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Synthesis of Indium Amide Compounds

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Indium trichloride reacts with 3 equiv of lithium amide in diethyl ether to give $In(NRR')_3$ (R = Ph or *t*-Bu, R′ = $SiMe_3$; R = *t*-Bu, R′ = $SiHMe_2$) and with 3 or 4 equiv of $LiNMe(SiMe_3)$ to yield $Li[In\{NMe(SiMe_3)\}_4]$. The chloride also reacts with $LiNPh_2$ in THF to give the salt $Li[In(NPh_2)_3Cl]$ and with LiNRR′ in pyridine to yield the neutral adduct $In(NRR')_3(py)$ (R = R′ = Ph; R = Me, R′ = $SiMe_3$). The volatile liquids $In[N(t\text{-}Bu)(SiHMe_2)]_3$ and $In[NMe(SiMe_3)]_3(py)$ react with *p*-Me_2Npy to form the solid compounds $In[N(t\text{-}Bu)(SiHMe_2)]_3(p\text{-}Me_2Npy)$ and $In[NMe(SiMe_3)]_3(p\text{-}Me_2Npy)$, respectively. X-ray crystallographic studies show that $In(NPh_2)_3(py)$, $In[N(t\text{-}Bu)(SiHMe_2)]_3(p\text{-}Me_2Npy)$, and the ether adduct of $In[NPh(SiMe_3)]_3$ contain nearly planar In(amide)$_3$ fragments. Crystallographic studies also show that the anion in the salt $[Li(THF)_4][In(NPh_2)_3Cl]$ is nearly tetrahedral and in $[Li(p\text{-}Me_2Npy)][In\{NMe(SiMe_3)\}_4]$ the tetrahedral-like anion is bound to the Li cation via two amide nitrogens. The Li in the latter structure is also bonded to *p*-Me_2Npy, resulting in a planar three-coordinate geometry for Li. Crystal data are the following. $C_{31}H_{52}N_3OSi_3In$ at −50 °C: $P2_1/n$ (monoclinic), $a = 11.003(2)$ Å, $b = 18.678(3)$ Å, $c = 17.618(3)$ Å, $\beta = 95.42(1)°$, and $Z = 4$. $C_{41}H_{35}N_4In{\cdot}C_7H_8$ at −50 °C: $P\bar{1}$ (triclinic), $a = 10.112(2)$ Å, $b = 12.786(3)$ Å, $c = 15.870(5)$ Å, $\alpha = 87.42(2)°$, $\beta = 74.95(2)°$, $\gamma = 78.15(2)°$, and $Z = 2$. $C_{25}H_{58}N_5Si_3In$ at −50 °C: $P2_1/c$ (monoclinic), $a = 9.797(3)$ Å, $b = 18.203(6)$ Å, $c = 19.592(5)$ Å, $\beta = 100.27(2)°$, and $Z = 4$. $C_{52}H_{62}ClInLiN_3O_4$ at 23 °C: $P2_1/n$ (monoclinic), $a = 16.076(2)$ Å, $b = 17.185(2)$ Å, $c = 18.447(3)$ Å, $\beta = 97.41(1)°$, and $Z = 4$. $C_{23}H_{58}InLiN_6Si_4$ at 23 °C: $P\bar{1}$ (triclinic), $a = 15.792(3)$ Å, $b = 16.345(3)$ Å, $c = 16.678(3)$ Å, $\alpha = 62.69(1)°$, $\beta = 81.00(1)°$, $\gamma = 86.94(1)°$, and $Z = 4$.

We have reported several examples of using low-temperature chemical vapor deposition (CVD) to deposit main group and transition metal nitride thin films from homoleptic amido compounds and ammonia precursors.[1] With this as background, we became interested in using homoleptic indium amido compounds as precursors to indium nitride films.[2] Only two examples of homoleptic indium amido complexes, $In[N(SiMe_3)_2]_3$ and $In(NEt_2)_3$, had been reported in the literature when we began this study.[3−5] The hexamethydisilazane compound, a solid, is involatile (dec <168 °C) and therefore not suitable for use as a CVD precursor. The diethylamido complex[5] $In(NEt_2)_3$ was particularly attractive to us because we showed earlier that $Ga(NMe_2)_3$ and ammonia precursors give clean GaN films at very low temperatures.[6,7] We found $In(NEt_2)_3$, however, to be difficult to purify and not very volatile.

Because of potential problems with using the known indium amido compounds as precursors to InN, we have prepared new derivatives. Herein we report the syntheses of $In(NRR')_3$ (R = Ph or *t*-Bu, R′ = $SiMe_3$; R = *t*-Bu, R′ = $SiHMe_2$), $In(NRR')_3L$ (R = *t*-Bu, R′ = $SiHMe_2$, L = *p*-Me_2Npy; R = R′ = Ph, L = py; R = Me, R′ = $SiMe_3$, L = py or *p*-Me_2Npy), $Li[In(NPh_2)_3Cl]$ and $Li[In\{NMe(SiMe_3)\}_4]$. Since we began this study, a new homoleptic compound, In(2,2,6,6-tetramethylpiperidino)$_3$, has been reported.[8]

Expermental Section

General Considerations. All manipulations were carried out in a glovebox or by using standard Schlenk techniques. Solvents were purified by using standard techniques, after which they were stored in the glovebox over 4-Å molecular sieves. $HNPh_2$ was purchased from Aldrich and H_2NMe from Matheson. Me_3SiCl, Me_2HSiCl, Me_2SiCl_2, *t*-$BuNH_2$, and *t*-$BuNH(SiMe_3)$ were purchased from Aldrich, degassed with an argon stream, and then stored in the refrigerator over 3-Å molecular sieves. $PhNH(SiMe_3)$ was synthesized by the literature method.[9] Infrared spectra were obtained by using an FTIR instruments and NMR spectra were collected on a 300-MHz instrument.

$HNMe(SiMe_3)$. This compound was prepared by using a modification of the literature procedure.[10] Methylamine (7.8 g, 0.25 mol) was added to a frozen solution of $ClSiMe_3$ (11 g, 0.10 mol) in ether (200 mL). A white solid formed while the mixture was being warmed slowly to room temperature. After warming to room temperature, the reaction mixture was stirred for an additional 4 h. The mixture was then cold-filtered (0 °C), and the filtrate was distilled at atmospheric pressure under argon, giving the product as a colorless liquid (bp 71 °C/760 mmHg; lit.[10] bp 71 °C/755 mmHg) (yield 6.0 g, 58%).

$LiNMe(SiMe_3)$. In the glovebox, a solution of *n*-BuLi (23 mL, 36 mmol; 1.6 M in hexane) was added slowly to a stirred solution of $HNMe(SiMe_3)$ (4.0 g, 39 mmol) in hexane (50 mL) at room temperature. A white solid formed immediately. The reaction mixture was stirred for 3 h after the addition was completed. The white solid was

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filtered off, washed with hexane, and then dried under vacuum for 6 h (yield 2.0 g, 50%).

^{1}H NMR (CD$_3$CN): δ −0.021 (s, 9, Si*Me*$_3$), 2.39 (s, 3, N*Me*).

HN(*t*-Bu)(SiHMe$_2$). A solution of *t*-BuNH$_2$ (7.3 g, 0.10 mol) in ether (10 mL) was added slowly to ClSiHMe$_2$ (4.7 g, 0.05 mol) in cold (−78 °C) ether (50 mL). A white solid formed immediately. The reaction mixture was stirred for 4 h while the temperature was allowed slowly to increase to room temperature. The mixture was filtered, and the filtrate was distilled at atmospheric pressure under argon, giving the product as a colorless liquid (bp 105 °C/760 mmHg) (yield 3.9 g, 60%).

^{1}H NMR (C$_6$D$_6$): δ 0.12 (d, $J_{\mathrm{HH}} = 2.7$ Hz, 6, Si*Me*$_2$H), 0.36 (broad, 1, N*H*), 1.10 (s, 9, C*Me*$_3$), 4.82 (octet, $^3J_{\mathrm{HH}} \approx {}^3J_{\mathrm{HH}}{}' = 3.0$, Hz, 1, HNSi*H*Me$_2$).

LiN(*t*-Bu)(SiHMe$_2$). In the glovebox, a solution of *n*-BuLi (7.5 mL, 12 mmol; 1.6 M in hexane) was added slowly to HN(*t*-Bu)(SiHMe$_2$) (1.7 g, 13 mmol) in hexane (50 mL) at room temperature. The reaction mixture was stirred for 3 h after the addition was completed. The solution was taken to dryness under vacuum, leaving the product as a white solid. The solid was dried in vacuo for 6 h (yield 1.6 g, 97%). The product was used without further purification.

^{1}H NMR (CD$_3$CN): δ 0.09 (d, $J_{\mathrm{HH}} = 3.0$ Hz, 6, Si*Me*$_2$H), 1.14 (s, 9, C*Me*$_3$), 4.49 (septet, $J_{\mathrm{HH}} = 3.0$ Hz, 1, SiMe$_2$*H*). IR (Nujol, CsI, cm^{-1}): 2052 vs, 1402 w, 1356 vs, 1303 w, 1246 vs, 1217 vs, 1192 vs, 1124 w, 1041 vs, 1016 s, 995 m, 922 vs, 887 vs, 833 vs, 769 vs, 750 vs, 696 m, 667 w, 623 w, 569 s, 461 w, 422 w.

In[NPh(SiMe$_3$)]$_3$. In the glovebox, a solution of LiNPh(SiMe$_3$) (0.52 g, 3.0 mmol) in ether (5 mL) was added slowly to a suspension of InCl$_3$ (0.22 g, 1.0 mmol) in ether (25 mL). The reaction mixture was stirred for 24 h. The mixture was taken to dryness in vacuo and then held in vacuo for 4 h. The residue was extracted with hexane (10 × 10 mL), and the extracts were filtered through Celite. The hexane was removed in vacuo, and the residue was held in vacuo for 24 h, leaving the product as a viscous liquid (yield 0.55 g, 90%). If the product is not held under dynamic vacuum for a long time, an ether adduct is obtained. Crystals of the ether adduct were grown from hexanes at low temperature (−35 °C). The ether can be removed from the etherate by dissolution in CH$_2$Cl$_2$ and then immediate removal of the CH$_2$Cl$_2$/ether in vacuo. A microanalysis was performed for the etherate. A satisfactory carbon analysis was not obtained. Anal. Calcd for C$_{31}$H$_{52}$N$_3$OInSi$_3$: C, 54.59; H, 7.70; N, 6.16. Found: C, 54.03; H, 7.73; N, 6.00.

^{1}H NMR (C$_6$D$_6$): δ 0.18 (s, 27, Si*Me*$_3$), 6.80 (t, 3, *p-Ph)*, 6.96 (d, 6, *o-Ph*), 7.08 (t, 6, *m-Ph*). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 2.35 (Si*Me*$_3$), 121.3 (*Ph*), 125.3 (*Ph*), 130.0 (*Ph*). IR (Nujol, CsI, cm^{-1}): 1589 vs, 1491 vs, 1423 w, 1248 vs, 996 w, 920 vs, 842 vs, 750 s, 696 s, 634 w, 511 s.

In[N(*t*-Bu)(SiMe$_3$)]$_3$. In the glovebox, a solution of LiN(*t*-Bu)(SiMe$_3$) (0.47 g, 3.1 mmol) in ether (5 mL) was added slowly to a suspension of InCl$_3$ (0.22 g, 1.0 mmol) in ether (25 mL). The reaction mixture was stirred in the glovebox for 24 h. The mixture was taken to dryness in vacuo and then held in vacuo for 4 h. The residue was extracted with hexane (5 × 10 mL), and the extracts were filtered through Celite. The hexane was removed in vacuo from the filtrate, leaving the product as a white solid (yield 0.43 g, 79%). Anal. Calcd for C$_{21}$H$_{54}$N$_3$InSi$_3$: C, 46.03; H, 9.95; N, 7.67. Found: C, 45.81; H, 9.76; N, 7.49.

^{1}H NMR (C$_6$D$_6$): δ 0.40 (s, 27, Si*Me*$_3$), 1.46 (s, 27, C*Me*$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 6.63 (Si*Me*$_3$), 36.9 (C*Me*$_3$), 55.7 (*C*Me$_3$). IR (Nujol, CsI, cm^{-1}): 1303 w, 1248 s, 1228 m, 1211 w, 1182 m, 1031 m, 1018 w, 981 m, 910 w, 858 s, 836 s, 775 m, 749 m, 671 w, 630 w, 603 w, 516 w, 470 m.

In[N(*t*-Bu)(SiHMe$_2$)]$_3$. LiN(*t*-Bu)(SiHMe$_2$) (0.42 g, 3.1 mmol) in ether (5 mL) was added dropwise to a slurry of InCl$_3$ (0.22 g, 1.0 mmol) in ether (25 mL) at −78 °C. The mixture was stirred while the temperature was allowed slowly to increase to room temperature over 24 h. A white precipitate formed. The ether was removed by vacuum distillation, and the residue was extracted with hexane (3 × 10 mL). The extracts were combined and filtered through Celite. Hexane was removed in vacuo from the filtrate, and the residue, a viscous light yellow liquid, was held in vacuo for 24 h (yield 0.28 g, 53%). Anal. Calcd for C$_{18}$H$_{48}$N$_3$InSi$_3$: C, 42.49; H, 9.53; N, 8.26. Found: C, 42.99; H, 9.76; N, 7.98.

^{1}H NMR (C$_6$D$_6$): δ 0.42 (d, $J_{\mathrm{HH}} = 3.6$ Hz, 18, Si*Me*$_2$H), 1.40 (s, 27, C*Me*$_3$), 4.80 (septet, $J_{\mathrm{HH}} = 3.0$ Hz, 3, SiMe$_2$*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 3.97 (SiH*Me*$_3$), 36.8 (C*Me*$_3$), 54.9 (*C*Me$_3$). IR (Nujol, CsI, cm^{-1}): 2075 vs, 1413 w, 1359 vs, 1303 w, 1246 vs, 1230 vs, 1196 vs, 1114 w, 1047 vs, 1020 s, 993 s, 922 vs, 883 vs, 844 vs, 790 vs, 754 vs, 677 m, 651 w, 630 w, 599 w, 524 w, 472 s, 420 w.

In[N(*t*-Bu)(SiHMe$_2$)]$_3$(*p*-Me$_2$Npy). In[N(*t*-Bu)(SiHMe$_2$)]$_3$ (0.20 g, 0.39 mmol) was dissolved in ether (10 mL), and *p*-(dimethylamino)pyridine (0.048 g, 0.39 mmol) was added quickly to the solution, resulting in a clear solution. The flask was transferred to the freezer (−35 °C), where it was kept for 48 h. Large, colorless crystals formed (yield 0.17 g, 69%).

^{1}H NMR (C$_6$D$_6$): δ 0.45 (d, $J_{\mathrm{HH}} = 3.3$ Hz, 18, Si*Me*$_2$H), 1.46 (s, 27, C*Me*$_3$), 2.13 (s, 6, N*Me*$_2$), 4.82 (septet, $J_{\mathrm{HH}} = 3.3$ Hz, 3, SiMe$_2$*H*), 6.03 (d, 2, *m*-py*)*, 8.51 (d, 2, *o*-py).

In(NPh$_2$)$_3$(py). In the glovebox, a solution of LiNPh$_2$ (0.53 g, 3.0 mmol) in pyridine (10 mL) was added slowly to a suspension of InCl$_3$ (0.22 g, 1.0 mmol) in pyridine (25 mL). The reaction mixture was stirred for 24 h. The solvent was removed in vacuo, and the residue was held in vacuo for 12 h. The residue was extracted with toluene (5 × 10 mL), and the extracts were filtered through Celite. The volume of the filtrate was reduced in vacuo to 20 mL. Cooling of the solution (−35 °C for 24 h) produced light yellow crystals, which were isolated by removal of the mother liquid with a pipet and drying in vacuo for 12 h (yield 0.48 g, 70%). Anal. Calcd for C$_{41}$H$_{35}$N$_4$In: C, 70.48; H, 5.06; N, 8.02. Found: C, 70.30; H, 4.87; N, 7.81.

^{1}H NMR (C$_6$D$_6$): δ 5.93 (t, 2, *m-py*), 6.32 (t, 1, *p-py*), 6.65 (t, 6, *p-Ph)*, 6.96 (t, 12, *m-Ph*), 7.11 (d, 12, *o-Ph*), 7.47 (d, 2, *o-py*). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 120.4 (*Ph*), 122.7 (*Ph*), 125.1 (*py*), 129.9 (*Ph*), 139.9 (*py*), 148.7 (*py*), 152.8 (*Ph*). IR (Nujol, CsI, cm^{-1}): 1584 s, 1524 w, 1491vs, 1338 m, 1296 vs, 1203 s, 1182 m, 1064 m, 1042 w, 989 m, 926 m, 873 m, 862 s, 839 w, 802 w, 779 w, 744 vs, 694 vs, 646 w, 617 w, 578 w, 530 w, 503 s, 447 w, 430 w, 421 s.

In[NMe(SiMe$_3$)]$_3$(py). In the glovebox, a solution of LiNMe(SiMe$_3$) (0.32 g, 3.0 mmol) in pyridine (10 mL) was added slowly to a suspension of InCl$_3$ (0.22 g, 1.0 mmol) in pyridine (25 mL). The reaction mixture was stirred for 24 h. The solvent was removed in vacuo, and the residue was held in vacuo for 12 h. The residue was extracted with hexane (3 × 10 mL), and the extracts were filtered through Celite. Hexane was removed in vacuo from the filtrate, and the residue, a viscous light red liquid, was held in vacuo for 12 h (yield 0.41 g, 82%). A similar yield is obtained using a 9:1 mixture of ether/pyridine as the reaction solvent. The compound distills at 70−75 °C, 0.01 mmHg, with some decomposition.

^{1}H NMR (C$_6$D$_6$): δ 0.32 (s, 27, Si*Me*$_3$), 2.94 (s, 9, N*Me*), 6.47 (t, 2, *m-py)*, 6.77 (t, 1, *p-py*), 8.46 (d, 2, *o-py*). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 1.23 (Si*Me*$_3$), 34.7 (N*Me*), 125, 139, 149 (*py*). IR (CsI, Nujol, cm^{-1}): 1604 vs, 1562 w, 1535 w, 1487 s, 1448 vs, 1427 s, 1400 s, 1338 w, 1286 s, 1244 vs, 1217 m, 1167 s, 1050 vs, 1012 m, 931 w, 926 s, 891 s, 862 vs, 831 vs, 748 m, 700 m, 677 w, 642 w, 619 w, 596 w, 572 w, 445 w, 420 w.

In[NMe(SiMe$_3$)]$_3$(*p*-Me$_2$Npy). In[NMe(SiMe$_3$)]$_3$(py) (0.20 g, 0.40 mmol) was dissolved in hexane (10 mL), and *p*-(dimethylamino)pyridine (0.049 g, 0.40 mmol) was added quickly to the solution, resulting in a clear solution. The flask was transferred to the freezer (−35 °C), where it was kept for 24 h. Large tan crystals formed (yield 0.18 g, 86%). Anal. Calcd for C$_{19}$H$_{46}$N$_5$InSi$_3$: C, 41.96; H, 8.54; N, 12.88. Found: C, 41.67; H, 8.50; N, 12.84.

^{1}H NMR (C$_6$D$_6$): δ 0.42 (s, 27, Si*Me*$_3$), 1.90 (s, 6, N*Me*$_2$), 3.13 (s, 9, N*Me*), 5.71 (d, 2, *m-py)*, 8.20 (d, 2, *o-py*).

[Li(THF)$_4$][In(NPh$_2$)$_3$Cl]. In the glovebox, a solution of LiNPh$_2$ (0.53 g, 3.0 mmol) in THF (10 mL) was added slowly to a suspension of InCl$_3$ (0.22 g, 1.0 mmol) in THF (25 mL). The reaction mixture was stirred for 24 h. The mixture was taken to dryness in vacuo and then held in vacuo for 8 h. The residue was extracted with benzene (5 × 10 mL), and extracts were filtered through Celite. The benzene was removed in vacuo, and the residue was held in vacuo for 24 h, leaving a viscous reddish brown liquid that is [Li(THF)][In(NPh$_2$)$_3$Cl] by ^{1}H NMR (i.e., one THF). Brownish yellow crystals were grown at low

Table 1. Crystal Data for In[NPh(SiMe$_3$)]$_3$(ether), In(NPh$_2$)$_3$(py)·toluene, In[N(*t*-Bu)(SiHMe$_2$)]$_3$(*p*-Me$_2$Npy), [Li(*p*-Me$_2$Npy)][In{NMe(SiMe$_3$)}$_4$], and [Li(THF)$_4$][In(NPh$_2$)$_3$Cl]

	In[NPh(SiMe$_3$)]$_3$ (ether)	In(NPh$_2$)$_3$(py)· toluene	In[N(*t*-Bu)(SiHMe$_2$)]$_3$ (*p*-Me$_2$Npy)	[Li(*p*-Me$_2$Npy)] [In{NMe(SiMe$_3$)}$_4$]	[Li(THF)$_4$] [In(NPh$_2$)$_3$Cl]
empirical formula	$C_{31}H_{52}N_{3O}Si_3In$	$C_{41}H_{35}N_4In \cdot C_7H_8$	$C_{25}H_{58}N_5Si_3In$	$C_{23}H_{58}InLiN_6Si_4$	$C_{52}H_{62}ClInLiN_3O_4$
fw	681.95	790.77	627.97	652.86	950.31
cryst dimens (mm)	0.66 × 0.38 × 0.30	0.12 × 0.24 × 0.28	0.30 × 0.45 × 0.55	0.08 × 0.15 × 0.17	0.07 × 0.09 × 0.10
radiation (Mo Kα), Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
space group	$P2_1/n$ (monoclinic)	$P\bar{1}$ (triclinic)	$P2_1/c$ (monoclinic)	$P\bar{1}$ (triclinic)	$P2_1/n$ (monoclinic)
a, Å	11.003(2)	10.112(2)	9.797(3)	15.792(3)	16.076(2)
b, Å	18.678(3)	12.786(3)	18.203(6)	16.345(3)	17.185(2)
c, Å	17.618(3)	15.870(5)	19.592(5)	16.678(3)	18.447(3)
α, deg		87.42(2)		62.69(1)	
β, deg	95.42(1)	74.95(2)	100.27(2)	81.00(1)	97.41(1)
γ, deg		78.15(2)		86.94(1)	
temp, °C	−50	−50	−50	23	23
Z	4	2	4	4	4
V, Å^3	3605	1939	3438	3777	5054
D_{calcd}, g/cm^3	1.26	1.35	1.21	1.15	1.25
μ, cm^{-1}	7.68	6.36	7.98	7.59	5.55
R, R_w[a]	0.022, 0.024[b]	0.032, 0.028[b]	0.026, 0.027[b]	0.067, 0.076[c]	0.057, 0.079[c]

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [b] $w = [\sigma(F)]^{-2}$. [c] $w = [0.04F^2 + (\sigma(F))^2]^{-1}$.

temperature (−35 °C) from toluene/THF (9:1). The crystals were then dried under dynamic vacuum for 12 h (yield 0.45 g, 47%). The microanalysis for this material suggests the formula [Li(THF)$_x$][In(NPh$_2$)$_3$Cl] where $x \cong 4$. Anal. Calcd for $C_{52}H_{62}N_3ClInLiO_4$: C, 65.71; H, 6.60; N, 4.40. Found: C, 65.08; H, 6.29; N, 4.23.

^{1}H NMR (CD$_3$CN): δ 0.18 (m, 8, THF), 3.64 (m, 8, THF), 6.62 (t, 6, *p-Ph*), 6.80 (d, 12, *o-Ph*), 6.96 (t, 12, *m-Ph*). ^{13}C{^{1}H} NMR (CD$_3$CN): δ 26.6 (*THF*), 68.7 (*THF*), 119.7 (*Ph*), 123.7 (*Ph*), 129.9 (*Ph*), 154.8 (*Ph*). IR (Nujol, CsI, cm^{-1}): 1581 m, 1340 m, 1288 s, 1207 m, 1166 m, 1041 m, 989 w, 887 s, 868 w, 852 s, 787 w, 744 s, 725 m, 692 m, 578 w, 515 w, 501 w, 470 w, 428 w.

Li[In{NMe(SiMe$_3$)}$_4$]. In the glovebox, a solution of LiNMe(SiMe$_3$) (0.44 g, 4.0 mmol) in ether (5 mL) was added slowly to a suspension of InCl$_3$ (0.22 g, 1.0 mmol) in ether (25 mL). The reaction mixture was stirred for 24 h. The ether was removed in vacuo, and the residue was then held in vacuo for 4 h. The residue was extracted with hexane (10 × 10 mL), and the extracts were filtered through Celite. The hexane was removed in vacuo from the filtrate, and the residue was held in vacuo for 24 h. The dried residue, a white solid, is the monoetherate by ^{1}H NMR (yield 0.44 g, 72%). The ether can be removed by dissolution of the etherate in CH$_2$Cl$_2$ and then immediate vacuum distillation to remove the CH$_2$Cl$_2$/ether. Anal. Calcd for $C_{16}H_{48}N_4InLiSi_4$: C, 36.20; H, 9.13; N, 10.56. Found: C, 36.07; H, 9.53; N, 10.24.

^{1}H NMR (C$_6$D$_6$): δ 0.29 (s, 36, Si*Me*$_3$), 2.75 (s, 12, N*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 1.74 (Si*Me*$_3$), 35.5 (N*Me*). IR (Nujol, CsI, cm^{-1}): 1246 vs, 1153 m, 1068 s, 1018 s, 956 w, 893 s, 854 s, 833 s, 769 s, 738 s, 678 w, 667 m, 580 w, 439 s.

[Li(*p*-Me$_2$Npy)][In{NMe(SiMe$_3$)}$_4$]. This compound was prepared by dissolving the etherate (0.10 g, 0.17 mmol) in toluene, adding *p*-(dimethylamino)pyridine (0.020 g, 0.17 mmol) to the solution, and keeping the mixture at −35 °C for 48 h. Light yellow crystals were obtained (yield 0.090 g, 81%).

^{1}H NMR (C$_6$D$_6$): δ 0.38 (s, 36, Si*Me*$_3$), 2.08 (s, 6, N*Me*$_2$), 3.10 (s, 12, N*Me*) 5.83 (d, 2, *m*-py), 7.77 (d, 2, *o*-py).

X-ray Crystallography. Crystal data are presented in Table 1.

Crystals of In(NPh$_2$)$_3$(py)·toluene and [Li(*p*-Me$_2$Npy)][In{NMe(SiMe$_3$)}$_4$] are yellow plates, and crystals of In[N(*t*-Bu)(SiHMe$_2$)]$_3$(*p*-Me$_2$Npy), In[NPh(SiMe$_3$)]$_3$(ether), and [Li(THF)$_4$][In(NPh$_2$)$_3$Cl] are colorless blocks. The crystals of In(NPh$_2$)$_3$(py)·toluene, In[N(*t*-Bu)(SiHMe$_2$)]$_3$(*p*-Me$_2$Npy), and In[NPh(SiMe$_3$)]$_3$(ether) were handled under mineral oil. For each of these compounds the crystal chosen for analysis was transferred to a cold nitrogen stream for data collection on a Nicolet R3m/V diffractometer. Crystals of [Li(THF)$_4$][In(NPh$_2$)$_3$Cl] and [Li(*p*-Me$_2$Npy)][In{NMe(SiMe$_3$)}$_4$] were mounted in capillaries, and the data were collected at room temperature on an Enraf-Nonius CAD-4F (κ geometry) diffractometer. Intensities were measured using the ω-scan technique except in the case of [Li(*p*-Me$_2$Npy)][In{NMe(SiMe$_3$)}$_4$], where the $\theta/2\theta$ method was used. Two standard reflections were monitored after every 2 h or every 100 data collected for In(NPh$_2$)$_3$(py)·toluene, In[N(*t*-Bu)(SiHMe$_2$)]$_3$(*p*-Me$_2$Npy), and In[NPh(SiMe$_3$)]$_3$(ether). The data showed no decay. Three standard reflections were monitored every 1 h of exposure time for [Li(THF)$_4$][In(NPh$_2$)$_3$Cl] and [Li(*p*-Me$_2$Npy)][In{NMe(SiMe$_3$)}$_4$]. The data for the diphenylamido complex showed no significant decay, but the data for [Li(*p*-Me$_2$Npy)][In{NMe(SiMe$_3$)}$_4$] showed a linear decay of <5%, which was corrected for by applying a normalization factor as a function of X-ray exposure time. In all cases Lorentz and polarization corrections were applied during data reduction. No absorption correction was applied for In(NPh$_2$)$_3$(py)·toluene, In[N(*t*-Bu)(SiHMe$_2$)]$_3$(*p*-Me$_2$Npy), and In[NPh(SiMe$_3$)]$_3$(ether) due to their small absorption coefficients. Semiempirical absorption corrections for [Li(THF)$_4$][In(NPh$_2$)$_3$Cl] and [Li(*p*-Me$_2$Npy)][In{NMe(SiMe$_3$)}$_4$] were applied based on Ψ scans of 10 reflections having χ angles between 70° and 90°. Calculations for In(NPh$_2$)$_3$(py)·toluene, In[N(*t*-Bu)(SiHMe$_2$)]$_3$(*p*-Me$_2$Npy), and In[NPh(SiMe$_3$)]$_3$(ether) were made using Nicolet's SHELXTL PLUS (1987) package of programs,[11] and those for [Li(THF)$_4$][In(NPh$_2$)$_3$Cl] and [Li(*p*-Me$_2$Npy)][In{NMe(SiMe$_3$)}$_4$] were made using the MolEN package.[12]

In[NPh(SiMe$_3$)]$_3$(ether). The Laue symmetry was determined to be 2/*m*, and from the systematic absences the space group was shown unambiguously to be $P2_1/n$. The structure was solved by using the SHELXTL Patterson interpretation program, which revealed the positions of most of the non-hydrogen atoms. The remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement followed. The hydrogen atoms attached to carbon were then entered in ideal calculated positions and constrained to riding motion with a single variable isotropic temperature factor for all of them. After all shift/esd ratios were less than 0.1, convergence was reached at the agreement factors listed in Table 1. No unusually high correlations were noted between any of the variables in the last cycle of refinement. The final difference map showed a maximum peak of about 0.25 e/Å^3.

In(NPh$_2$)$_3$(py)·toluene. The Laue symmetry was determined to be $\bar{1}$, and the space group was shown to be $P1$ or $P\bar{1}$. Because the unitary structure factors displayed centric statistics, space group $P\bar{1}$ was assumed to be correct. The structure was solved by using the SHELXTL Patterson interpretation program, which revealed the position of the In atom. The remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. The usual sequence of

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(11) Sheldrick, G. M. *SHELXTL PLUS, Release 3.4 for the Nicolet R3m/v Crystallographic System*; Nicolet Instrument Corp.: Madison, WI, 1987.

(12) *MolEN, An Interactive Structure Solution Program*; Enraf-Nonius: Delft, The Netherlands, 1990.

isotropic and anisotropic refinement followed. Hydrogen atoms attached to carbon were then entered in ideal calculated positions and constrained to riding motion with a single variable isotropic temperature factor for the nonsolvent hydrogens and a separate variable for the toluene hydrogens. The toluene methyl group was treated as an ideal rigid body and allowed to refine independently. After all shift/esd ratios were less than 0.2, convergence was reached at the agreement factors listed in Table 1. No unusually high correlations were noted between any of the variables in the last cycle of full-matrix least-squares refinement, and the final difference map showed a maximum peak of about 0.5 e/Å^3.

In[N(*t*-Bu)(SiHMe$_2$)]$_3$(*p*-Me$_2$Npy). The Laue symmetry was determined to be 2/*m*, and from the systematic absences the space group was shown unambiguously to be $P2_1/n$. The structure was solved by using the SHELXTL Patterson interpretation program, which revealed the position of the In atom. The remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement followed. The hydrogen atoms attached to carbon were then entered in ideal calculated positions and constrained to riding motion with a single variable isotropic temperature factor for all of them. The hydrogens attached to Si were located in difference maps and allowed to refine independently. The two methyl groups attached to N5 were refined as ideal rigid bodies and allowed to rotate independently. After all shift/esd ratios were less than 0.1, convergence was reached at the agreement factors listed in Table 1. No unusually high correlations were noted between any of the variables in the last cycle of refinement. The final difference map showed a maximum peak of about 0.5 e/Å^3.

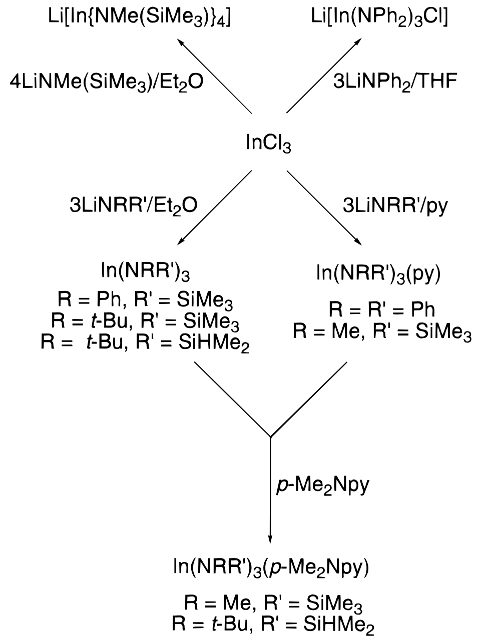
[Li(*p*-Me$_2$Npy)][In{NMe(SiMe$_3$)}$_4$]. The Laue symmetry was determined to be $\bar{1}$, and the space group was shown to be $P1$ or $P\bar{1}$. Because the unitary structure factors displayed centric statistics, the space group $P\bar{1}$ was assumed to be the correct setting. The structure was solved by using the MolEN Patterson interpretation program, which revealed the position of the In atoms. The remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. A disorder observed for one of the N(Me)SiMe$_3$ groups resolved as two Si and four Me positions with site occupancies refined to 0.5. The In, N, and full-occupancy Si atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to carbon were then entered in ideal calculated positions and constrained to riding motion such that $U(\mathrm{H}) = 1.3U(\text{attached C})$. After all shift/esd ratios were less than 0.01, convergence was reached at the agreement factors listed in Table 1. No unusually high correlations were noted between any of the variables in the last cycle of full-matrix least-squares refinement, and the final difference map showed a maximum peak of about 1.0 e/A^3 located near In(1).

[Li(THF)$_4$][In(NPh$_2$)$_3$Cl]. The Laue symmetry was determined to be 2/*m*, and from the systematic absences the space group was shown unambiguously to be $P2_1/n$. The structure was solved by using the MolEN Patterson interpretation program, which revealed the position of the In atom. The remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses, but due in part to the weak scattering by the crystal, the phenyl groups and THF molecules were difficult to locate and refine. Attempts to model both either as rigid groups or with bond length and angle restraints led to unreasonable geometries and/or thermal parameters. The disorder for only one THF molecule was eventually resolved. For all the THF molecules, the best refinements were obtained by assigning a common thermal parameter to each residue. Due to the paucity of data, only the In atom was refined with anisotropic thermal parameters. The hydrogen atoms attached to carbon were entered in ideal calculated positions and constrained to riding motion such that $U(\mathrm{H}) = 1.3U(\text{attached C})$. After all shift/esd ratios were less than 0.1, convergence was reached at the agreement factors listed in Table 1. No unusually high correlations were noted between any of the variables in the last cycle of refinement. The final difference map showed a maximum peak of about 0.5 e/A^3.

Results and Discussion

Syntheses and Spectroscopic Characterization. A summary of our synthetic results is presented in Scheme 1.

Scheme 1



In diethyl ether, InCl$_3$ reacts with 3 equiv of lithium amide to give In(NRR′)$_3$ (R = Ph or *t*-Bu, R′ = SiMe$_3$; R = *t*-Bu, R′ = SiHMe$_2$). The ether adduct of the phenyl silyl amide derivative, In[NPh(SiMe$_3$)]$_3$(ether), a colorless crystalline solid, can be isolated from the synthesis if the product is held under vacuum only briefly. The ether can also be removed from the etherate by dissolution in CH$_2$Cl$_2$ and then removal of the CH$_2$Cl$_2$/ether in vacuo. In[N(*t*-Bu)(SiMe$_3$)]$_3$ is a volatile white solid (subl 70 °C, 10^{-2} Torr, with some decomposition) while In[NPh(SiMe$_3$)]$_3$ is a yellow-orange liquid that decomposes at ≈70 °C under vacuum and In[N(*t*-Bu)(SiHMe$_2$)]$_3$ is a light yellow liquid that distills at 30 °C, 10^{-2} Torr. In[N(*t*-Bu)(SiHMe$_2$)]$_3$ reacts with *p*-(dimethylamino)pyridine to form the adduct In[N(*t*-Bu)(SiHMe$_2$)]$_3$(*p*-Me$_2$Npy), a colorless crystalline solid. This compound was prepared to have a solid sample for an X-ray crystallographic analysis (see below). Attempted reactions of InCl$_3$ with LiN(SiHMe$_2$)$_2$ in ether and pyridine solvents produced copious amounts of a gray insoluble precipitate that is presumably In metal.

When less sterically encumbered amides are reacted with indium chloride in weakly coordinating ether solvents, salts are isolated. Thus, indium trichloride reacts with 3 equiv of LiNMe(SiMe$_3$) in diethyl ether to give [Li(ether)][In{NMe(SiMe$_3$)}$_4$] instead of the intended tris(amide) product. The yield of the salt is nearly doubled (to 72%) by carrying out the reaction with the correct 1:4 stoichiometry. Similarly, InCl$_3$ reacts with 3 equiv of LiNPh$_2$ in THF to give [Li(THF)$_4$][In(NPh$_2$)$_3$Cl], which forms yellow crystals upon low-temperature crystallization from toluene/THF. Both [Li(ether)][In{NMe(SiMe$_3$)}$_4$] and [Li(THF)$_4$][In(NPh$_2$)$_3$Cl] show moderate solubility in benzene. To have a sample of Li[In{NMe(SiMe$_3$)}$_4$] suitable for X-ray analysis, the *p*-(dimethylamino)pyridine adduct [Li(*p*-Me$_2$Npy)][In{NMe(SiMe$_3$)}$_4$] was prepared by reacting the etherate with *p*-Me$_2$Npy and crystallizing from toluene.

The isolation of the salt compounds from reactions carried out in ether solvents contrasts with the results of reactions between InCl$_3$ and 3 equiv of LiNRR′ (R = R′ = Ph; R = Me, R′ = SiMe$_3$) carried out in pyridine, which produce the neutral complexes In(NRR′)$_3$(py). In[NMe(SiMe$_3$)]$_3$(py) can also be prepared by carrying out the reaction in a 9:1 mixture of ether/

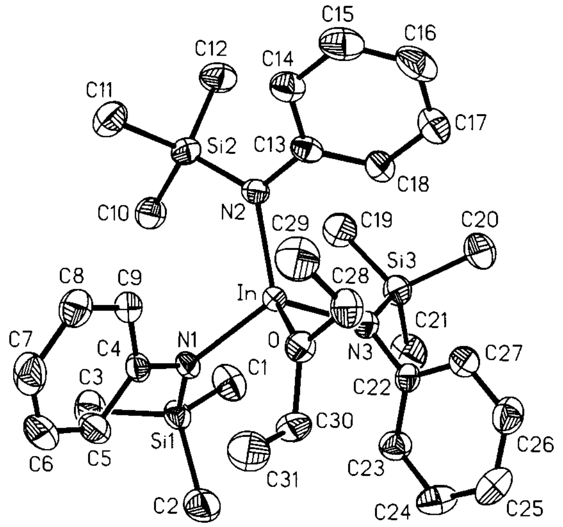


Figure 1. View of In[NPh(SiMe$_3$)]$_3$(ether) showing the atom-numbering scheme (50% probability ellipsoids).

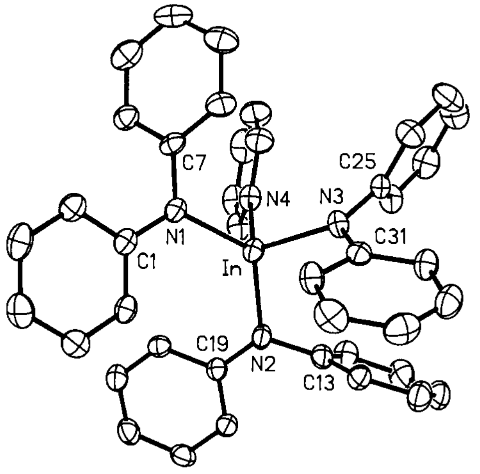


Figure 2. View of In(NPh$_2$)$_3$(py) showing the atom-numbering scheme (40% probability ellipsoids).

pyridine. In(NPh$_2$)$_3$(py) is a yellow crystalline solid, and In[NMe(SiMe$_3$)]$_3$(py) is a viscous light red liquid that distills at 70−75 °C with decomposition. The py ligand in In[NMe(SiMe$_3$)]$_3$(py) is displaced by *p*-(dimethylamino)pyridine, a better donor than unsubstituted pyridine, to yield In[NMe(SiMe$_3$)]$_3$(*p*-Me$_2$Npy) as a crystalline light tan solid after workup.

We considered the possibility that in the reactions described in the previous paragraph the pyridine solvent prevents formation of [In{NMe(SiMe$_3$)}$_4$]$^-$ and [In(NPh$_2$)$_3$Cl]$^-$ by blocking open coordination sites. To test this idea, we reacted In[NMe(SiMe$_3$)]$_3$(py) with excess LiNMe(SiMe$_3$) (4−5 equiv) in neat pyridine. After stirring for 24 h, the pyridine was removed in vacuo, and the residue was extracted with benzene-d_6 (some insoluble material remained). The ^{1}H NMR specrum of the extract showed only the presence of the salt [Li(pyridine)][In{NMe(SiMe$_3$)}$_4$]. Because the pyridine did not prevent formation of the salt in the aforementioned experiment, we also examined the possibility that the neutral In(NRR′)$_3$(py) compounds are formed via [In(NRR′)$_4$]$^-$ intermediates. To test this idea, we reacted preformed [Li(ether)][In{NMe(SiMe$_3$)}$_4$] with $^1/_3$ equiv of InCl$_3$ in neat pyridine under the same reaction conditions (23 °C/24 h) used to prepare In[NMe(SiMe$_3$)]$_3$(py) from LiNMe(SiMe$_3$) and InCl$_3$. After the specified time the pyridine solvent was removed in vacuo. The ^{1}H NMR spectrum of the residue (benzene-d_6) revealed the soluble components to be a 60:40 mixture of [Li(py)$_x$][In{NMe(SiMe$_3$)}$_4$] and In[NMe(SiMe$_3$)]$_3$(py). This result suggests that the formation of In[NMe(SiMe$_3$)]$_3$(py) from InCl$_3$/LiNMe(NSiMe$_3$) in pyridine is not entirely through an anion intermediate. On the basis of these two sets of experiments, the role pyridine solvent plays to allow isolation of the neutral adducts In[NMe(SiMe$_3$)]$_3$(py) and In(NPh$_2$)$_3$(py) rather than the anions [In{NMe(SiMe$_3$)}$_4$]$^-$ and [In(NPh$_2$)$_3$Cl]$^-$ is not clear. It is reasonable to suggest, however,

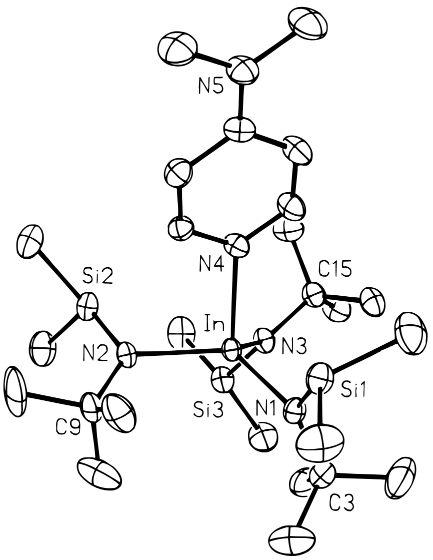


Figure 3. View of In[N(*t*-Bu)(SiHMe$_2$)]$_3$(*p*-Me$_2$Npy) showing the atom-numbering scheme (40% probability ellipsoids).

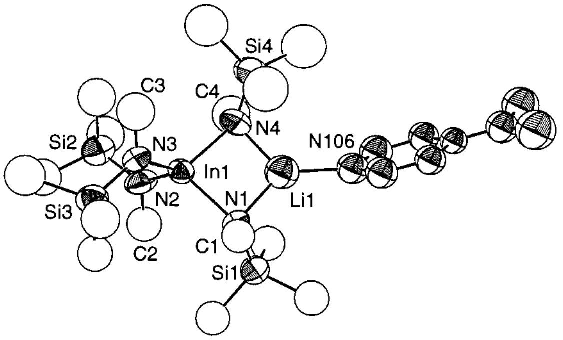


Figure 4. View of [Li(*p*-Me$_2$Npy)][In{NMe(SiMe$_3$)}$_4$] showing the atom-numbering scheme for one of the two independent molecules in the unit cell (50% probability ellipsoids).

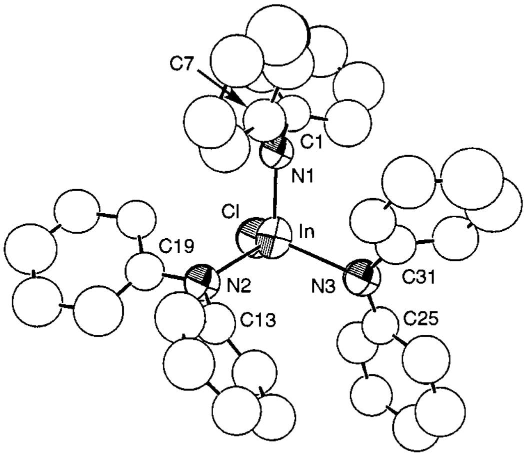


Figure 5. View of [In(NPh$_2$)$_3$Cl]$^-$ from [Li(THF)$_4$][In(NPh$_2$)$_3$Cl] showing the atom-numbering scheme (50% probability ellipsoids).

Table 2. Selected Bond Distances (Å) and Angles (deg) for In[NPh(SiMe$_3$)]$_3$(ether), In(NPh$_2$)$_3$(py)·toluene, In[N(*t*-Bu)(SiHMe$_2$)]$_3$(*p*-Me$_2$Npy), [Li(*p*-Me$_2$Npy)][In{NMe(SiMe$_3$)}$_4$], and [Li(THF)$_4$][In(NPh$_2$)$_3$Cl]

	In[NPh(SiMe$_3$)]$_3$ (ether)	In(NPh$_2$)$_3$(py)· toluene	In[N(*t*-Bu)(SiHMe$_2$)]$_3$ (*p*-Me$_2$Npy)	[Li(*p*-Me$_2$Npy)] [In{NMe(SiMe$_3$)}$_4$]^a	[Li(THF)$_4$] [In(NPh$_2$)$_3$Cl]
			Distances		
In−N1	2.098(2)	2.079(3)	2.130(3)	2.17(1)	2.02(2)
In−N2	2.103(2)	2.072(3)	2.124(3)	2.05(1)	2.11(1)
In−N3	2.083(2)	2.099(3)	2.122(3)	2.08(1)	2.15(1)
In−Z	2.283(2) (Z = O)	2.264(4) (Z = N4)	2.327(3) (Z = N4)	2.17(2) (Z = N4)	2.384(6) (Z = Cl)
Li1−N1				2.02(4)	
Li1−N4				1.98(4)	
Li1−N106				1.99(4)	
			Angles		
N1−In−N2	117.3(1)	128.0(1)	119.3(1)	119.9(5)	114.9(6)
N1−In−N3	121.4(1)	111.3(1)	115.0(1)	107.2(6)	109.6(6)
N2−In−N3	115.9(1)	109.5(1)	114.8(1)	110.7(5)	113.2(5)
Z−In−N1	90.0(1)	99.0(1)	100.7(1)	89.9(6)	100.9(4)
Z−In−N2	106.3(1)	100.0(1)	92.4(1)	109.4(6)	106.8(4)
Z−In−N3	97.3(1)	105.3(1)	110.4(1)	118.7(5)	110.7(4)
X−N1−Y	120.8(2)	119.5(3)	121.4(3)	111.(1)	110.(2)
	(X = Si1, Y = C4)	(X = C1, Y = C7)	(X = Si1, Y = C3)	(X = Si1, Y = C1)	((X = C1, Y = C7)
In−N1−X	123.3(1)	127.5(3)	117.4(1)	128.3(6)	123.(1)
In−N1−Y	115.8(2)	113.0(2)	121.0(2)	112.(1)	127.(1)
X−N2−Y	120.1(2)	117.2(3)	123.2(2)	113.(1)	121.(1)
	(X= Si2, Y = C13)	(X = C13, Y = C19)	(X = Si2, Y = C9)	(X = Si2, Y = C2)	((X = C13, Y = C19)
In−N2−X	122.8(1)	114.7(3)	114.9(1)	125.7(7)	117.(1)
In−N2−Y	117.0(2)	127.1(3)	121.1(2)	120.(1)	121.(1)
X−N3−Y	116.2(2)	118.8(3)	124.4(2)	115.(1)	123.(2)
	(X = Si3, Y = C22)	(X = C25, Y = C31)	(X = Si3, Y = C15)	(X = Si3, Y = C3)	(X = C25, Y = C31)
In−N3−X	128.6(1)	121.6(3)	115.3(1)	122.7(5)	124.(1)
In−N3−Y	115.2(2)	119.0(2)	119.9(2)	122.(1)	113.(1)
X−N4−Y				107.(1)	
				(X = Si4, Y = C4)	
In−N4−X				129.7(9)	
In−N4−Y				109.(1)	
N1−Li1−N4				100.(2)	
N1−Li1−N106				131.(2)	
N4−Li1−N106				128.(2)	

[a] Distances and angles for only one of the two independent molecules in the asymmetric unit are presented. See the Supporting Information for full details.

that the pyridine slows formation of the anions, thereby allowing isolation of the neutral complexes.

There is no evidence to suggest the existence of dimer solution structures in room temperature ^{1}H NMR spectra of In[N(*t*-Bu)(SiMe$_3$)]$_3$, In[NPh(SiMe$_3$)]$_3$, and In[N(*t*-Bu)(SiHMe$_2$)]$_3$ or in low-temperature spectra of In[NPh(SiMe$_3$)]$_3$ (toluene-d_8, down to −60 °C). A molecular weight determination of In[NPh(SiMe$_3$)]$_3$ gave a mass of 710 ± 40 g/mol (isothermal distillation, pentane solvent, Ta[N(SiMe$_3$)$_2$]$_2$Cl$_3$ standard), which is about 17% higher than the monomer molecular weight of 608 g/mol.

In the ^{1}H NMR spectra of In[N(*t*-Bu)(SiHMe$_2$)]$_3$ and In(N(*t*-Bu)(SiHMe$_2$))$_3$(*p*-Me$_2$Npy) the Si−H protons appear as septets due to coupling with the methyl groups attached to Si. Similarly, the Si−H proton in the parent amine HN(*t*-Bu)(SiHMe$_2$) gives rise to an “octet” due to coupling with Si*Me*$_2$ and N*H* (i.e., $^3J_{HH} \approx {^3J_{HH}}' \approx 3$ Hz). The IR spectrum of In[N(*t*-Bu)(SiHMe$_2$)]$_3$ has a strong band at 2075 cm^{-1} that can be assigned to the Si−H stretch.

X-ray Crystallographic Studies. X-ray crystal structure determinations of In[NPh(SiMe$_3$)]$_3$(ether) (Figure 1), In(NPh$_2$)$_3$(py)·toluene (Figure 2), In[N(*t*-Bu)(SiHMe$_2$)]$_3$(*p*-Me$_2$Npy) (Figure 3), [Li(*p*-Me$_2$Npy)][In{NMe(SiMe$_3$)}$_4$] (Figure 4), and [Li(THF)$_4$][In(NPh$_2$)$_3$Cl] (Figure 5) were carried out. The results of the analyses for the two salt compounds are poor because of the crystal quality.

The overall geometries of the four-coordinate In atoms can be loosely described as severely distorted tetrahedral with the exception of [In(NPh$_2$)$_3$Cl]$^-$, which approaches an ideal tetrahedral geometry. In In[NPh(SiMe$_3$)]$_3$(ether), In(NPh$_2$)$_3$(py), and In[N(*t*-Bu)(SiHMe$_2$)]$_3$(*p*-Me$_2$Npy), the amide nitrogens and the In atoms are close to planar, with the sum of the N−In−N angles being 355°, 350° and 349°, respectively (Table 2). The N−In−N angles associated with the amide ligands in the neutral compounds vary widely, with the biggest difference found in In(NPh$_2$)$_3$(py), where N1−In−N2 is more than 17° larger than N2−In−N3 and N1−In−N3. On the other hand, the N−In−N angles in In[N(*t*-Bu)(SiHMe$_2$)]$_3$(*p*-Me$_2$Npy) fall in a narrow 4° range. The amide nitrogen coordination geometries are all planar with the exception of N1 and N4 in [Li(*p*-Me$_2$Npy)][In{NMe(SiMe$_3$)}$_4$], which show slight pyramidalization (≈10°) because they are bound to the Li cation. The X−N−Y angles at the amide nitrogens in the neutral compounds are all within 4° of 120°, but the associated In−N−X,Y angles span a large range, 113−129°, suggesting that the energy barrier for bending is low and the angle is set by steric factors.

The In−N(amide) distances in In[N(*t*-Bu)(SiHMe$_2$)]$_3$(*p*-Me$_2$Npy) (average 2.125(3) Å) are significantly longer than those in In[NPh(SiMe$_3$)]$_3$(ether) (average 2.095(2) Å) and In(NPh$_2$)$_3$(py) (average 2.083(3) Å). The In−N(amide) distances in the new compounds can be compared to those found in In[N(SiMe$_3$)$_2$]$_3$ (2.049(1) Å),[4] In(2,2,6,6-tetramethylpiperidino)$_3$ (average 2.078(5) Å),[8] (Me$_3$C)$_2$In[N(SiPh$_3$)(2,6-*i*-PrPh)] (2.104(3)

Å),[4] and $Et_2In(NC_5H_4)$ (2.166(4) Å).[13] In $In[NPh(SiMe_3)]_3$(ether) the In−O distance (2.283(2) Å) is in the range of dative In−O bond distances found in $In(mesityl)_3(THF)$ (2.414(4) Å),[14] $In(SC_6(CF_3)_3H_2)_3$(ether) (2.224(6) Å),[15] and $InCl_3(THF)_2$ (2.265(5) Å),[16] and the In−N(py) bond lengths in $In(NPh_2)_3(py)$ (2.264(4) Å) and $In[N(t\text{-}Bu)(SiHMe_2)]_3(p\text{-}Me_2Npy)$ (2.327(3) Å) are close to the corresponding distances found in $InX_3(py)_3$ where X = Cl or Br (2.28(3)−2.38(2) Å)[17,18] and $InCl_2$(1,3-diphenyltriazide)(3,5-dimethylpyridine)$_2$ (average 2.307(7) Å).[19]

In $[Li(THF)_4][In(NPh_2)_3Cl]$, the $[Li(THF)_4]^+$ fragment is not close to the anion, but in $[Li(p\text{-}Me_2Npy)][In\{NMe(SiMe_3)\}_4]$, the lithium cation interacts with two of the amide nitrogens (N1 and N4) and p-Me_2Npy (N106), giving lithium a planar, three-coordinate geometry. The N−Li−N angle associated with the two amide ligands is nearly 30° smaller than the other two angles, and the three Li−N bond distances are the same within experimental error. The Li coordination geometry in $[Li(p\text{-}Me_2Npy)][In\{NMe(SiMe_3)\}_4]$ is similar to that found in $[Li(py)]_2[Cr(NEt_2)_4]$.[20]

Conclusion

$In(NRR')_3$ (R = Ph or t-Bu, R′ = $SiMe_3$; R = t-Bu, R′ = $SiHMe_2$) compounds are synthesized by reacting $InCl_3$ with lithium amides in diethyl ether. In contrast, $InCl_3$ reacts with the less sterically demanding amides $LiNPh_2$ and $LiNMe(SiMe_3)$ in ether solvents to give the salt compounds $Li[In(NPh_2)_3Cl]$ and $Li[In\{NMe(SiMe_3)\}_4]$, respectively. Similar reactions carried out in the presence of pyridine yield the neutral adducts $In(NPh_2)_3(py)$ and $In[NMe(SiMe_3)]_3(py)$. In the latter reactions the role pyridine plays to prevent formation of $[In\{NMe(SiMe_3)\}_4]^-$ and $[In(NPh_2)_3Cl]^-$ is not clear. The result suggests, however, that other neutral In(amide)$_3$L compounds may be accessible by using similar coordinating solvents, such as liquefied NMe_3, or by using preformed $InCl_3L_n$ (L = amine) complexes as starting materials. $In[N(t\text{-}Bu)(SiHMe_2)]_3$ and $In[NMe(SiMe_3)]_3(py)$ react with the strong donor p-(dimethylamino)pyridine to give $In(NRR')_3(p\text{-}Me_2Npy)$ compounds.

In the solid state, $In[NPh(SiMe_3)]_3$(ether), $In(NPh_2)_3(py)$, and $In[N(t\text{-}Bu)(SiHMe_2)]_3(p\text{-}Me_2Npy)$ have nearly planar In(amide)$_3$ cores. The anion in $[Li(THF)_4][In(NPh_2)_3Cl]$ is separated from the cation in the solid state, but in $[Li(p\text{-}Me_2Npy)][In\{NMe(SiMe_3)\}_4]$, the tetrahedral-like anion is bound to the Li cation via two amide nitrogens. In the latter compound, the Li is also bonded to p-Me_2Npy, resulting in a planar three-coordinate geometry for Li.

A goal of this study was to prepare CVD precursors for use in combination with ammonia to give InN. Of the new compounds, $In[N(t\text{-}Bu)(SiHMe_2)]_3$ is the most promising precursor candidate because it is a liquid and it can be volatilized without appreciable decomposition, two essential attributes of a CVD precursor.

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Supporting Information Available: Complete tables of crystal data, atomic coordinates, thermal parameters, and bond distances and angles for $In[NPh(SiMe_3)]_3$(ether), $In(NPh_2)_3(py)$, $In[N(t\text{-}Bu)(SiHMe_2)]_3(p\text{-}Me_2Npy)$, $[Li(THF)_4][In(NPh_2)_3Cl]$, and $[Li(p\text{-}Me_2Npy)][In\{NMe(SiMe_3)\}_4]$ (44 pages). Ordering information is given on any current masthead page.

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