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Notes

Five-Coordinate Organometallic Complexes of Gallium and Indium

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Summary: Using 2-benzylaminopyridine anion as a ligand, we have prepared a family of five- and six-coordinate organometallic complexes of Ga^{III} *and* In^{III}*. The monomeric nature and unusual distorted square-based pyramidal coordination geometries of the metal centers for* $M\{2\text{-}[N(CH_2C_6H_5)]NC_5H_4\}_2Me$ *(M = Ga,* **1***; M = In,* **2***) were confirmed through single-crystal X-ray diffraction analyses. An intermediate in the formation of the gallium complex,* $Ga\{2\text{-}[N(CH_2C_6H_5)]NC_5H_4\}Me_2(OEt_2)$*, has been characterized spectroscopically. Further reaction of* **2** *with a third equivalent of amine yields a six-coordinate tris-ligand complex,* $\{2\text{-}[N(CH_2C_6H_5)]NC_5H_4\}_3In$*.*

The organometallic complexes of aluminum, gallium, and indium are dominated by the appearance of four-coordinate metal centers.[1] Stimulated by efforts to clarify the steric and electronic effects on both the structure and the reactivity of group 13 organometallic species, there has been a recent resurgence of interest in the preparation of alkyl complexes of these elements having uncommon coordination geometries. For example, there are now several structurally characterized polynuclear and monomeric five- and six-coordinate organoaluminum complexes.[2−5] However, as one moves down the group toward gallium and indium, the examples of such species decline.[6−14] In fact, the dominant profile of aluminum is illustrated by the fact that the first structurally characterized five- and six-coordinate organometallic complexes of indium have been only very recently reported.[7]

Motivated by an interest in the effects of ligand geometry on the coordination environments of post-transition elements in general and of gallium and indium specifically, we began a systematic study of the use of bidentate, three-atom bridging ligands for organometallic gallium and indium compounds. This family of ligands has been important in preparing a wide variety of dinuclear transition-metal complexes, and a member of this class of ligands, the triazenide anion, has recently been used to stabilize unusual aluminum and indium alkyls.[4,7] In addition, modification of the organic substituents on these ligands should allow tuning of their steric bulk and, as a result, the aggregation of the product compounds. This note reports the ready reaction of gallium and indium trialkyl complexes with 2-(benzylamino)pyridine to eliminate alkane and yield stable monomeric five-coordinate organometallic Ga^{III} and In^{III} compounds of the general formula $M\{2\text{-}[N(CH_2C_6H_5)]NC_5H_4\}_2Me$ (M = Ga, In). An intermediate in the formation of the gallium complex, $Ga\{2\text{-}[N(CH_2C_6H_5)]NC_5H_4\}Me_2(OEt_2)$ has been characterized spectroscopically. Further reaction of the indium species with a third equivalent of amine yields a six-coordinate tris-ligand complex, $\{2\text{-}[N(CH_2C_6H_5)]NC_5H_4\}_3In$.

Reaction of an ether solution of $Ga(CH_3)_3$ or $In(CH_3)_3$ (prepared *in situ* from a stoichiometric reaction of MCl_3 and MeLi) with 2 equiv of 2-(benzylamino)pyridine afforded, after crystallization, the new species **1** and **2** (Scheme 1) in 70% and 73% yield, respectively. The ^1H NMR spectra for the two compounds are similar and consistent with a 2:1 ratio of bidentate ligand to CH_3 as well as a single environment for the amido ligands. For example, the benzylic protons (4.34 ppm, M = Ga; 4.15 ppm, M = In) and carbon atoms (48.7 ppm, M = Ga; 48.8 ppm, M = In) exhibit single resonance signals. Elemental analysis confirmed the formulas of these species to be $[M\{2\text{-}[N(CH_2C_6H_5)]NC_5H_4\}_2(CH_3)]_n$. On the basis of the ready solubility of both **1** and **2** in organic solvents, the comparable ionic radius of In(III) with those of the transition metals, and the ability of indium to accommodate 5- or 6-fold coordination, we could not rule out the possibility that these complexes may be dinuclear species.[15] A lantern-type arrangement with four bridging ligands was recently discovered in

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[1] For a summary of Ga and In organometallic chemistry see: Tuck, D. G. In *Comprehensive Organometallic Chemmistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Vol. 1, Chapter 7.

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[15] (a) Gerstner, F.; Weidlein, J. *Z. Naturforsch.* **1978**, *33B*, 24. (b) Hausen, H. D.; Gerstner, F.; Schwarz, W. *J. Organomet. Chem.* **1978**, *145*, 277.

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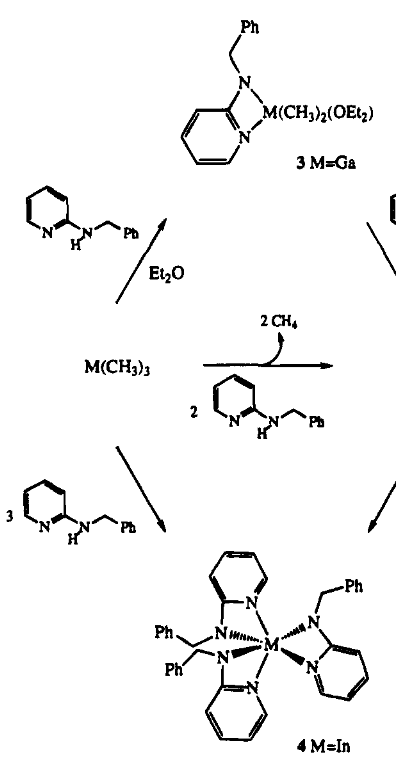
Scheme 1



our laboratory for the indium formamidinate complex $Cl_2In_2(CyNCHNCy)_4$ (Cy = cyclohexyl).[16]

The monomeric nature and the coordination geometries of the metal centers for both **1** and **2** were confirmed through single-crystal X-ray diffraction analyses. Complex **1** crystallized in the monoclinic space group *C*2/*c* ($a = 20.884(5)$ Å, $b = 9.335(4)$ Å, $c = 25.769(9)$ Å, $\beta = 103.32(4)°$) with one molecule of **1** and half of a solvent molecule (Et_2O) in the asymmetric unit. There are no anomalously short intermolecular contacts. The molecular geometry and atom-numbering scheme are shown in Figure 1. Complex **2** crystallized in the triclinic space group $P\bar{1}$ ($a = 10.475(4)$ Å, $b = 11.917(7)$ Å, $c = 9.683(5)$ Å, $\alpha = 97.16(5)°$, $\beta = 101.08(4)°$, $\gamma = 69.45(3)°$, $Z = 2$). The molecular geometry and atom-numbering scheme are shown in Figure 2.

In both cases the structural analysis revealed a molecular core with the metal center in an unusual distorted square-based pyramidal environment consisting of the four nitrogen atoms of the two 2-(benzylamino)pyridine anions with an apical methyl group completing the coordination sphere.[17] Within a given complex, the two nitrogen atoms of the pyridine rings as well as those of the amido groups are oriented in a trans configuration. Tables 1 and 2 present a summary of selected bond distances and angles for the two complexes. The principal structural parameter differences between **1** and **2**, including M−C and M−N distances and angles, are in accord with the increased ionic radius of indium with respect to that of gallium.

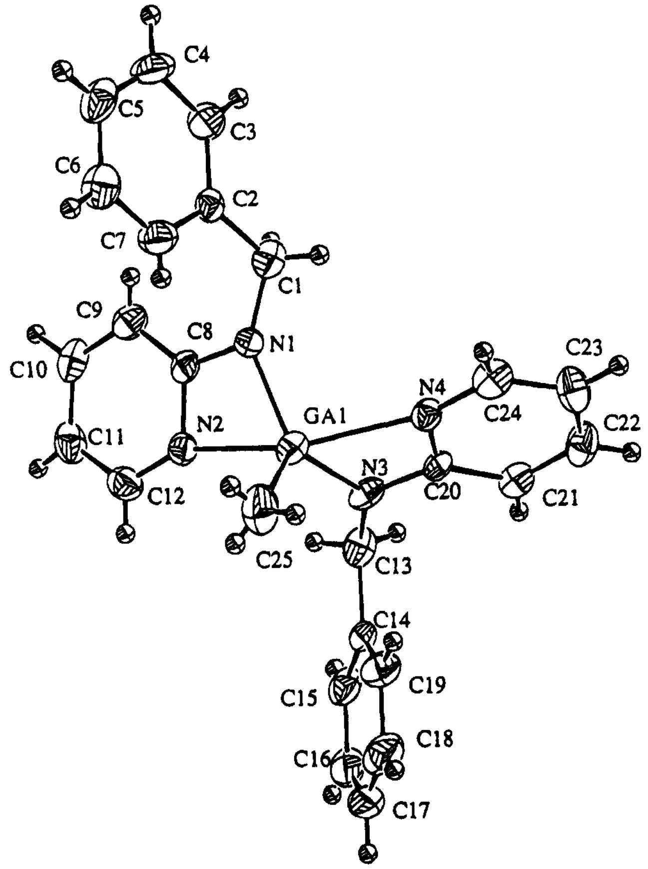


Figure 1. Molecular structure and atom-numbering scheme for $MeGa(C_6H_5CH_2NC_5H_4)_2$ (**1**). The solvent of crystallization has been omitted for clarity.

Table 1. Selected Atomic Bond Distances (in angstroms) for Compounds 1 and 2

compd 1		compd 2	
Ga1−N1	1.933(3)	In1−N1	2.146(2)
Ga1−N2	2.216(3)	In1−N2	2.349(3)
Ga1−N3	1.933(3)	In1−N3	2.169(2)
Ga1−N4	2.236(3)	In1−N4	2.341(3)
Ga1−C25	1.924(5)	In1−C25	2.158(3)
N1−C1	1.433(5)	N1−C1	1.443(4)
N1−C8	1.340(5)	N1−C8	1.343(4)
N2−C8	1.363(5)	N2−C8	1.365(4)
N2−C12	1.331(5)	N2−C12	1.338(4)
N3−C13	1.442(5)	N3−C13	1.434(4)
N3−C20	1.333(5)	N3−C20	1.340(4)
N4−C20	1.356(5)	N4−C20	1.365(4)
N4−C24	1.311(5)	N4−C24	1.335(4)
C1−C2	1.521(5)	C1−C2	1.499(5)
C8−C9	1.396(6)	C8−C9	1.416(4)

In both **1** and **2**, the metal center lies at the intersection of two planes; one contains the two pyridine nitrogens, the metal, and the methyl carbon with the other consisting of the two amido nitrogens, the metal center, and the methyl carbon. The planarity of these groups is confirmed by the fact that the sum of the appropriate angles is 360°. Both compounds display M−N(amido) distances that are slightly shorter than the M−N(Py) bond lengths, a feature consistent with the literature.[1,7,18,19] The $Ga-CH_3$ and $In-CH_3$ bond

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[16] Zhou, Y.; Richeson, D. S. Unpublished results.

[17] References 6, 7, 13, and 14 present crystal structures of five-coordinate gallium and indium complexes in distorted-trigonal-bipyramidal coordination environments. The values for the angle along the pseudo-axial vectors in these reports fall in the range 149.7−157.2°. In all cases the methyl group is in the equatorial plane.

[18] For a summary of Ga coordination chemistry see: Taylor, M. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987; Vol. 3, Chapter 25.1.

[19] For a summary of In coordination chemistry see: Tuck, D. G. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987; Vol. 3, Chapter 25.2.

Table 2. Selected Atomic Bond Angles (in Degrees) for Compounds 1 and 2

compd 1		compd 2	
N1−Ga1−N2	63.7(1)	N1−In1−N2	59.46(9)
N1−Ga1−N3	113.2(1)	N1−In1−N3	115.5(1)
N1−Ga1−N4	99.2(1)	N1−In1−N4	101.6(9)
N1−Ga1−C25	124.7(2)	N1−In1−C25	123.8(1)
N2−Ga1−N3	97.2(1)	N2−In1−N3	98.2(9)
N2−Ga1−N4	148.1(1)	N2−In1−N4	143.0(9)
N2−Ga1−C25	106.2(2)	N2−In1−C25	110.9(1)
N3−Ga1−N4	63.5(1)	N3−In1−N4	59.3(9)
N3−Ga1−C25	122.0(2)	N3−In1−C25	120.6(1)
N4−Ga1−C25	105.7(2)	N4−In1−C25	105.9(1)
Ga1−N1−C1	138.8(3)	In1−N1−C1	139.3(2)
Ga1−N1−C8	100.2(2)	In1−N1−C8	99.4(2)
C1−N1−C8	121.0(3)	C1−N1−C8	120.9(3)
Ga1−N2−C8	87.0(2)	In1−N2−C8	89.7(2)
Ga1−N2−C12	154.6(3)	In1−N2−C12	149.4(2)
C8−N2−C12	118.4(3)	C8−N2−C12	120.2(3)
Ga1−N3−C13	135.8(3)	In1−N3−C13	141.0(2)
Ga1−N3−C20	99.9(2)	In1−N3−C20	98.6(2)
C13−N3−C20	124.0(3)	C13−N3−C20	120.3(3)
Ga1−N4−C20	85.9(2)	In1−N4−C20	90.3(2)
Ga1−N4−C24	155.0(3)	In1−N4−C24	148.5(2)
C20−N4−C24	118.8(3)	C20−N4−C24	120.2(3)
N1−C1−C2	117.1(3)	N1−C1−C2	112.7(3)
N1−C8−N2	109.1(3)	N1−C8−N2	111.3(3)
N3−C20−N4	110.4(3)	N3−C20−N4	111.6(3)

lengths correlate with the few reported values for five-coordinate complexes.[7,13,14]

In an effort to isolate an intermediate in the formation of **1**, an ether solution of $Ga(CH_3)_3$ was mixed with 1 equiv of 2-(benzylamino)pyridine (Scheme 1). Various attempts were made to isolate the resulting material, but unfortunately, complex **3** proved to be too unstable and its identification relied on ^1H and ^{13}C NMR and subsequent reactivity. The molecular formula for **3**, $Me_2Ga\{2\text{-}[N(CH_2C_6H_5)]NC_5H_4\}(OEt_2)$, is confirmed by ^1H NMR and by the fact that reaction of **3** with a second equivalent of $2\text{-}[HN(CH_2C_6H_5)]NC_5H_4$ resulted in isolation of complex **1**. We feel confident in assigning a coordinated Et_2O molecule as part of the five-coordinate structure of **3** on the basis of NMR integrations and the characteristic upfield shift of coordinated versus free diethyl ether (free ether, 3.27 ppm (q, CH_2), 1.13 ppm (t, CH_3); coordinated ether in **3**, 2.97 ppm (q, CH_2), 0.77 ppm (t, CH_3)). In addition, the presence of the gallium methyl carbon signal at −6.1 ppm is consistent with what we observed for complex **1**.

On the basis of the observation that the 2-(benzylamino)pyridine anion led to the ready formation of five-coordinate complexes, we were interested in the possibility of generating six-coordinate tris-ligand compounds. The interaction of $In(CH_3)_3$ with 3 equiv of $2\text{-}[HN(CH_2C_6H_5)]NC_5H_4$ followed by crystallization from diethyl ether resulted in the isolation of the tris-ligand product $In\{2\text{-}[N(CH_2C_6H_5)]NC_5H_4\}_3$ (**4**) (Scheme 1). Microanalysis confirmed the stoichiometry of this product, and the spectroscopic parameters are consistent with the formulation of **4** as a six-coordinate complex. Alternatively, the same material can be prepared by the reaction of **2** with 2-(benzylamino)pyridine in a 1:1 mole ratio. Surprisingly, direct reaction of MCl_3 (M = Ga, In) with 1, 2, or 3 equiv of the lithium salt of the 2-(benzylamino)pyridine anion have, so far, led only to intractable mixtures.

The use of the 2-(benzylamino)pyridine anion as a ligand in the organometallic chemistry of gallium and indium leads to a family of five- and six-coordinate organometallic complexes of these metals. X-ray crystallographic studies and spectroscopic parameters confirm that these complexes represent examples of rather unusual five- and six-coordinate geomtries. Our continuing investigations are oriented at dissecting the steric and electronic features that influence the formation and reactivity of high-coordination-number organogallium and organoindium compounds.

Experimental Section

General Procedure. All reactions were carried out either in a nitrogen filled drybox or under nitrogen using standard Schlenk-line techniques. Diethyl ether, hexane, and benzene were distilled under nitrogen from potassium. Deuterated benzene was dried by vacuum transfer from potassium. 2-(Benzylamino)pyridine and MeLi (in diethyl ether) were purchased from Aldrich and used without further purification. $InCl_3$ and $GaCl_3$ (Aldrich) were sublimed prior to use.

Synthesis of $MeGa(C_6H_5CH_2NC_5H_4)_2$ (1). To a suspension of $GaCl_3$ (0.44 g, 2.50 mmol) in diethyl ether (30 mL) was added MeLi (5.4 mL, 1.4 M, 7.50 mmol) dropwise, and the mixture was then stirred for an additional 30 min. 2-(Benzylamino)pyridine (0.92 g, 5.00 mmol) was added, and the reaction mixture was stirred 24 h 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: yield 0.79 g, 70%, 1.75 mmol; mp (sealed) 84−86 C. Spectroscopic data: IR (Nujol, cm^{-1}) 1605 (s), 1487 (s); ^1H NMR (C_6D_6, ppm) 7.30−7.05 (m, 14H, C_6H_5, and NC_5H_4), 5.91 (m, 4H, NC_5H_4), 4.34 (s, 4H, CH_2), 3.27 (q, 2H, CH_2, ether of crystallization), 1.13 (t, 3H, CH_3, ether of crystallization), 0.42 (s, 3H, GaMe); ^{13}C NMR (C_6D_6, ppm) 165.9, 145.3, 141.6, 139.7, 128.7, 127.2, 126.7, 108.7, 104.2 (9 s, C_6H_5 and NC_5H_4), 65.9 (s, CH_2, ether of crystallization), 48.7 (s, CH_2), 15.6 (s, CH_3, ether of crystallization), −6.5 (s, $GaCH_3$). Elemental analysis was performed on a sample dried under vacuum. Anal. Calcd for $C_{25}H_{25}GaN_4$: C, 66.55; H, 5.58; N, 12.42. Found: C, 66.15; H, 5.72; N, 12.37.

Synthesis of $MeIn(C_6H_5CH_2NC_5H_4)_2$ (2). To a suspension of $InCl_3$ (0.71 g, 3.21 mmol) in diethyl ether (30 mL) was added MeLi (6.9 mL, 1.4 M, 9.63 mmol) dropwise, and the mixture was then stirred for an additional 20 min. 2-(Benzylamino)pyridine (1.18 g, 6.42 mmol) was added, and 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: yield 1.16 g, 73%, 2.34 mmol; mp (sealed) 119−121 °C. Spectroscopic data: IR (Nujol, cm^{-1}) 1604 (s), 1484 (s); ^1H NMR (C_6D_6, ppm) 7.18−6.85 (m, 14H, C_6H_5 and NC_5H_4), 5.85 (m, 4H, NC_5H_4), 4.15 (s, 4H, CH_2), 0.23 (s, 3H, $InCH_3$); ^{13}C NMR (C_6D_6, ppm) 165.4, 146.4, 141.8, 138.9, 128.5, 127.6, 126.9, 108.9, 105.0 (9 s, C_6H_5 and NC_5H_4), 48.8 (s, CH_2), −8.2 (s, $InCH_3$). Anal. Calcd for $C_{25}H_{25}InN_4$: C, 60.50; H, 5.18; N, 11.29. Found: C, 60.55; H, 5.16; N, 11.33.

Synthesis of $Me_2Ga(C_6H_5CH_2NC_5H_4)$ (3). To a suspension of $GaCl_3$ (0.68 g, 3.86 mmol) in diethyl ether (30 mL) was added MeLi (8.3 mL, 1.4 M, 11.58 mmol) dropwise, and the mixture was then stirred for an additional 30 min. 2-(Benzylamino)pyridine (0.71 g, 5.00 mmol) was added, and the reaction mixture was stirred 24 h and then filtered. The solution was removed under oil pump vacuum. The residue was dissolved in 10 mL of hexane/diethyl ether (9:1), and the solution was cooled to −30 °C. The resulting white crystalline solid was collected by filtration and dried under oil pump vacuum: yield 0.99 g, 73%, 2.82 mmol; mp (sealed) 78−80 °C. Spectroscopic data: IR (Nujol, cm^{-1}) 1606 (s), 1485 (s); ^1H NMR (C_6D_6, ppm) 7.55−6.05 (m, 9H, C_6H_5 and NC_5H_4), 4.69 (s, 2H, CH_2), 2.97 (q, 4H, CH_2, ether), 0.77 (t, 6H, CH_3, ether), −0.04 (s, 6H, GaMe); ^{13}C NMR (C_6D_6, ppm) 167.5, 146.0, 142.8, 137.9,

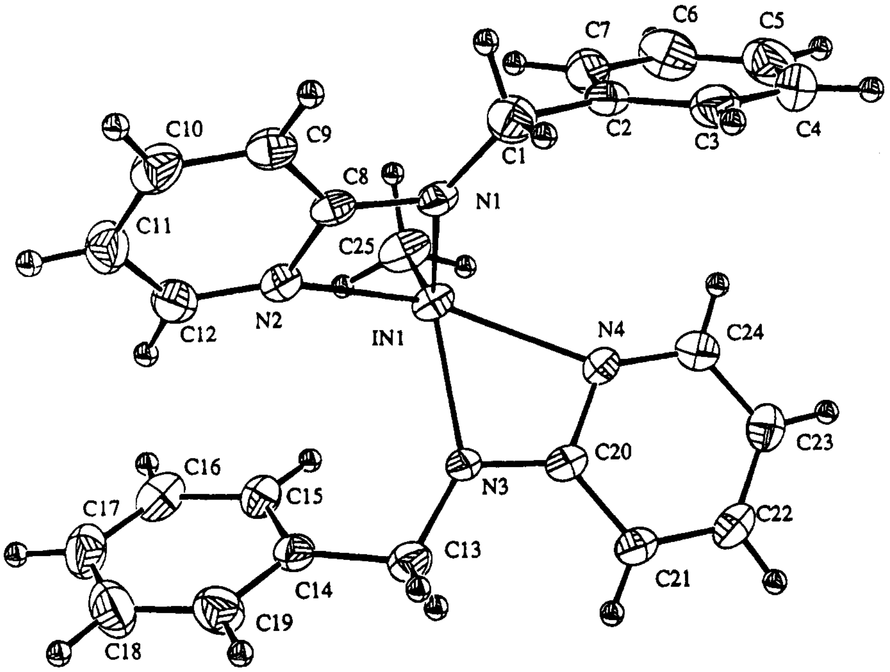

Figure 2. Molecular structure and atom-numbering scheme for $MeIn(C_6H_5CH_2NC_5H_4)_2$ (**2**).

128.3, 127.0, 126.2, 110.3, 108.3 (9 s, C_6H_5 and NC_5H_4), 65.9 (s, CH_2, ether), 51.5 (s, CH_2), 14.5 (s, CH_3, ether), −6.1 (s, $GaCH_3$).

Synthesis of $In(C_6H_5CH_2NC_5H_4)_3$ (4). To a suspension of $InCl_3$ (0.34 g, 1.54 mmol) in diethyl ether (25 mL) was added MeLi (3.3 mL, 1.4 M, 4.62 mmol) dropwise, and the mixture was then stirred for an additional 20 min. 2-(Benzylamino)pyridine (0.85 g, 4.62 mmol) was added, and the reaction mixture was stirred for 2 h and then filtered. The solution was concentrated to ca. 8 mL and cooled to −30 °C. The resulting crystalline solid was collected by filtration and dried under oil pump vacuum: yield 0.66 g, 65%, 1.00 mmol; mp (sealed) 98−100 °C. Spectroscopic data: IR (Nujol, cm^{-1}) 1602 (s), 1485 (s); ^1H NMR (C_6D_6, ppm) 7.21−6.93 (m, 21H, C_6H_5 and NC_5H_4), 5.93 (m, 6H, NC_5H_4), 4.23 (s, 6H, CH_2). Anal. Calcd for $C_{36}H_{33}InN_6$: C, 65.07; H, 5.01; N, 12.65. Found: C, 65.17; H, 5.25; N, 12.32.

X-ray Crystallography. Intensity data were collected on a Rigaku diffractometer at −153 °C using the $\omega-2\Theta$ scan technique to a maximum 2Θ value of 47° (complex **1**) and 50° (complex **2**) 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 3 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 structures were 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 case 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 F_c. All calculations were performed using the NRCVAX package. Details of the data collection and refinement and final atomic coordinates are reported in the supporting information.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada.

Supporting Information Available: Text giving a description of the structural solutions, tables of atomic positions, thermal parameters, crystallographic data, and bond distances and angles, and ORTEP drawings for compounds **1** and **2** (20 pages). Ordering information is given on any current masthead page.

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