-withdrawing CF_3 groups.[41] Namely, the In–N [2.321(2) Å] and In–O [2.251(3) Å] distances are slightly greater than those of **6** [In–N: 2.242(2) Å, In–O:

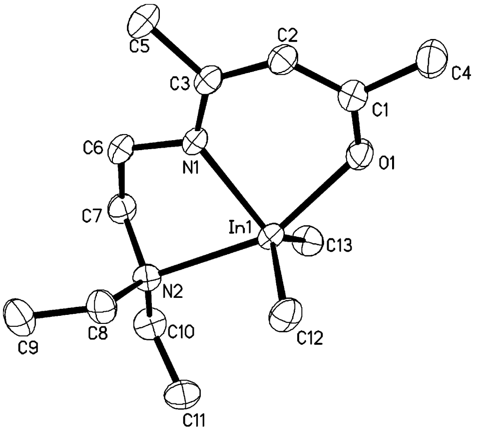


Figure 9. Molecular structure of **6**. Thermal ellipsoids drawn at 30% probability. Hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: In(1)–C(12) 2.153(3), In(1)–C(13) 2.156(3), In(1)–O(1) 2.238(2), In(1)–N(1) 2.242(2), In(1)–N(2) 2.538(2), C(12)–In(1)–C(13) 131.76(14), C(12)–In(1)–O(1) 95.38(11), C(13)–In(1)–O(1) 93.65(11), O(1)–In(1)–N(1) 82.61(8), N(1)–In(1)–N(2) 74.10(9), O(1)–In(1)–N(2) 156.47(8).

2.238(2) Å], making the In–C bonds slightly stronger and shorter in the CF_3 complex [2.141(2), 2.142(2) Å] than in **6** [2.153(3), 2.156(3) Å].

Conclusions

The coordination preferences of bidentate ArL^1 and tridentate L^2 were investigated with several group 13 precursors, affording a range of products. Aside from the expected *N*,*O*-chelation, a monomeric adduct (in the case of gallium) and two novel LiCl cages were synthesized, one of which featured an $InMe_2$ moiety bridging two ketiminate ligands. Despite some variability in the favorability of deprotonation in both ArL^1 and L^2, the commonality among these complexes is the ability of L^2 to better stabilize metal centers with its 3 ligand contacts, relative to ArL^1, with 2 ligand contacts. In addition, the isolation of bimetallic cage **4** shows the versatility of ketiminato ligands and highlights their diverse coordination modes.

Experimental Section

General: All manipulations were performed under anaerobic conditions using standard Schlenk techniques. Hexane and toluene were dried using an MBraun-SPS solvent purification system. The ligands, L^1H and L^2H were prepared according to published procedures.[6a,42] All other reagents were purchased from Aldrich and used as received. Crystal data were collected with a Bruker SMART 1000 diffractometer, molybdenum radiation (λ = 0.7107 Å) at –50 or –60 °C. Crystals were mounted on glass fibers using paratone oil. The data were corrected for absorption. Structures were solved by direct methods[43] and refined[43] via full-matrix least-squares. Crystal data for **1**–**6** can be found in Table 3. Hydrogen atoms were placed in idealized positions except certain M-CH_3 groups and NH groups that were localized from the electron-density map and refined with distant restraints. The ^1H and ^{13}C NMR spectra were recorded at 300.05 and 75.45 MHz, respectively, on a Varian XL-300, IR analysis was conducted as Nujol mulls with NaCl plates on a MIDAC M4000 Fourier transform infrared (FT IR) spectrometer, and mass spectrometry analysis was carried out using a Bruker Esquire 6000 Mass Spectrometer and North Carolina, Mass Spectrometry Facility. Melting or decomp. points were determined in capillaries under a nitrogen atmosphere.

Synthesis of [DmpL^{1}BF$_2$] (1): To a stirring CH_2Cl_2 solution of DmpL^{1}Li (0.35 g, 1.57 mmol) was slowly added via syringe a threefold excess of $BF_3{\cdot}Et_2O$ (0.59 mL, 4.7 mmol) at room temperature. Within minutes, the initially pale yellow reaction mixture became darker yellow. After stirring overnight, the reaction mixture became cloudy and straw colored. Following removal of the volatiles in vacuo and extraction into a hexane/diethyl ether mix, colorless needles of **1** were obtained; yield 51%; m.p. 102–106 °C. ^1H NMR ($CDCl_3$, 25 °C): δ = 1.80 (s, 3 H, backbone γ C*Me*), 1.88 (s, 3 H, NC*Me*), 2.09 (s, 6 H, Ar*Me*), 2.1 (s, 3 H, OC*Me*), 7.02–7.10 (m, 3 H, Ar*H*) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 13.7 (backbone *Me*), 18.27 (backbone *Me*), 18.30 (Ar*Me*), 4.7 (Ar*Me*), 103.0 (γ backbone *C*), 128.0 (*para* Ar*C*), 128.9 (*meta* Ar*C*), 134.4 (*ortho* Ar*C*), 138.8 (Ar*C*-N), 172.9 (backbone *C*N), 173.2 (backbone *C*O) ppm. ^{11}B NMR (28.88 MHz, $CDCl_3$, 25 °C): δ (ppm) 0.91 (t, J = 14.1 Hz) ppm. ^{19}F NMR ($CDCl_3$, 25 °C): δ = –139.5 ppm. IR (Nujol mull): $\tilde{\nu}$ = 772 (w), 892 (w), 1078 (m), 1162 (m), 167 (m), 1309 (s), 1613 (m) cm^{-1}.

Synthesis of [L^{2}Al(Me)Cl] (2A and 2B): To a Schlenk flask that had not been flame dried was added L^2H (0.29 g, 1.5 mmol) under a

Table 3. Crystal data for compounds **1**–**6**.

	1	**2B (2A)**	**3**	**4**	**5**	**6**
Chemical formula	$C_{14}H_{18}BF_2NO$	$C_{12}H_{24}AlClN_2O$ ($C_{11.70}H_{23.11}AlCl_{1.29}N_2O$)	$C_{36}H_{53}Cl_6Ga_2N_2O_2$	$C_{68}H_{106}Cl_3InLi_7N_3O_6$	$C_{86}H_{121}ClLi_5N_4O_4$	$C_{13}H_{27}InN_2O$
Formula weight	265.10	274.76 (280.78)	897.94	1331.31	1344.01	342.19
Crystal system	orthorhombic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$Pna2_1$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
T /K	213(2)	213(2)	213(2)	223(2)	223(2)	213(2)
a /Å	24.2280(18)	11.6821(13), [11.6627(13)]	27.085(11)	15.1948(10)	18.257(2)	8.8945(19)
b /Å	14.2005(10)	11.1958(19), [11.1893(12)]	9.660(4)	15.6781(10)	26.669(3)	13.435(3)
c /Å	8.1794(6)	14.456(2)/[14.4605(12)]	16.725(7)	17.3832(11)	17.976(2)	27.261(6)
α /°	90	90	90	95.8990(10)	90	90
β /°	90	128.223(6)/[128.209(6)]	90	103.5820(10)	107.875(2)	91.387(4)
γ /°	90	90	90	107.6320(10)	90	90
V /Å^3	2814.1(4)	1485.4(4)/[1482.8(3)]	4376(3)	3768.0(4)	8329.9(16)	3256.7(12)
Z	8	4	4	2	4	8
Reflections collected	13671	4995/(7655)	18102	32460	65797	27186
Independent reflections	4781	2363/(2668)	6678	13551	15051	5902
Data/restraints/ parameter ratio	4781/1/353	2363/0/159/ (2668/0/158)	6678/0/448	13551/7/814	15051/0/931	5902/0/319
R_{int}	0.0235	0.0361/(0.0220)	0.0979	0.0502	0.0468	0.0290
D_{calc} /Mg m^{-3}	1.251	1.229/(1.258)	1.363	1.173	1.072	1.396
Absorption coefficient /mm^{-1}	0.095	0.305/(0.358)	1.629	0.466	0.094	1.441
F(000)	1120	592/(601)	1852	1408	2912	1408
R indices (all data)	$R1$ = 0.0417 $wR2$ = 0.0908	$R1$ = 0.0709, $wR2$ = 0.1450/ ($R1$ = 0.0469, $wR2$ = 0.1024)	$R1$ = 0.1554, $wR2$ = 0.1915	$R1$ = 0.1052, $wR2$ = 0.1676	$R1$ = 0.1089, $wR2$ = 0.1840	$R1$ = 0.0320, $wR2$ = 0.0647
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0315 $wR2$ = 0.0809	$R1$ = 0.0505, $wR2$ = 0.1348/ ($R1$ = 0.0356, $wR2$ = 0.0917)	$R1$ = 0.0649, $wR2$ = 0.1464	$R1$ = 0.0580, $wR2$ = 0.1339	$R1$ = 0.0646, $wR2$ = 0.1573	$R1$ = 0.0237, $wR2$ = 0.0571
Largest difference in peak and hole /e Å^{-3}	0.194 and –0.134	0.458 and –0.224/ (0.372 and –0.315)	0.462 and –0.829	2.348 and –0.572	0.466 and –0.289	0.536 and –0.358

nitrogen atmosphere. Approximately 10 mL of undried hexane (from the reagent bottle) was poured in and the stirring solution cooled to –78 °C. $AlMe_2Cl$ (1.0 M in hexanes, 1.5 mL, 1.5 mmol) was syringed in dropwise, immediately resulting in a bright yellow solution and precipitate. The cooling bath was removed after 10 min, and stirring was maintained at room temp. overnight. Extraction into toluene, concentration, and storage overnight at room temp. yielded large colorless rectangular crystalline blocks of **2A**; yield 0.11 g, 28 %. **2B** was prepared in same manner, using strictly anaerobic conditions and toluene as the solvent; yield 0.16 g, 39 %; m.p. 111–113 °C. ^{1}H NMR ($CDCl_3$, 25 °C): δ = –0.68 (s, 3 H, Al-$C\mathit{H}_3$), 1.08 (t, $^1J_{H,H}$ = 7.0 Hz, 6 H, $CH_2\mathit{Me}$), 1.98 (s, 3 H, backbone NC*Me*), 2.02 (s, 3 H, OC*Me*), 2.69, 2.90 (overlapping multiplets, 6 H, $NC\mathit{H}_2CH_3$ and $NC\mathit{H}_2CH_2N$), 3.30 (t, $^1J_{H,H}$ = 5.9 Hz, 2 H, $NCH_2C\mathit{H}_2N$), 5.16 (s, 1 H, backbone γ C*H*) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 8.4 ($CH_2\mathit{Me}$), 6.0 (NC*Me*), 9.0 (OC*Me*), 43.9, 44.3, 48.5 ($N\mathit{C}H_2$), 99.9 (backbone γ *C*H), 176.5 (*C*N), 183.5 (*C*O) ppm, Al-$\mathit{C}H_3$ not observed. IR (Nujol mull): ṽ = 1347 (w), 1532 (w), 1581 (w) cm^{-1}.

Synthesis of [$GaCl_3$·DippL^{1}H] (3): To a stirring THF solution of DippL^{1}H (0.35 g, 1.3 mmol) at –78 °C was added dropwise *n*BuLi (2.5 M in hexanes, 0.51 mL, 1.3 mmol). The cooling bath was immediately removed and the lithiation reaction was stirred overnight at room temperature. The ligand solution was then added to a stirring THF suspension of $GaCl_3$ at –78 °C, resulting in the evolution of colorless gas and the formation of a yellow solution. Stirring was maintained at low temperature for 10 min, at which time the THF was removed and the white solid extracted into toluene. Crystals of **3** were obtained at room temperature from a toluene/hexane mix; yield 0.12 g, 20 %; m.p. 92–95 °C. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 1.16, 1.20 (overlapping doublets, $^1J_{H,H}$ = 7.0 Hz, 12 H, *i*Pr $C\mathit{Me}_2$), 1.80 (s, 3 H, γ backbone *Me*), 1.95 (s, 3 H, backbone NC*Me*), 2.35 (s, 3 H, backbone OC*Me*), 2.92 (sept, $^1J_{H,H}$ = 6.7 Hz, 2 H, *i*Pr $C\mathit{H}Me_2$), 7.20 (d, $^1J_{H,H}$ = 7.6 Hz, 2 H, *meta* Ar*H*), 7.32 (t, $^1J_{H,H}$ = 7.6 Hz, 1 H, *para* Ar*H*), 13.01 (broad s, 1 H, N*H*) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 15.0, 17.6 (*i*Pr *Me*), 5.9, 7.7, 27.6 (backbone *Me*), 28.8 (*i*Pr *C*H), 100.4 (backbone γ *C*Me), 17.0 (*para* Ar*C*), 128.8 (*meta* Ar*C*), 133.6 (*ortho* Ar*C*), 145.9 (N-Ar*C*), 166.8 (*C*N), 12.7 (*C*O) ppm. IR (Nujol mull): ṽ = 773 (w), 974 (m), 1136 (m), 1151 (m), 1170 (m), 1592 (w), 3285 (w, br) cm^{-1}. MS *m*/*z*; found (calcd.) 273.3 (273.4) L^H.

Synthesis of [$InMe_2Li_7Cl_5$(DippL^{1-})$_2$(DippL^1)(THF)$_3$] (4): A THF solution of DippL^{1}H (0.35 g, 1.3 mmol) was cooled to –78 °C and *n*BuLi (2.5 M in hexanes, 0.51 mL, 1.3 mmol) added dropwise, and was then allowed to stir for 1 h at low temperature. In a separate Schlenk flask, 3 equiv. of MeLi (1.6 M in diethyl ether, 2.4 mL, 3.9 mmol) were added dropwise to a stirring suspension of $InCl_3$ at –78 °C, and stirring was maintained at this temperature for 30 min. Following that, the cold solution of DippL^{1}Li was added rapidly by cannula to the stirring $InMe_3$ solution at –78 °C. After 15 min, the cooling bath was removed, and the resultant clear bright yellow solution was allowed to stir overnight at ambient temperature. A clear amber solution was observed, from which the volatiles were removed in vacuo. After extraction of the foamy yellow solid into PhMe, filtration, and storage at –30 °C, large colorless crystalline chunks of **4** were afforded; yield 0.43 g, 25 %; decomp. point 92–94 °C (turns orange), 122–126 °C (turns red), 135–139 °C (turns maroon), 191–194 °C (turns black). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 0.30 (s, 6 H, $In\mathit{Me}_2$), 0.37 [s, 4 H, $In(C\mathit{H}_2)_2$]; 1.30, 1.37, 1.41, 1.43, 1.45, 1.48 (overlapping doublets, $^1J_{H,H}$ = 6.7 Hz, 36 H, *i*Pr $C\mathit{Me}_2$), 1.87 (s, 3 H, backbone *Me*), 2.02 (m, THF $OCC\mathit{H}_2$), 2.07 (s, 3 H, backbone *Me*), 2.14, 2.20 (s, 6 H each, backbone *Me*), 2.42 (s, 3 H, backbone *Me*), 3.02 (sept, $^1J_{H,H}$ = 6.7 Hz, 2 H, *i*Pr $C\mathit{H}Me_2$), 3.9 (sept, $^1J_{H,H}$ = 6.7 Hz, 4 H, *i*Pr $C\mathit{H}Me_2$), 4.05 (m, THF $OC\mathit{H}_2$), 7.46 (d, $^1J_{H,H}$ = 7.6 Hz, 8 H, *meta* Ar*H*), 7.57 (t, $^1J_{H,H}$ = 7.7 Hz, 4 H, *para* Ar*H*) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ (ppm) = –8.4 [$In(\mathit{C}H_3)_2$]; –3.1 [$In(\mathit{C}H_2)_2$]; 15.0, 17.4, 1.9, 20.9, 4.6, 4.7 (*i*Pr *Me*), 6.0, 6.1, 7.4, 8.6, 8.8 (backbone *Me*), 7.4, 7.6, 9.8,28.0 (*i*Pr *C*H), 8.8 (THF $OC\mathit{C}H_2$), 68.2 (THF $O\mathit{C}H_2$), 90.6, 96.2 (backbone γ *C*Me), 16.7, 17.1, 18.5, 1.0, 128.5, 129.3, 132.5, 138.1, 138.9, 141.5, 142.8, 146.3 (Ar*C*), 166.5, 169.7 (*C*N), 171.0, 174.4 (*C*O) ppm. IR (Nujol mull): ṽ = 770 (s), 891 (m), 971 (s), 1159 (m), 1561 (s), 1606 (s) cm^{-1}. MS *m*/*z*; found (calcd.): 1130 (1130.6) M – 4Li – $In(CH_3)_2$-$(CH_2)_2$; 274 (274.4) DippL^{1}H.

Synthesis of [Li_5(Cl)(DippL^1)$_4$]·2PhMe (5): Compound **5** was synthesized and worked up analogously to **4** but carried out in diethyl ether rather than THF. Alternatively, **5** was prepared in THF as described in the synthesis of **6** but by using 2 equiv. of $InMe_3$ (rather than 1), prepared from $InCl_3$ (0.57 g, 2.6 mmol) and MeLi (1.6 M in diethyl ether, 4.8 mL, 7.8 mmol), yield 0.33 g, 79 %; decomp. point 93–95 °C (turns yellow), 129–133 °C (turns orange), 142–145 °C (turns maroon), 188–191 °C (turns black). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 0.39, 0.61, 1.01, 1.07 (doublets, $^1J_{H,H}$ = 6.7 Hz, 12 H each, *i*Pr $C\mathit{Me}_2$), 1.57 (s, 12 H, γ backbone *Me*), 1.84 (s, 12 H, backbone NC*Me*), 1.89 (s, 12 H, backbone OC*Me*), 2.33, 2.72 (2 sept, $^1J_{H,H}$ = 6.5 Hz, 4 H each, *i*Pr $C\mathit{H}Me_2$), 2.38 (s, Ph*Me*), 6.91–7.04 (m, 12 H, Ar*H*), 7.1 (m, toluene Ar*H*), 7.9 (m, toluene Ar*H*) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ (ppm) 17.4, 20.9, 6.1, 7.1 (*i*Pr *Me*), 7.5, 8.3, 27.5 (backbone *Me*), 28.2, 28.7 (*i*Pr *C*H), 101.6 (backbone γ *C*Me), 15.9, 16.3, 16.5, 16.6, 16.7, 18.5, 128.5 129.3, 138.9, 139.4, 146.1, 146.5 (Ar*C*), 168.7(*C*N), 171.0 (*C*O) ppm. IR (Nujol mull): ṽ = 880 (w), 1534 (m), 1598 (m) cm^{-1}. MS *m*/*z*; found (calcd.): 827 (827.2) 3DippL^{1}H + Li; 553 (553.8) 2DippL^{1}H + Li; 274 (274.4) DippL^{1}H.

Synthesis of [L^2$InMe_2$] (6): To a stirring THF solution of L^{2}H (0.25 g, 1.3 mmol) at –78 °C was added dropwise *n*BuLi (2.5 M in hexanes, 0.51 mL, 1.3 mmol). The reaction warmed to room temp. slowly and stirring was continued an additional 2 h. In a separate Schlenk flask, a cloudy, colorless THF suspension of $InCl_3$ (0.28 g, 1.3 mmol) was cooled to –78 °C and MeLi (1.6 M in diethyl ether, 2.4 mL, 3.9 mmol) added dropwise. Stirring at –78 °C of the $InMe_3$ was maintained for 30 min, after which time the L^{2}Li was added rapidly via cannula. After 10 min, the cooling bath was removed and the reaction mixture became clear yellow with a small amount of yellow solid. After stirring overnight at room temp., the volatiles were removed in vacuo and the yellow oily residue extracted into toluene. Colorless crystals of **6** suitable for X-ray diffraction were grown from hexane at –10 °C; yield 0.11 g, 25 %. Complex **6** can also be prepared deliberately with analogous conditions, using L^{2}H, rather than L^{2}Li; yield 0.33 g, 75 % and spectroscopic data matched that of the originally obtained crystals; m.p. 88–91 °C. ^{1}H NMR ($CDCl_3$, 25 °C): δ = –0.32 (s, 6 H, $In\mathit{Me}_2$), 0.97 (t, $^1J_{H,H}$ = 7.0 Hz, 6 H, $CH_2C\mathit{H}_3$), 1.88 (s, 3 H, NC*Me*), 1.93 (s, 3 H, OC*Me*), 2.61 (quart, $^1J_{H,H}$ = 7.9 Hz, 4 H, $NC\mathit{H}_2CH_3$), 2.71 (t, $^1J_{H,H}$ = 5.9 Hz, 2 H, $NC\mathit{H}_2CH_2N$), 3.32 (t, $^1J_{H,H}$ = 5.9 Hz, 2 H, $NCH_2C\mathit{H}_2N$), 4.79 (s, 1 H, backbone γ C*H*) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = –8.1 ($In\mathit{Me}_2$), 8.2 ($CH_2\mathit{Me}$), 6.5 (NC*Me*), 28.0 (OC*Me*), 42.2, 45.9, 51.2 ($N\mathit{C}H_2$), 97.0 (backbone γ *C*H), 173.9 (*C*N), 184.4 (*C*O) ppm. IR (Nujol mull): ṽ = 939 (w), 1346 (m), 1407 (m), 151 (s), 1575 (s) cm^{-1}. MS *m*/*z*; found (calcd.) 341.1 (342.2) M$^+$, 199.2 (198.2) $Et_2NCH_2CH_2N(H)C(Me)CHC(Me)O$.

CCDC-755673 (for **1**), -755674 (for **2A**), -755675 (for **2B**), -755676 (for **3**), -755677 (for **4**), -755678 (for **5**), and -755679 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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