Synthesis and Characterization of Five-Coordinate Gallium and Indium Complexes Stabilized by Tridentate, Substituted Pyrrole Ligands

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Five-coordinate gallium and indium complexes stabilized by tridentate, substituted pyrrole ligands have been synthesized and characterized. The reaction of MCl_3 with 1 equiv. of $Li[NC_4H_2(CH_2NMe_2)_2\text{-}2,5]$ in diethyl ether affords $[\{NC_4H_2(CH_2NMe_2)_2\text{-}2,5\}MCl_2]$ [M = Ga (**1**), In (**2**)] in high yield. Reaction of **1** with 2 equiv. of MeLi in diethyl ether at –78 °C followed by heating to reflux for 30 min affords the alkylated product $[\{NC_4H_2(CH_2NMe_2)_2\text{-}2,5\}GaMe_2]$ (**3**). Similarly, the reaction of **2** with 2 equiv. of MeLi or *n*BuLi affords the dialkylated complexes **4** and **5**, respectively. Complex **2** is a strong Lewis acid which readily absorbs H_2O forming $[\{[C_4H_2N(CH_2NMe_2)_2\text{-}2,5]InCl_2\}_2(\mu\text{-}OH_2)]$ (**6**). Complexes **3**, **4**, and **6** have been characterized by X-ray crystallography.

Introduction

Lewis acids catalyze a wide range of reactions. The reactivity and selectivity of these reactions are often related to the Lewis acid's electronic and steric properties.[1] Among the Lewis acid catalysts derived from group-13 metals, those of aluminum are well known for serving as catalysts in organic synthesis, and more recently for polymerization reactions.[2–4] The number of metal complexes reported, however, declines upon descending the group from aluminum to indium. Indium-mediated organometallic reactions have received considerable attention recently, due to their tolerance of polar solvents, including water.[5–11] Lewis acidic indium complexes are dominated by a low coordination number at the metal center (three or four)[12–14] but a few complexes of higher coordination number (five and six) have been reported.[15–21]

We have been interested in the chemistry of group-13[22–23] and early transition metal complexes[24–25] stabilized by bi- or tridentate substituted pyrrole ligands.[26–27] These complexes are Lewis acids with the potential to serve as catalysts in organic synthesis or for the polymerization of olefins. We report here the syntheses, intramolecular rearrangement, and X-ray crystal structures of Ga and In complexes.

Results and Discussion

Synthesis and Characterization

Reaction of $Li[NC_4H_2(CH_2NMe_2)_2\text{-}2,5]$ with MCl_3 (M = Ga, In) in diethyl ether affords $[\{NC_4H_2(CH_2NMe_2)_2\text{-}2,5\}MCl_2]$ [M = Ga (**1**), In (**2**)] in yields of 98 and 81%, respectively (Scheme 1). However, suitable crystals of complexes **1** and **2** could not be obtained. The ^1H and ^{13}C NMR spectra of both **1** and **2** show the signals of one type of CH_2 and NMe_2 units at $\delta \approx 3.6$ and 2.5 ppm, respectively, which are consistent with symmetrical structures.

Reaction of complex **1** with 2 equiv. of 1.6 M methyllithium in diethyl ether solution at −78 °C followed by heating to reflux for 30 min afforded the dimethylgallium complex $[\{NC_4H_2(CH_2NMe_2)_2\text{-}2,5\}GaMe_2]$ (**3**) in 75% yield. The ^1H NMR spectrum of **3** shows signals of one set of CH_2, NMe_2, and GaMe units at $\delta = 3.47$, 2.29, and −0.37 ppm, respectively.

Similarly, treatment of **2** with 2 equiv. of MeLi or *n*BuLi in a diethyl ether solution at −78 °C, allowing to warm to room temperature, and then heating to reflux for 30 min generated the pure dimethyl complex **4** and the dibutyl complex **5** in yields of 61 and 65%, respectively. Complexes **3**, **4**, and **5** are thermally robust and show no decomposition upon heating in toluene at 100 °C for over 12 h.

Complex **2** is very Lewis acidic and reacts readily with moisture upon exposure to air. During recrystallization of **2** from a toluene solution at −20 °C, the Schlenk flask was occasionally opened to air resulting in the deposition of the water-bridged complex $[\{[C_4H_2N(CH_2NMe_2)_2\text{-}2,5]InCl_2\}_2(\mu\text{-}OH_2)]$ (**6**). The procedure was carried out several times in both toluene and diethyl ether, and the same result was obtained. Attempts to let **2** react with 0.5 equiv. of H_2O

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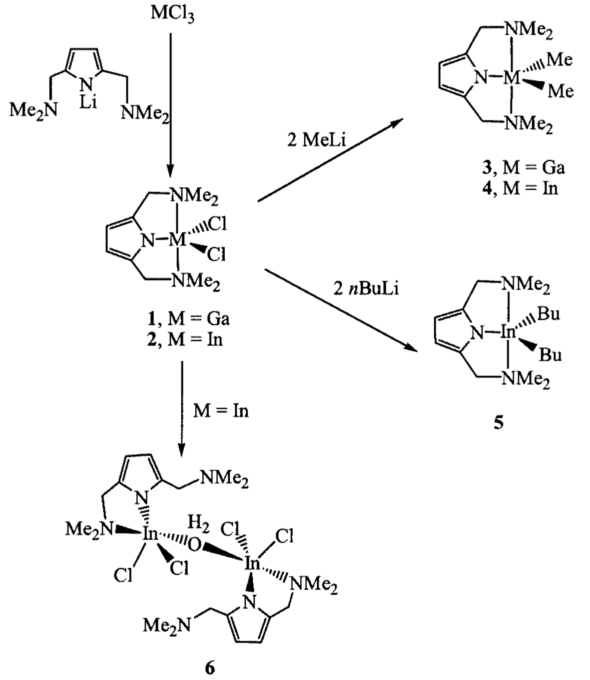

Scheme 1

in either toluene or diethyl ether afforded a mixture, from which only a small amount of **6** was isolated. Similarly, diffusion of H_2O vapor into a toluene solution of **2** yielded the same results. The ^1H NMR spectrum of **6** in CD_2Cl_2 at room temperature indicates an asymmetric arrangement, which is consistent with the X-ray crystal structure (vide infra). Complex **6** gives rise to three methyl resonances for the two NMe_2 units at $\delta = 2.50$, 2.59, and 2.84 ppm in the ratio of 1:1:2. Four doublets for the two AB systems of the CH_2N units were observed at $\delta = 3.16$, 3.70, 4.56, and 4.72 ppm in the ratio of 1:1:1:1. Selective homonuclear decoupling of the ^1H NMR spectrum of **6** revealed that one AB pattern of a CH_2N unit gives rise to the resonances at $\delta =$ 3.16 and 4.56 ppm while the other unit can be attributed to the resonances at $\delta = 3.70$ and 4.72 ppm.

Solid-State Structures of Complexes 3, 4, and 6

Crystals of **3** suitable for X-ray structure determination were obtained from a saturated diethyl ether solution stored at −20 °C. Crystals of **4** were obtained by sublimation from a flask in the glove box under nitrogen. Details of the data collections for **3** and **4** are summarized in Table 2 with selected bond lengths and angles listed in Table 1. The ORTEP diagram of complex **3** is depicted in Figure 1. The gallium atom is surrounded by two methyl groups and three nitrogen atoms of the tridentate pyrrolyl ligand, $[NC_4H_2(CH_2NMe_2)_2\text{-}2,5]$, forming a distorted trigonal-bipyramidal structure. The tridentate pyrrolyl ligand is arranged at the meridional positions, with the pyrrolyl nitrogen atom occupying the equatorial position and the two NMe_2 units occupying the axial positions. The axial N(1)−Ga−N(3) angle of 146.68(6)° deviates from linearity

Table 1. Selected bond lengths [Å] and angles [°] for compounds **3**, **4**, and **6**

3							
Ga−N(2)	1.920(2)	Ga−C(2)	1.953(2)	Ga−C(1)	1.969(2)	Ga−N(1)	2.307(2)
Ga−N(3)	2.736(2)						
N(2)−Ga−C(2)	121.38(10)	N(2)−Ga−C(1)	114.36(9)	C(2)−Ga−C(1)	123.10(11)	N(2)−Ga−N(1)	77.13(7)
C(2)−Ga−N(1)	102.57(9)	C(1)−Ga−N(1)	99.66(9)	N(2)−Ga−N(3)	69.92(6)	C(2)−Ga−N(3)	90.63(8)
C(1)−Ga−N(3)	98.27(9)	N(1)−Ga−N(3)	146.68(6)				
4							
In(1)−N(2)	2.108(5)	In(1)−C(2)	2.173(6)	In(1)−C(1)	2.187 (6)	In(1)−N(1)	2.519(5)
In(1)−N(3)	2.681(6)	In(2)−N(5)	2.117(5)	In(2)−C(14)	2.087(7)	In(2)−C(13)	2.161(6)
In(2)−N(4)	2.516(6)	In(2)−N(6)	2.670(6)				
N(2)−In(1)−C(2)	113.1(2)	N(2)−In(1)−C(1)	121.2(2)	C(2)−In(1)−C(1)	124.6(3)	N(2)−In(1)−N(1)	71.9(2)
C(2)−In(1)−N(1)	105.4(2)	C(1)−In(1)−N(1)	101.3(2)	N(2)−In(1)−N(3)	69.5(2)	C(2)−In(1)−N(3)	94.5(3)
C(1)−In(1)−N(3)	94.0(2)	N(1)−In(1)−N(3)	140.96(19)	N(5)−In(2)−C(14)	112.7(3)	N(5)−In(2)−C(13)	119.5(2)
C(14)−In(2)−C(13)	127.0(3)	N(5)−In(2)−N(4)	71.5(2)	C(14)−In(2)−N(4)	106.1(3)	C(13)−In(2)−N(4)	98.4(2)
N(5)−In(2)−N(6)	68.5(2)	C(14)−In(2)−N(6)	95.2(3)	C(13)−In(2)−N(6)	95.6(2)	N(4)−In(2)−N(6)	139.5(2)
6·C_7H_8							
In(1)−O(1)	2.136(4)	In(1)−N(2)	2.167(5)	In(1)−N(1)	2.334(5)	In(1)−Cl(1)	2.434(2)
In(1)−Cl(1)	2.519(2)	In(2)−N(5)	2.146(5)	In(2)−O(1)	2.175(4)	In(2)−N(4)	2.366(5)
In(2)−Cl(3)	2.462(2)	In(2)−Cl(4)	2.4750(14)				
O(1)−In(1)−N(2)	97.5(2)	O(1)−In(1)−N(1)	156.9(2)	N(2)−In(1)−N(1)	78.7(2)	O(1)−In(1)−Cl(1)	106.64(10)
N(2)−In(1)−Cl(1)	102.8(1)	N(1)−In(1)−Cl(1)	96.4(1)	O(1)−In(1)−Cl(2)	84.7(1)	N(2)−In(1)−Cl(2)	154.2(1)
N(1)−In(1)−Cl(2)	89.2(1)	Cl(1)−In(1)−Cl(2)	101.14(6)	N(5)−In(2)−O(1)	96.9(2)	N(5)−In(2)−N(4)	77.6(2)
O(1)−In(2)−N(4)	161.3(2)	N(5)−In(2)−Cl(3)	98.7(1)	O(1)−In(2)−Cl(3)	98.2(1)	N(4)−In(2)−Cl(3)	100.4(1)
N(5)−In(2)−Cl(4)	163.8(1)	O(1)−In(2)−Cl(4)	84.7(1)	N(4)−In(2)−Cl(4)	95.8(1)	Cl(3)−In(2)−Cl(4)	97.03(6)
In(1)−O(1)−In(2)	108.6(2)						

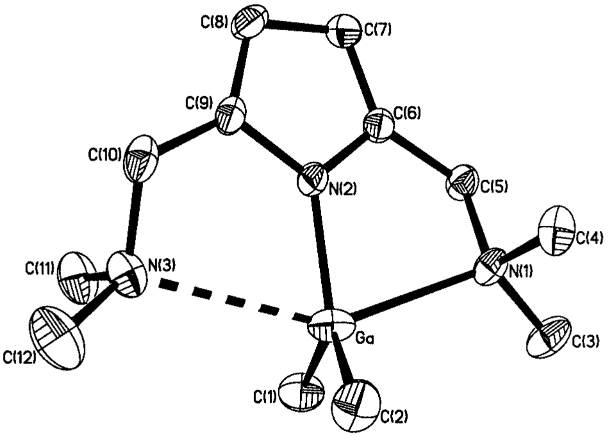

Figure 1. ORTEP diagram of complex **3**; thermal ellipsoids at the 50% probability level and hydrogen atoms are omitted for clarity

by 33.32° due to the geometrical constraints of the two fused five-membered rings. It is noteworthy that the N(1)−Ga and N(3)−Ga bond distances of 2.307(2) and 2.736(2) Å, respectively, are significantly different. The unit cell of **4** contains two independent molecules and the structure of one of these is shown in Figure 2. The structure of **4** is very similar to that of complex **3**. However, the difference of 0.14 Å in the metal-to-axial-nitrogen bond lengths In(1)−N(1) [2.519(5) Å] and In(1)−N(3) [2.661(6) Å] is smaller in **4** than in the corresponding gallium species. This is consistent with the larger atomic radius of indium. The axial angle, N(1)−In−N(3) [140.96(19)°], deviates from linearity by 39.04° due to the steric constraints imposed by the two fused five-membered rings.

Crystals of complex **6** were obtained by dissolving **2** in toluene and cooling to −20 °C. The reaction of **2** with moisture was effected by slowly exposing the solution to air occasionally. This caused crystals of **6** to appear in the flask. The crystals were collected and characterized by ^{1}H NMR spectroscopy and a single-crystal X-ray diffraction study. Details of the data collection for complex **6** are summarized in Table 2 with selected bond lengths and angles listed in Table 1. The ORTEP diagram of **6** is shown in Figure 3. The structure of **6** can be described as corner-sharing bis(square-pyramidal), in which the oxygen atom acts as the corner atom with Cl(1) and Cl(3) occupying the apical positions. A view of the coordination spheres of the two indium centers is shown in Figure 4, where the two square planes are joined by the oxygen atom. The In(1) and In(2) atoms are displaced from the planes defined by N(1)−N(2)−O(1)−Cl(2) and N(4)−N(5)−O(1)−Cl(4) by 0.4717 and 0.3389 Å, respectively. The question has been raised as to whether the oxygen-containing bridging groups should be viewed as water molecules or dianionic oxo groups. Although the hydrogen atoms of the bridging group were not found either in the ^{1}H NMR spectrum or in the X-ray crystal structure, three points support the water-bridged formulation for the dinuclear indium complex: (1) In both **4** and **6**, both pyrrolyl groups exist as σ-coordinated ligands with similar In−N distances [2.108(5) vs. 2.17 Å]. Furthermore, accommodation of the two methyl groups results in an oxidation state of +3 for the In center. These data suggest that the oxygen atom is coordinated to the indium

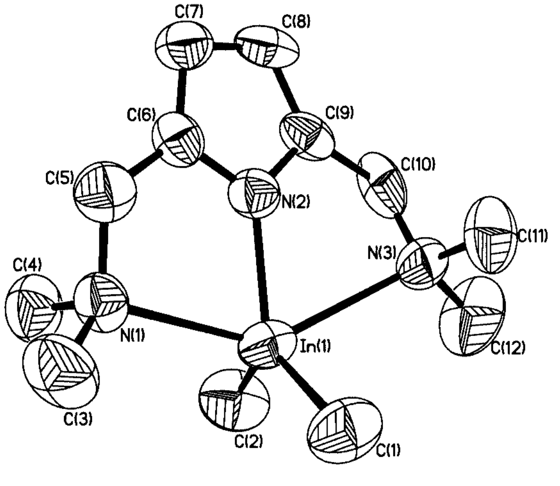

Figure 2. ORTEP diagram of complex **4**; thermal ellipsoids are at the 50% probability level and hydrogen atoms are omitted for clarity

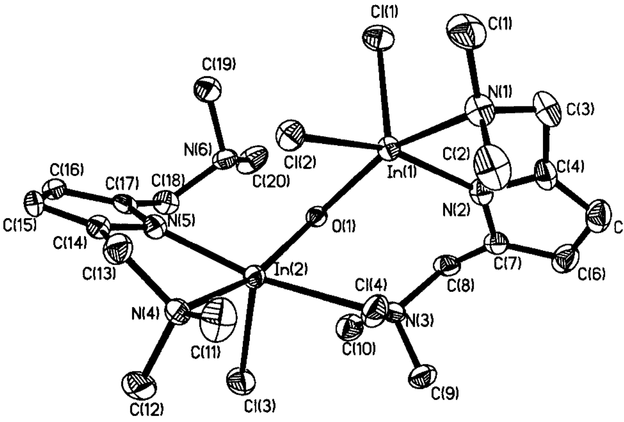

Figure 3. ORTEP diagram of complex **6**; thermal ellipsoids are at the 50% probability level and hydrogen atoms are omitted for clarity

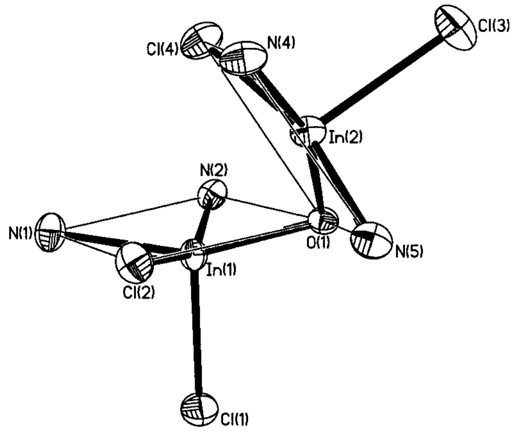

Figure 4. View of the coordination spheres of complex **6** showing only atoms coordinated to the indium atom; thermal ellipsoids are at the 50% probability level

atom via a lone pair of electrons. (2) The bond angle subtended by In(2)−O(1)−In(1) in complex **6** is 108.6(2)°, which is very close to the sp^3 bonding angle of 109.28. (3) Finally, an IR spectrum of **6** supports the existence of the bridged H_2O molecule, since a broad characteristic OH stretching peak was observed at 3460 cm^{-1}. Oxygen-atom-bridged dinuclear indium complexes have been observed often,[28−30] however, water-bridged diindium complexes have not been reported.

Experimental Section

General Procedures: All reactions were performed under dry nitrogen using standard Schlenk techniques or a glove box. Toluene, diethyl ether, and tetrahydrofuran were dried by heating to reflux in the presence of sodium benzophenone ketyl. CH_2Cl_2 was dried with P_2O_5. All solvents were distilled and stored under nitrogen in solvent reservoirs containing 4-Å molecular sieves. ^1H and ^{13}C NMR spectra were recorded with a Bruker AC 200 spectrometer. Chemical shifts for ^1H and ^{13}C spectra were recorded in ppm relative to the residual protons of the solvent or the ^{13}C resonances of the deuterated solvent: $CDCl_3$ (δ = 7.24, 77.0 ppm), C_6D_6 (δ = 7.15, 128.0 ppm), or CD_2Cl_2 (δ = 5.24, 54.0 ppm). Elemental analyses were performed with a Heraeus CHN-OS Rapid Elemental Analyzer at the Instrument Center, NCHU. $[C_4H_3N(CH_2NMe_2)_2\text{-}2,5]$ and $Li[C_4H_2N(CH_2NMe_2)_2\text{-}2,5]$ were prepared according to previously reported procedures.[23−25] $InCl_3$ (Strem) and MeLi (Aldrich) were used as received.

$[\{C_4H_2N(CH_2NMe_2)_2\text{-}2,5\}GaCl_2]$ (1): A 100-mL Schlenk flask was charged with a solution of $GaCl_3$ (5.0 g, 28.57 mmol) in diethyl ether (30 mL). This solution was added dropwise to a suspension of $Li[C_4H_2N(CH_2NMe_2)\text{-}2,5]$ (5.34 g, 28.57 mmol) in diethyl ether (20 mL) with stirring at −78 °C. The mixture was allowed to warm to room temperature and stirred for 5 h. The resultant suspension was filtered through Celite. The filtrate was concentrated to dryness and the resultant solid was recrystallized from diethyl ether to afford **1** (9.0 g, 98%). ^1H NMR ($CDCl_3$): δ = 2.52 (s, 12 H, NMe_2), 3.63(s, 4 H, CH_2N), 5.95 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 47.0 (q, $J_{C,H}$ = 136 Hz, NMe_2), 58.8 (t, $J_{C,H}$ = 139 Hz, CH_2N), 105.2 (d, $J_{C,H}$ = 167 Hz), 128.0 (s) ppm. $C_{10}H_{18}Cl_2GaN_3$ (320.90): calcd. C 37.43, H 5.65, N 13.09; found C 36.93, H 5.68, N 12.55.

$[\{C_4H_2N(CH_2NMe_2)_2\text{-}2,5\}InCl_2]$ (2): This complex was prepared in a similar way to that described for **1**, starting from $InCl_3$ (3.0 g, 13.6 mmol) and $Li[C_4H_2N(CH_2NMe_2)\text{-}2,5]$ (2.53 g, 13.6 mmol). Yield: 4.03 g (81%). ^1H NMR ($CDCl_3$): δ = 2.54 (s, 12 H, NMe_2), 3.65 (s, 4 H, CH_2N), 5.99 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 46.5 (q, $J_{C,H}$ = 137 Hz, NMe_2), 59.3 (t, $J_{C,H}$ = 138 Hz, CH_2N), 106.4 (d, $J_{C,H}$ = 167 Hz), 129.5 (s) ppm. $C_{10}H_{18}Cl_2InN_3$ (365.99): calcd. C 32.82, H 4.96, N 11.48; found C 32.26, H 4.54, N 10.92.

$[\{C_4H_2N(CH_2NMe_2)_2\text{-}2,5\}GaMe_2]$ (3): A 50-mL Schlenk flask was charged with diethyl ether (20 mL) and **1** (2.0 g, 6.23 mmol) and the resultant solution was cooled to −78 °C. To this solution was added MeLi (1.4 M in diethyl ether, 4.45 mL, 12.5 mmol) via syringe. The mixture was stirred at room temperature for 5 h, and the resultant suspension was heated to reflux for 30 min and filtered through Celite. The filtrate was concentrated to dryness affording **3** in 75% yield (1.30 g). ^1H NMR ($CDCl_3$): δ = −0.37 (s, 6 H, $GaMe$), 2.29 (s, 12 H, NMe_2), 3.48 (s, 4 H, CH_2N), 5.89 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = −9.32 (q, $J_{C,H}$ = 121 Hz), 45.9 (q, $J_{C,H}$ = 137 Hz, NMe_2), 58.9 (t, $J_{C,H}$ = 136 Hz, CH_2N), 103.0 (d, $J_{C,H}$ = 163 Hz), 131.9 (s) ppm. $C_{12}H_{24}GaN_3$ (280.06): calcd. C 51.46, H 8.64, N 15.00; found C 49.802, H 8.036, N 14.51. The error in the elemental analysis may be due to traces of LiBr in the final product.

$[\{C_4H_2N(CH_2NMe_2)_2\text{-}2,5\}InMe_2]$ (4) and $[\{C_4H_2N(CH_2NMe_2)_2\text{-}2,5\}InBu_2]$ (5): A similar procedure described for the preparation of complexe **3** was applied for the preparation of **4** and **5**. The yield of **4** was 61% (0.54 g, based on 1.0 g of **2**). ^1H NMR ($CDCl_3$): δ = −0.31 (s, 6 H, $InMe$), 2.31 (s, 12 H, NMe_2), 3.47 (s, 4 H, CH_2N), 5.91 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = −10.6 (q, $J_{C,H}$ = 126 Hz), 46.1 (q, $J_{C,H}$ = 135 Hz, NMe_2), 59.4 (t, $J_{C,H}$ = 135 Hz, CH_2N), 103.0 (d, $J_{C,H}$ = 164 Hz), 131.9 (s) ppm. $C_{12}H_{24}InN_3$ (325.16): calcd. C 44.33, H 7.44, N 12.92; found C 44.92, H 6.96, N 12.65. For **5** the yield was 65% (0.73 g, based on 1.0 g of **2**) of a brown viscous liquid after removing all volatiles. Due to the viscosity of complex **5**, it could not be purified by recrystallization or distillation. ^1H NMR ($CDCl_3$): δ = 0.66 (t, 4 H, $InCH_2CH_2CH_2CH_3$), 0.89 (t, 6 H, $InCH_2CH_2CH_2CH_3$), 1.31 (m, 4 H, $InCH_2CH_2CH_2CH_3$), 1.57 (m, 4 H, $InCH_2CH_2CH_2CH_3$), 2.34 (s, 12 H, NMe_2), 3.45 (s, 4 H, CH_2N), 5.91 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.2 (t, $J_{C,H}$ = 140 Hz), 13.7 (q, $J_{C,H}$ = 123 Hz), 28.8 (t, $J_{C,H}$ = 125 Hz), 30.3 (t, $J_{C,H}$ = 128 Hz), 46.8 (q, $J_{C,H}$ = 137 Hz, NMe_2), 60.0 (t, $J_{C,H}$ = 135 Hz, CH_2N), 103.0 (d, $J_{C,H}$ = 164 Hz), 132.7 (s). No elemental analysis was performed due to a small amount of impurity present in the product.

$[\{[C_4H_2N(CH_2NMe_2)_2\text{-}2,5]InCl_2\}_2(\mu\text{-}OH_2)]$ (6): The same procedure was applied for the preparation of **6** as that used to synthesize **2**, with the exception that during recrystallization of complex **2** from a toluene solution at −20 °C the Schlenk flask was periodically opened to air. This resulted in the deposition of **6** on the bottom of the flask (1.03 g,13%, based on 5 g of $InCl_3$). ^1H NMR (CD_2Cl_2): δ = 2.50 (br. s, 6 H, NMe_2), 2.59 (br. s, 6 H, NMe_2), 2.84 (br. s, 12 H, NMe_2), 3.16 (d, 4 H, CH_2N), 3.70 (d, 4 H, CH_2N), 4.56 (d, 4 H, CH_2N), 4.72 (d, 4 H, CH_2N), 6.01 (d, 2 H), 6.26 (d, 2 H) ppm. ^{13}C NMR (CD_2Cl_2): 47.8 (q, $J_{C,H}$ = 136 Hz, NMe_2), 49.6 (q, $J_{C,H}$ = 135 Hz, NMe_2), 50.2 (q, $J_{C,H}$ = 135 Hz, NMe_2), 60.6 (t, $J_{C,H}$ = 139 Hz, CH_2N), 61.3 (t, $J_{C,H}$ = 145 Hz, CH_2N), 106.3 (d, $J_{C,H}$ = 167 Hz), 114.9 (d, $J_{C,H}$ = 164 Hz), 122.5 (s), 136.0 (s). A small amount of complex **2** was present in **6** (less than 3% by ^1H NMR spectroscopy), which prevented a reasonable elemental analysis from being obtained.

X-ray Structure Determination of Complexes 3, 4, and 6: Crystals were mounted on a glass fiber using epoxy resin and transferred to the goniostat. Data collections were preformed at 150 K under liquid nitrogen vapor for complexes **3** and **6** and at 293 K for complex **4**. Data were collected with a Bruker SMART CCD diffractometer with graphite-monochromated Mo-K_α radiation. Structural determinations were carried out using the SHELXTL package of programs. All refinements were carried out by the full-matrix least-squares method using anisotropic displacement parameters for all non-hydrogen atoms. All the hydrogen atoms were placed in calculated positions. The crystal data are summarized in Table 2. CCDC-185057 and -185059 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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Table 2. Summary of crystallographic data for compounds **3**, **4**, and **6**

	3	**4**	**6**
Empirical formula	$C_{12}H_{24}GaN_3$	$C_{24}H_{48}In2N_6$	$C_{27}H_{46}Cl_4In_2N_6O$
Formula mass	280.06	650.32	842.14
Temperature [K]	150(1)	293(2)	150(1)
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	Pbca	*C*2/*c*	*P*2$_1$/*c*
a [Å]	12.1751(6)	27.4334(17)	9.3723(1)
b [Å]	15.2278(7)	9.1830(6)	17.6586(3)
c [Å]	15.6050(7)	27.5320(17)	21.9571(2)
β [°]	90	117.23(1)	92.704(1)
Volume [$Å^3$]/*Z*	2893.2(2)/8	6173.1(7)/8	3629.89(8)/4
Density (calcd.) [Mg/m^3]	1.286	1.399	1.541
Absorption coefficient [mm^{-1}]	1.884	1.514	1.594
F(000)	1184	2656	1696
Crystal size [mm]	0.50 × 0.40 × 0.10	0.36 × 0.31 × 0.07	0.20 × 0.10 × 0.10
θ range [°]	2.51 to 27.50	1.66 to 27.51	1.48 to 27.50
No. of reflns. collected	16753	19182	20140
No. of indep. reflns.	3318 (R_{int} = 0.0375)	7066 (R_{int} = 0.0339)	8096 (R_{int} = 0.08533)
Max./min. trans.	0.6471/0.4120	0.9486/0.8740	0.8621/0.5674
No. of data/restraints/params.	3318/0/146	7066/0/297	8095/0/362
Goodness of fit on F^2	1.094	1.014	1.017
Final *R* indices [$I > 2\sigma(I)$], R_1[a]	0.0363	0.0409	0.0581
wR_2[b]	0.0754	0.0830	0.1007
R indices (all data), R_1[a]	0.0463	0.1177	0.1045
wR_2[b]	0.0793	0.1137	0.1169
Largest diff. peak/hole [$e\cdot Å^{-3}$]	0.674/−0.615	0.765/−0.739	1.812/−1.210

[a] $R_1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}\}$.

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