Bulky Amidinate Complexes of Indium(III). Synthesis and Structure of [CyNC(tBu)NCy]2InCl

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Reaction of 2 equiv of lithium dicyclohexylacetamidinate with $InCl_3$ affords the new species $In[CyNC(Me)NCy]_2$-Cl (Cy = cyclohexyl) (**1**). Compound **1** reacts with MeLi to yield $In[CyNC(Me)NCy]_2CH_3$ (**2**) and also reacts with a third equivalent of amidinate to yield $In[CyNC(Me)NCy]_3$ (**3**). Two new bulky amidinate ligands are prepared by the addition of tBuLi to CyN=C=NCy and $Me_3SiN=C=CSiMe_3$, respectively. Subsequent reactions with $InCl_3$ lead to the high-yield syntheses of $In[CyNC(CMe_3)NCy]_2Cl$ (**4**) and $[Me_3SiN(CMe_3)NSiMe_3]_2InCl$ (**5**). Spectroscopic and elemental analyses confirm the formulas of all of these new species. Compound **4** is further characterized by X-ray crystallography and shown to possess a distorted trigonal bipyramidal coordination geometry around the metal center with the chloride group in the equatorial position. Crystal data for **4**: triclinic, $P\bar{1}$, $a = 12.545(7)$ Å, $b = 13.482(8)$ Å, $c = 11.965(6)$ Å, $\alpha = 102.08(5)°$, $\beta = 92.00(5)°$, $\gamma = 64.36(4)°$, $Z = 2$, $R = 0.029$, $R_w = 0.045$.

Introduction

The recent resurgence of interest in the preparation of inorganic and organometallic complexes of Al, Ga, and In stems from their appearance in a variety of technologically important electronic materials and from a more basic effort to clarify the steric and electronic effects on both the structure and reactivity of group 13 species.[1] The latter endeavor is reflected by an increasing number of reported complexes of these elements having novel ligands and uncommon coordination geometries.[2−17] Motivated by an interest in the effects of ligand geometry on the coordination environments of post-transition elements in general and of indium specifically, we began a systematic study of the use of bidentate, three-atom bridging ligands for the preparation of indium compounds. This family of ligands has been important in preparing a variety of dinuclear transition metal complexes,[18] and a member of this class of ligands, the triazenide anion, was recently used to stabilize unusual aluminum and indium alkyls.[4,7,8] In particular, we have focused on the use of amidinates, formamidinates, and triazenates ($RNXNR^-$; X = CR′, CH, N) as ligands for In and Sn. Through modification of the organic substituents on the nitrogen atoms and at the bridge position, these ligands should present an ideal system to explore the effects of steric bulk and electronic features on the product compounds. For example, formamidinate ligands are known to favor unusual structural features in both transition metal and main group metal chemistry.[17,19,20]

Herein we report, as part of our ongoing investigation, the synthesis and characterization, including preliminary reactivity, of a novel family of monomeric five-coordinate In^{III} compounds of the general formula $In[RNC(R′)NR]_2Cl$ (R = cyclohexyl, $SiMe_3$; R′ = Me, tBu). The introduction of the tBu group at the bridging position adds two new sterically demanding members to the amidinate family of ligands. The complexes within this series show substantial differences in reactivity with respect to alkylation and formation of tris(ligand) complexes.

Results and Discussion

Complexes of the $[CyNC(Me)NCy]^-$ Anion. Reaction of the lithium salt of dicyclohexylacetamidinate, prepared by the combination of dicylohexylcarbodiimide and MeLi, with $InCl_3$ in a 2:1 stoichiometry afforded the new species **1** (Scheme 1) in 78% yield. The ^1H NMR spectrum for **1** is consistent with a single environment for the acetamidinate ligand. Elemental analysis confirmed the formula of this species to be $In[CyNC(Me)NCy]_2Cl$ (Cy = cyclohexyl). We propose the structure shown in Scheme 1.[7,17,20]
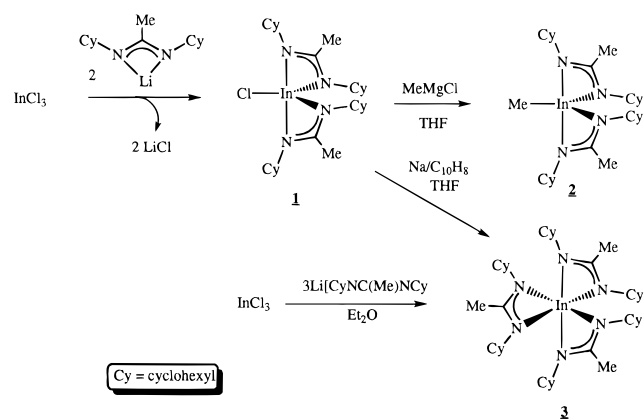
Complex **1** undergoes a facile alkylation reaction with 1 equiv of MeMgCl to yield the new organometallic species $In[CyNC(Me)NCy]_2CH_3$ (**2**). The spectroscopic features are consistent our proposed composition of **2** as an organoindium species.

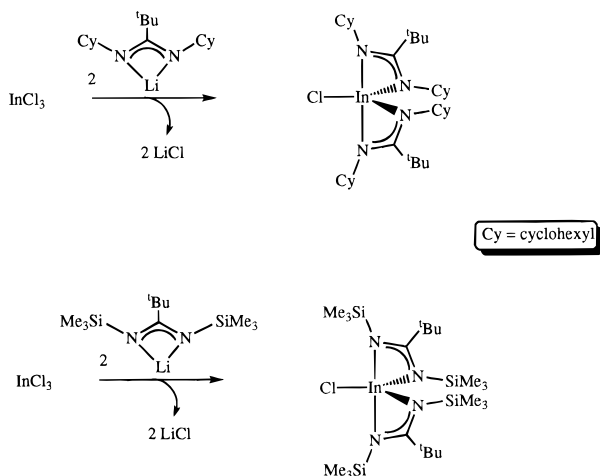⊗ Abstract published in *Advance ACS Abstracts,* April 1, 1996.

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Scheme 1

Cy = cyclohexyl

Scheme 2

Cy = cyclohexyl

Table 1. Summary of Crystal Data for **4**

empirical formula	In Cl N$_4$ C$_{34}$ H$_{62}$
fw	677.16
space group	$P\bar{1}$
a, Å	12.545(7)
b, Å	13.482(8)
c, Å	11.965(6)
α, deg	102.08(5)
β, deg	92.00(5)
γ, deg	64.36(4)
V, Å^3	1780.3(16)
Z	2
no. of reflns for cell	24
D_{calc}, Mg·m^{-3}	1.263
μ, mm^{-1}	0.74
T, °C	−153
radiation (λ, Å)	Mo Kα (0.710 69)
R, R_w, GoF^a	0.029, 0.045, 4.50

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$; GoF $= [(\Sigma w(|F_o| - |F_c|)^2)/(n_{reflns} - n_{params})]^{1/2}$.

establish the monomeric nature, coordination geometry of the metal center, and connectivity of the ligand for complex **4** (Figure 1 and following section).

The reactivity of complex **4** contrasts with the methyl analog, **1**. So far, attempts to alkylate this material with Grignard and lithium reagents have been unsuccessful. Both reaction of complex **4** with Na/C$_{10}$H$_8$ and attempts to incorporate a third equivalent of ligand to generate the analogous complex to **3** have resulted in a complex mixture of products, a fact which is most clearly demonstrated by the appearance of several resonances in the ^{1}H NMR ascribed to ^{t}Bu groups. We attribute this difference in reactivity to the increased steric bulk of CyNC-(CMe$_3$)NCy compared to CyNC(Me)NCy.

A similar reaction of ^{t}BuLi with 1,3-bis(trimethylsilyl)-carbodiimide in ether generates Li[Me$_3$SiN(CMe$_3$)NSiMe$_3$]. Reaction of this species with InCl$_3$ in a 2:1 ratio yields the corresponding bis(amidinato) chloro complex [Me$_3$SiN(CMe$_3$)-NSiMe$_3$]$_2$InCl (**5**) (Scheme 2). The formulation and proposed structure for **5** were confirmed by spectroscopic evidence, microanalysis, and analogy with **4**. Like complex **4** and in contrast to **1**, **5** does not react cleanly with alkylating or reducing agents and will not incorporate a third amidinate ligand.

Crystal Structure of 4. Complex **4** crystallized in the triclinic space group $P\bar{1}$ with two molecules in the unit cell (see Table 1). There are no anomalously short intermolecular contacts. The molecular geometry and atom-numbering scheme are shown in Figure 1.

The structural analysis revealed a molecular core with the metal center in a distorted trigonal bipyramidal (TBP) environment consisting of the two amidinate anions with an equatorial chloride group completing the coordination sphere.[22] Tables 2−4 provide a summary of heavy atom positions and selected bond distances and angles for **4**. The bonding parameters within the two amidinate ligands are not dramatically different, resulting in a molecular geometry that is of approximately C_2 symmetry. The fact that the Cy groups are equivalent in the ^{1}H and ^{13}C NMR spectra indicates the possibility that complex may be fluxional in solution.

The metal center lies at the intersection of two planes: the pseudoequatorial plane consisting of Cl1, N1, and N4 with the pseudoaxial plane described by Cl1, N2, and N3. Planarity of these groups is confirmed by the fact that the sum of the appropriate angles is 360°. As expected for the trigonal

Because bulky groups are known to stabilize a reduced In center, we attempted the reduction of **1** with Na/C$_{10}$H$_8$ as shown in Scheme 1.[21] The product of this reaction, **3**, possessed only the NMR resonances for equivalent dicyclohexylamidinate ligands. Microanalysis confirmed the formulation as the tris-(acetamidinate) complex, In[CyNC(Me)NCy]$_3$, which likely arises through a disproportionation reaction from a reduced In complex. We propose a six-coordinate structure on the basis of the high-yield, independent synthesis of **3** from the reaction of InCl$_3$ with 3 equiv of Li[CyNC(Me)NCy], the spectroscopic evidence, and the report of the six-coordinate complex In{2-[N(CH$_2$C$_6$H$_5$)]NC$_5$H$_4$}$_3$ from our laboratory (Scheme 1).[17]

Complexes of the [RNC(CMe$_3$)NR]$^-$ Anion (R = Cy, SiMe$_3$). In an effort to extend this family of complexes as well as to enlarge the range of available amidinate ligands, we have been investigating the introduction of sterically demanding groups into the bridge position. Our synthetic methodology is based on the reaction of organolithium reagents with carbodi-imide to generate the appropriate amidinate species. Complex preparation is achieved by addition of a stoichiometric amount of InCl$_3$ to this solution.

The addition of ^{t}BuLi to dicyclohexylcarbodiimide proceeds smoothly in ether at room temperature. Subsequent addition of 0.5 equiv of InCl$_3$ followed by recrystallization resulted in isolation of an 86% yield of In[CyNC(CMe$_3$)NCy]$_2$Cl (**4**) (Scheme 2). Spectroscopic characterization and microanalysis confirmed the formula of the complex. However, a single-crystal X-ray diffraction analysis was needed in order to

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(22) References 6, 7, 9, 13, 14, and 16 present crystal structures of five-coordinate gallium and indium complexes in distorted trigonal bipyramidal coordination environments. The values for the angle along the pseudoaxial vectors in these reports fall in the range 149.7−178.4°.
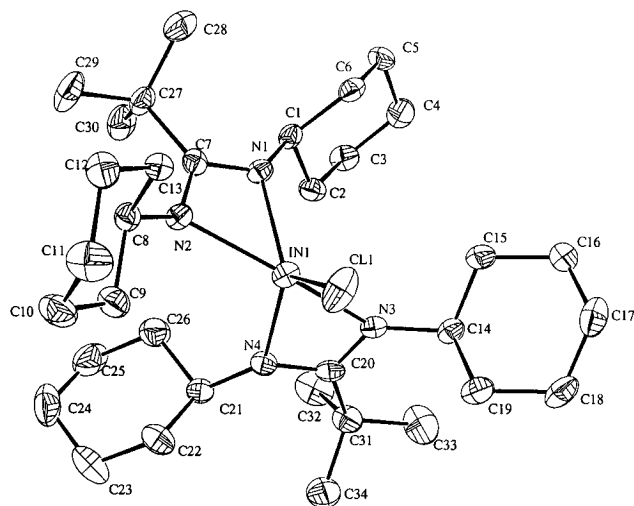
Figure 1. Molecular structure and atom-numbering scheme for ClIn-[C$_6$H$_{11}$NC(CMe$_3$)NC$_6$H$_{11}$]$_2$ (**4**). Hydrogen atoms have been omitted for clarity.

Table 2. Atomic Parameters x, y, z and B_{iso} Values

	x	y	z	B_{iso},^{a} Å^2
In1	0.85965(3)	0.15234(3)	0.28369(3)	1.9(1)
Cl1	1.0139(1)	−0.03710(9)	0.2366(1)	3.3(6)
N1	0.7841(3)	0.2443(2)	0.4582(2)	1.8(2)
N2	0.7224(3)	0.1202(2)	0.3636(2)	1.7(2)
N3	0.9552(3)	0.2361(2)	0.2152(2)	1.8(2)
N4	0.7797(3)	0.2551(2)	0.1572(2)	1.8(2)
C1	0.7895(3)	0.3414(3)	0.5348(3)	1.8(2)
C2	0.7878(3)	0.4249(3)	0.4654(3)	2.2(2)
C3	0.7996(4)	0.5261(3)	0.5400(3)	2.5(2)
C4	0.9074(4)	0.4895(3)	0.6097(3)	2.8(2)
C5	0.9082(4)	0.4076(3)	0.6796(3)	2.3(2)
C6	0.8995(3)	0.3064(3)	0.6030(3)	2.0(2)
C7	0.7102(3)	0.1964(3)	0.4612(3)	1.8(2)
C8	0.6993(3)	0.0211(3)	0.3448(3)	1.8(2)
C9	0.7002(4)	−0.0223(3)	0.2163(3)	2.4(2)
C10	0.6840(4)	−0.1304(3)	0.1898(3)	3.0(3)
C11	0.7741(4)	−0.2198(3)	0.2443(3)	3.3(3)
C12	0.7710(4)	−0.1775(3)	0.3724(3)	2.4(2)
C13	0.7896(3)	−0.0711(3)	0.3992(3)	2.1(2)
C14	1.0796(3)	0.2133(3)	0.2082(3)	1.9(2)
C15	1.1346(3)	0.1848(3)	0.3199(3)	2.3(2)
C16	1.2651(4)	0.1596(4)	0.3178(3)	3.0(3)
C17	1.3344(4)	0.0663(3)	0.2154(4)	3.2(3)
C18	1.2798(4)	0.0933(3)	0.1049(3)	2.9(2)
C19	1.1499(4)	0.1173(3)	0.1075(3)	2.5(2)
C20	0.8688(3)	0.2835(3)	0.1491(3)	2.0(2)
C21	0.6613(3)	0.3003(3)	0.1158(3)	2.0(2)
C22	0.6406(4)	0.2095(3)	0.0318(3)	2.8(2)
C23	0.5166(4)	0.2524(4)	−0.0083(4)	4.0(3)
C24	0.4240(4)	0.3069(4)	0.0901(4)	4.4(3)
C25	0.4437(4)	0.3968(4)	0.1726(4)	4.2(3)
C26	0.5681(4)	0.3530(3)	0.2148(3)	3.1(3)
C27	0.6161(3)	0.2351(3)	0.5625(3)	2.2(2)
C28	0.6755(4)	0.2328(4)	0.6774(3)	3.3(3)
C29	0.5458(4)	0.1662(4)	0.5579(4)	3.5(3)
C30	0.5237(4)	0.3548(3)	0.5557(4)	3.2(3)
C31	0.8600(4)	0.3706(3)	0.0772(3)	2.6(2)
C32	0.7609(4)	0.4852(3)	0.1362(4)	3.7(3)
C33	0.9691(4)	0.3918(4)	0.0706(4)	4.3(3)
C34	0.8357(4)	0.3317(4)	−0.0470(3)	3.5(3)

^{a} B_{iso} is the mean of the principal axes of the thermal ellipsoid.

bipyramidal geometry, the equatorial In−N bond lengths are slightly shorter than the axial distances.[23] These two planes are not perpendicular (e.g. N1−In−N2 = 60.2(1)° and N3−In−N4 = 59.8(1)°), as in a strict TBP geometry, a feature which

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Table 3. Selected Bond Distances (Å) for **4**

In1−Cl1	2.405(1)	N2−C8	1.457(5)
In1−N1	2.198(3)	N3−C14	1.456(5)
In1−N2	2.236(3)	N3−C20	1.327(5)
In1−N3	2.239(3)	N4−C20	1.341(5)
In1−N4	2.188(3)	N4−C21	1.455(5)
N1−C1	1.459(5)	C7−C27	1.561(5)
N1−C7	1.345(5)	C20−C31	1.560(5)
N2−C7	1.347(5)		

Table 4. Selected Bond Angles in (deg) for **4**

Cl1−In1−N1	124.43(8)	In1−N2−C8	131.4(2)
Cl1−In1−N2	99.25(8)	C7−N2−C8	129.4(3)
Cl1−In1−N3	97.57(8)	In1−N3−C14	132.7(2)
Cl1−In1−N4	123.74(8)	In1−N3−C20	93.3(2)
N1−In1−N2	60.2(1)	C14−N3−C20	130.2(3)
N1−In1−N3	109.7(1)	In1−N4−C20	95.2(2)
N1−In1−N4	111.8(1)	In1−N4−C21	133.0(2)
N2−In1−N3	163.2(1)	C20−N4−C21	130.4(3)
N2−In1−N4	109.6(1)	N1−C7−N2	111.4(3)
N3−In1−N4	59.8(1)	N1−C7−C27	122.3(3)
In1−N1−C1	133.0(2)	N2−C7−C27	126.1(3)
In1−N1−C7	95.1(2)	N3−C20−N4	111.7(3)
C1−N1−C7	130.6(3)	N3−C20−C31	126.9(4)
In1−N2−C7	93.3(2)	N4−C20−C31	121.2(3)

is likely due to the constraints imposed by the three-atom bite of the ligand. Although direct comparisons are difficult due to the lack of known In amidinate complexes, the In−N and In−Cl bond lengths of **4** correlate favorably with the few reported values for five-coordinate TBP complexes.[7,9,16]

Conclusion

Amidinate ligands have proven to be useful in the preparation of a family of unusual In complexes. We have extended the available amidinate ligands by demonstrating the synthesis and reactivity of two new bulky anionic ligands, [Me$_3$SiN(CMe$_3$)-NSiMe$_3$]$^-$ and [CyNC(CMe$_3$)NCy]$^-$. A combination of X-ray crystallographic and spectroscopic studies confirms the nature of these compounds. The subsequent reactivity of these indium species is dependent on the nature of the group bound to the bridging C atom of the amidinate; at this stage, the acetamidinate complexes appear to be more reactive toward substitution and the ligand is sufficiently small to accommodate the 6-fold coordination at the metal center. Our continuing investigations are oriented toward discerning the steric and electronic features that influence the formation and reactivity of high-coordination-number indium compounds and toward extending this work to other post-transition metals.

Experimental Section

General Procedures. All reactions were carried out either in a nitrogen-filled drybox or under nitrogen using standard Schlenk-line techniques. Diethyl ether, hexamethyldisiloxane, hexane, and benzene were distilled under nitrogen from potassium. Deuterated benzene was dried by vacuum transfer from potassium. MeLi (1.4 M in diethyl ether), ^{t}BuLi (1.7 M in hexane), dicyclohexylcarbodiimide, and 1,3-bis(trimethylsilyl)carbodiimide were purchased from Aldrich and used without further purification. InCl$_3$ was sublimed prior to use.

Synthesis of ClIn[C$_6$H$_{11}$NC(Me)NC$_6$H$_{11}$]$_2$ (1). A Schlenk flask was charged with dicyclohexylcarbodiimide (0.93 g, 4.51 mmol), diethyl ether (30 mL), and a stir bar. To this solution was added MeLi (3.2 mL, 1.4 M, 4.51 mmol) dropwise, and the mixture was stirred for 30 min, followed by the addition of InCl$_3$ (0.50 g, 2.26 mmol). The reaction mixture was stirred overnight. A white solid was removed by filtration, and the solution was concentrated to ca. 8 mL and cooled to −30 °C. The resulting white crystalline solid was collected by filtration and dried under oil pump vacuum (1.05 g, 78%, 1.76 mmol); mp (sealed) 158−160 °C. IR (Nujol, cm^{-1}): 1502 (s). ^{1}H NMR (C$_6$D$_6$, ppm): 3.13 (m, C$_6$H$_{11}$, 4H); 1.96−1.16 (m, C$_6$H$_{11}$, 40H);1.50 (s, Me,

6H). Anal. Calcd for $C_{28}H_{50}ClInN_4$: C, 56.71; H, 8.50; N, 9.45. Found: C, 57.11; H, 8.66; N, 9.53.

Synthesis of MeIn[C_6H_{11}NC(Me)NC_6H_{11}]$_2$ (2). Complex **1** (0.50 g, 0.84 mmol) was dissolved in 10 mL of THF, and the solution was cooled to −78 °C in a dry ice−acetone bath. MeMgCl (0.2 mL, 0.84 mmol, 3 M in diethyl ether) was added via syringe. The solution was allowed to slowly warm to room temperature and then stirred overnight. The THF was removed under oil pump vacuum, and the residue was extracted with 15 mL of diethyl ether. After filtration, the solution was concentrated to ca. 5 mL and cooled to −30 °C. The resulting crystalline solid was collected by filtration and dried under oil pump vacuum (0.35 g, 73%, 0.61 mmol); mp (sealed) 139−140 °C. IR (Nujol, cm^{-1}): 1520 (s). ^{1}H NMR (C_6D_6, ppm): 3.21 (m, C_6H_{11}, 4H); 1.96−1.23 (m, C_6H_{11}, 40H); 1.63 (s, CMe, 6H); 0.32 (s, 3H, InMe). ^{13}C NMR (C_6D_6, ppm): 166.5 (s, N*C*(Me)N); 55.8, 37.6, 26.3, 26.2 (4s, C_6H_{11},); 11.92 (s, NC(*Me*)N) (In*C*H$_3$). Anal. Calcd for $C_{29}H_{53}$-InN$_4$: C 60.73; H, 9.33; N, 9.78. Found: C, 60.39; H, 9.47; N, 9.80.

Synthesis of In[C_6H_{11}NC(Me)NC_6H_{11}]$_3$ (3). Method A. A Schlenk flask was charged with sodium (0.020 g, 0.84 mmol), naphthalene (0.11 g, 0.84 mmol), THF (15 mL), and a stir bar, and the resultant deep green solution was stirred for 5 h at room temperature. The solution was then cooled to −78 °C in a dry ice−acetone bath. To this solution was added dropwise complex **1** (0.50 g, 0.84 mmol) dissolved in 5 mL of THF. The reaction mixture was allowed to warm to room temperature and then stirred overnight. The THF was removed under oil pump vacuum, and the residue was extracted with 20 mL of diethyl ether. After filtration, the solution was concentrated to ca. 7 mL and cooled to −30 °C. The resulting white solid was collected by filtration and dried under oil pump vacuum (0.31 g, 0.39 mmol).

Method B. A Schlenk flask was charged with dicyclohexylcarbo-diimide (0.57 g, 2.76 mmol), diethyl ether (15 mL), and a stir bar. To this solution was added MeLi (2.0 mL, 1.4 M, 2.76 mmol) dropwise, and the mixture was stirred for 30 min, followed by the addition of InCl$_3$ (0.20 g, 0.92 mmol). The reaction mixture was stirred overnight and then filtered. The solution was concentrated to ca. 8 mL and cooled to −30 °C. The resulting white solid was collected by filtration and dried under oil pump vacuum (0.57 g, 80%, 0.74 mmol); mp (sealed) 248−251 °C. IR (Nujol, cm^{-1}): 1516 (s). ^{1}H NMR (C_6D_6, ppm): 3.25 (m, C_6H_{11}, 6H); 2.10−1.25 (m, C_6H_{11}, 60H); 1.71 (s, CMe, 9H). ^{13}C NMR (C_6D_6, ppm): 164.5 (s, N*C*(Me)N); 56.6, 37.6, 35.5, 26.7, 26.6 (5s, C_6H_{11},); 11.93 (Me). Anal. Calcd for $C_{42}H_{75}$InN$_6$: C 64.76; H, 9.71. Found: C, 64.59; H, 9.84.

Synthesis of ClIn[C_6H_{11}NC(CMe$_3$)NC_6H_{11}]$_2$ (4). A Schlenk flask was charged with dicyclohexylcarbodiimide (0.57 g, 2.76 mmol), diethyl ether (20 mL), and a stir bar. To this solution was added ^{t}BuLi (1.6 mL, 1.7 M in hexane, 2.76 mmol) dropwise, and the mixture was stirred for 30 min, followed by the addition of InCl$_3$ (0.31 g, 1.38 mmol). The reaction mixture was stirred overnight and then filtered. The solution was concentrated to ca. 8 mL and cooled to −30 °C. The resulting

white crystalline solid was collected by filtration and dried under oil pump vacuum (0.80 g, 86%, 1.19 mmol); mp (sealed) 189−194 °C dec. IR (thin film, cm^{-1}): 1487 (m), 1446 (s), 1427 (s). ^{1}H NMR (C_6D_6, ppm): 3.89 (m, C_6H_{11}, 4H); 2.13−1.15 (m, C_6H_{11}, 40H); 1.27 (s, CMe$_3$, 18H). ^{13}C NMR (C_6D_6, ppm): 174.4 (s, N*C*(C(Me)$_3$)N); 56.1, 36.1, 26.2, 25.8 (4s, C_6H_{11},); 39.5 (s, *C*(CH$_3$)$_3$); 30.1 (C(*C*H$_3$)$_3$). Anal. Calcd for $C_{34}H_{62}$ClInN$_4$: C 60.13; H, 9.23; N, 8.27. Found: C, 59.71; H, 9.39; N, 8.39.

Synthesis of ClIn[Me$_3$SiN(CMe$_3$)NSiMe$_3$]$_2$ (5). A Schlenk flask was charged with 1,3-bis(trimethylsilyl)carbodiimide (0.71 g, 3.81 mmol), diethyl ether (20 mL), and a stir bar. To this solution was added ^{t}BuLi (2.2 mL, 1.7 M in hexane, 3.81 mmol) dropwise, and the mixture was stirred for 30 min, followed by the addition of InCl$_3$ (0.42 g, 1.91 mmol). The reaction mixture was stirred overnight and then filtered. The solution was removed under oil pump vacuum, the residue was extracted with 10 mL of (Me$_3$Si)$_2$O, and the extract was cooled to −30 °C. The resulting white crystalline solid was collected by filtration and dried under oil pump vacuum (0.90 g, 74%, 1.41 mmol); mp (sealed) 122−124 °C. ^{1}H NMR (C_6D_6, ppm): 1.14 (s, CMe$_3$, 18H); 0.46 (s, 36H, Me$_3$Si). Anal. Calcd for $C_{22}H_{54}$ClInN$_4$Si$_4$: C 41.46; H, 8.54. Found: C, 41.08; H, 8.64.

X-ray Crystallography. Data were collected on a Rigaku diffractometer at −153 °C using the θ−2θ scan technique to a maximum 2θ value of 50° for crystals mounted on glass fibers. Cell constants and orientation matrices were obtained from the least-squares refinement of 24 carefully centered high-angle reflections. Redundant reflections were removed from the data set. The intensities of three representative reflections were measured after every 150 reflections to monitor the crystal and instrument stability. Data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were located in the difference Fourier maps and refined isotropically in the cases of favorable observation/parameter ratios. The final cycle of full-matrix least-squares refinement was based on the number of observed reflections with [$I > 2.5\sigma(I)$]. Anomalous-dispersion effects were included in the F_c values. All calculations were performed using the NRCVAX package. Details of the data collection and structure refinement and final atomic coordinates are reported in the Supporting Information.