Organometallics 1993, 12, 2986-2990

Five- and Six-Coordinate Organometallic Compounds of Indium

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Received January 19, 1993

The interaction of $InMe_3(3,5\text{-}Me_2py)$ (**1**) with 1 and 2 equiv of 1,3-diphenyltriazine (Hdpt) yields the five- and six-coordinate indium alkyls $InMe_2(dpt)(3,5\text{-}Me_2py)$ (**2**) and $InMe(dpt)_2(3,5\text{-}Me_2py)$ (**3**), respectively. Compound **3** may also be prepared in high yield directly from **2** by the reaction with Hdpt. The interaction of $InCl_2(dpt)(3,5\text{-}Me_2py)_2$ with 2 molar equiv of MeLi in hexane leads to the formation of **2** as the major product with **3** and **1** as minor products. Compound **3** undergoes ligand exchange upon thermolysis in solution to give $In(dpt)_3$ (**4**) and **2**. All compounds have been characterized by ^1H and ^{13}C NMR and IR spectroscopy, and the structures of **2**–**4** have been confirmed by X-ray crystallography. Compound **3** represents the first example of a monomeric six-coordinate alkylindium compound. Crystal data for **2**: monoclinic, $P2_1/c$, a = 9.475(3) Å, b = 11.135(2) Å, c = 19.814(4) Å, β = 101.92(2)°, Z = 4, R = 0.049, R_w = 0.059. Crystal data for **3**: monoclinic, $P2_1/c$, a = 9.932(3) Å, b = 17.027(5) Å, c = 18.436(5) Å, β = 94.94(2)°, Z = 4, R = 0.042, R_w = 0.067. Crystal data for **4**: orthorhombic, $Pna2_1$, a = 18.591(5) Å, b = 10.043(4) Å, c = 18.365(8) Å, Z = 4, R = 0.040, R_w = 0.054.

Introduction

Tetrahedral coordination has for many years dominated the organometallic chemistry of the group 13 metals aluminum, gallium, and indium.[1] While five-coordinate organometallic compounds were for many years limited to those using macrocyclic ligands,[2] the last few years has seen an increase in the number of all types of five-coordinate group 13 compounds.[3] By contrast, examples of six-coordinate organometallic compounds remain scarce; the first examples to be crystallographically characterized were cluster compounds isolated in this laboratory.[4] The first monomeric six-coordinate organoaluminum compound $AlMe(dpt)_2(3,5\text{-}Me_2py)$ (Hdpt = 1,3-diphenyltriazene) was prepared from the reaction of $AlMe_3$ with Hdpt in the presence of a large excess of 3,5-dimethylpyridine.[5] The possibility that the reactivity of six-coordinate group 13 alkyls would be different from that of the more usual four-coordinate geometry prompted further study of $AlMe(dpt)_2(3,5\text{-}Me_2py)$; however, this was hindered by the fact that it could only be isolated in low yield (<30%). Since the presence of a ligand exchange was found to account for the low yield[6] and we have observed that similar reactions are less accessible for the indium analogs,[7] we chose to concentrate on an investigation of the 1,3-diphenyltriazenide complexes of indium(III) as a route to easily accessible six-coordinate organometallic compounds.[8] We report herein the synthesis and structural characterization of the first monomeric six-coordinate alkylindium compound, as well as an unusual monomeric, five-coordinate alkylindium derivative.

Results and Discussion

The interaction of $InMe_3(3,5\text{-}Me_2py)$ (**1**) (prepared *in situ* from the addition of 3,5-Me_2py to $InMe_3$ in pentane) with 1 and 2 molar equiv of 1,3-diphenyltriazene yields the five- and six-coordinate indium alkyls $InMe_2(dpt)(3,5\text{-}Me_2py)$ (**2**) and $InMe(dpt)_2(3,5\text{-}Me_2py)$ (**3**), respectively. Compound **3** may also be prepared in high yield from **2** by the reaction with Hdpt (eq 1).

$$\underset{1}{\mathrm{InMe_3(3,5\text{-}Me_2py)}} \xrightarrow[-\mathrm{MeH}]{+\mathrm{Hdpt}} \underset{2}{\mathrm{InMe_2(dpt)(3,5\text{-}Me_2py)}} \xrightarrow[-\mathrm{MeH}]{+\mathrm{Hdpt}} \underset{3}{\mathrm{InMe(dpt)_2(3,5\text{-}Me_2py)}} \tag{1}$$

Compound **3** decomposes (eq 2) upon thermolysis via ligand redistribution to yield $In(dpt)_3$ (**4**) and **2** as the only isolable products. Compound **4** has previously been prepared from $InMe_3$.[9]

$$2\underset{3}{\mathrm{InMe(dpt)_2(3,5\text{-}Me_2py)}} \rightarrow \underset{2}{\mathrm{InMe_2(dpt)(3,5\text{-}Me_2py)}} + \underset{4}{\mathrm{In(dpt)_3}} + \mathrm{3,5\text{-}Me_2py} \tag{2}$$

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[1] For summaries see: (a) Eisch, J. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1983; Vol. 1, Chapter 6. (b) Tuck, D. G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1983; Vol. 1, Chapter 7.

[2] See: Oliver, J. P.; Kumar, R. *Polyhedron* **1990**, *9*, 409 and references therein.

[3] See for example: (a) Robinson, G. H.; Sangokoya, S. A. *J. Am. Chem. Soc.* **1987**, *109*, 6852. (b) Khan, M.; Steevensz, R. C.; Tuck, D. G.; Noltes, T. G.; Corfield, P. W. R. *Inorg. Chem.* **1980**, *19*, 3407. (c) Reger, D. L.; Knox, S. J.; Rheingold, A. L.; Haggerty, B. S. *Organometallics* **1990**, *9*, 2581.

[4] (a) Arif, A. M.; Barron, A. R. *Polyhedron* **1988**, *7*, 2091. (b) Healy, M. D.; Barron, A. R. *J. Am. Chem. Soc.* **1989**, *111*, 398.

[5] Leman, J. T.; Barron, A. R. *Organometallics* **1989**, *8*, 1828.

[6] Leman, J. T.; Braddock-Wilking, J.; Coolong, A. J.; Barron, A. R. *Inorg. Chem.*, in press.

[7] Leman, J. T.; Roman, H. A.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1992**, 2183.

[8] We note that related ligand-exchange reactions have been observed for four-coordinate indium compounds: Wells, R. L.; McPhail, A. T.; Jones, L. J.; Self, M. F. *Organometallics* **1992**, *11*, 2694.

[9] Leman, J. T.; Barron, A. R.; Ziller, J. W.; Kren, R. M. *Polyhedron* **1989**, *8*, 1909.

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A mixture of compounds **2** and **3** may also be formed by the interaction of $InCl_2(dpt)(3,5\text{-}Me_2py)_2$[7] with 2 molar equiv of MeLi (eq 3). Compounds **2** and **3** are readily separated by fractional crystallization.

$$InCl_2(dpt)(3,5\text{-}Me_2py)_2 \xrightarrow{+2MeLi} \underset{\mathbf{2}\ (60\%)}{InMe_2(dpt)(3,5\text{-}Me_2py)} + \underset{\mathbf{3}\ (12\%)}{InMe(dpt)_2(3,5\text{-}Me_2py)} \quad (3)$$

Although we have little direct evidence for the reaction pathway by which **3** forms during the reaction of $InCl_2(dpt)(3,5\text{-}Me_2py)_2$ with MeLi, we propose the following: Compound **3** is not formed by the same reaction pathway as **2**. Instead, monoalkylation of the dichloride complex may yield the chloro–methyl derivative whose Lewis acidity is expected to be reduced as compared to that of the dichloride, leading to the dissociation of one of the $3,5\text{-}Me_2py$ ligands and the formation of the five-coordinate complex $InCl(Me)(dpt)(3,5\text{-}Me_2py)$. This coordinately unsaturated compound may either react further with MeLi (to give **2**) or undergo ligand exchange to give the six-coordinate compound **3** and $InCl_2Me(3,5\text{-}Me_2py)$, the latter being alkylated (to give $InMe_3(3,5\text{-}Me_2py)$; see above) and removed during reaction workup. Supporting evidence for such a reaction scheme is obtained from the following: (i) Compound **3** does not form spontaneously upon the thermolysis of **2**. (ii) The addition of excess $3,5\text{-}Me_2py$ to **2** does not result in the formation of the bis-$3,5\text{-}Me_2py$ complex. Furthermore, there is no reaction between **2** and 2,2′-bipy, demonstrating the lack of affinity of **2** for an additional Lewis base, to become six-coordinate, i.e., $InMe_2(dpt)(bipy)$ [*cf.* $InCl_2(dpt)(bipy)$].[7] (iii) The five-coordinate triazenido compounds $Al(X)(dpt)_2$ (X = ^iBu, $OC_6H_2\text{-}2,6\text{-}^tBu_2\text{-}4\text{-}Me$) undergo a facile irreversible ligand exchange reaction (eq 4).[6] (iv) Resonances due to $InMe_3(3,5\text{-}Me_2py)$ (**1**) are observed in the ^1H NMR spectrum of the crude product mixture (prior to recrystallization) for the reaction between $InCl_2(dpt)(3,5\text{-}Me_2py)_2$ and MeLi.

$$Al(X)(dpt)_2 \rightarrow Al(dpt)_3 + AlX_2(dpt) \quad (4)$$

$$X = {}^iBu,\ OC_6H_2\text{-}2,6\text{-}{}^tBu_2\text{-}4\text{-}Me$$

Compounds **1**–**4** have been fully characterized (see Experimental Section); however, two points should be noted. The IR spectra of **2**–**4** show bands characteristic of a chelating triazenide group [1327, 1302, and 1280 cm^{-1} (**2**), 1331, 1305, and 1277 cm^{-1} (**3**), 1325, 1310, and 1280 cm^{-1} (**4**)]. The chelating coordination mode for all three compounds has been confirmed by X-ray crystallography. We have previously shown that the ^{13}C NMR shift of aluminum methyl groups may be directly correlated with the coordination geometry about the aluminum.[10] A similar linear correlation exists between the ^{13}C NMR shift of the indium methyl and the coordination number of compounds **1** (δ −7.1), **2** (δ −5.6), and **3** (δ −3.2).

Compound **3** represents the first monomeric six-coordinate organometallic indium compound to be structurally characterized, and its high-yield synthesis opens the door to further studies of the reactivity of high coordination number group 13 alkyls.

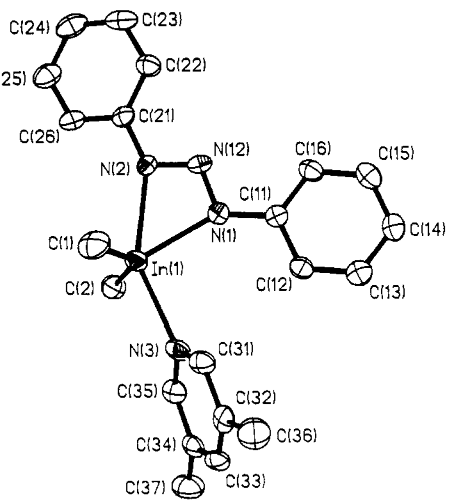

Figure 1. Molecular structure of $InMe_2(dpt)(3,5\text{-}Me_2py)$ (**2**). Thermal ellipsoids show 50% probability levels. Hydrogen atoms have been omitted for clarity.

Table I. Selected Bond Lengths (Å) and Angles (deg) in $InMe_2(dpt)(3,5\text{-}Me_2py)$ (2)

In(1)–C(1)	2.147(6)	In(1)–C(2)	2.153(6)
In(1)–N(1)	2.293(4)	In(1)–N(2)	2.430(4)
In(1)–N(3)	2.425(4)	N(1)–N(12)	1.324(5)
N(1)–C(11)	1.407(7)	N(2)–N(12)	1.292(6)
N(2)–C(21)	1.404(6)		
C(1)–In(1)–C(2)	137.1(2)	C(1)–In(1)–N(1)	110.1(2)
C(1)–In(1)–N(2)	96.3(2)	C(1)–In(1)–N(3)	94.4(2)
C(2)–In(1)–N(1)	110.2(2)	C(2)–In(1)–N(2)	95.5(2)
C(2)–In(1)–N(3)	95.7(2)	N(1)–In(1)–N(2)	53.9(1)
N(1)–In(1)–N(3)	95.8(1)	N(2)–In(1)–N(3)	149.7(1)
In(1)–N(1)–N(12)	100.8(3)	In(1)–N(1)–C(11)	145.4(3)
N(12)–N(1)–C(11)	113.8(4)	In(1)–N(2)–N(12)	95.2(3)
In(1)–N(2)–C(21)	149.6(4)	N(12)–N(2)–C(21)	115.0(4)
N(1)–N(12)–N(2)	110.1(4)		

X-ray Crystallography Studies. The molecular structure of **2** is shown in Figure 1; selected bond lengths and angles are given in Table I. The structure consists of discrete monomeric units with the indium atom in a distorted trigonal bipyramidal configuration. The equatorial plane is defined by N(1), C(1), and C(2) ($\sum$X–In–Y = 357.4°), and N(2) and N(3) occupy the pseudoaxial positions [N(2)–In(1)–N(3) = 149.7(1)°]. The axial In(1)–N bond distances are significantly longer than the equatorial one, as would be expected from a consideration of the relative In s and p character in the respective In–N bonds, i.e., five-coordinate axial (p) > five-coordinate equatorial (sp^2).[11] It is also worth noting that the axial In–N bond distances in **2** (Table I) are also significantly larger than those found for the mutually *trans* In–N distances in the six-coordinate compounds **3** and **4** [2.250(7)–2.360(8) Å] (vide infra). This may be due to the lower Lewis acidity of the indium center in **2**; alternatively, it may indicate that the In–N bonds in the six-coordinate compounds have significant s character.

The molecular structure of **3** is shown in Figure 2; selected bond lengths and angles are given in Table II. The structure consists of discrete monomeric units with the indium atoms in a highly distorted octahedral configuration [N(1)–In(1)–N(4) = 138.7(2)°, N(2)–In(1)–N(5) = 152.3(2)°, C(1)–In(1)–N(3) = 164.0(3)°]. The methyl

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[10] (a) Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1988**, 3047. (b) Wierda, D. A.; Barron, A. R. *Polyhedron* **1989**, *8*, 831.

[11] Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; Chapter 14, p 273.

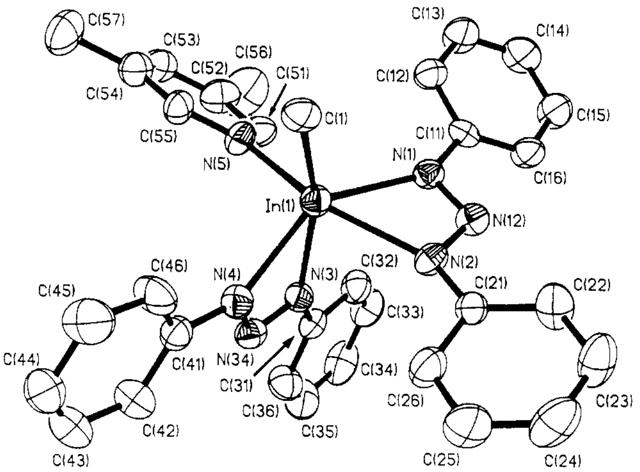

Figure 2. Molecular structure of InMe(dpt)$_2$(3,5-Me$_2$py) (**3**). Thermal ellipsoids show 40% probability levels. Hydrogen atoms have been omitted for clarity.

Table II. Selected Bond Lengths (Å) and Angles (deg) in InMe(dpt)$_2$(3,5-Me$_2$py) (3)

In(1)-C(1)	2.179(9)	In(1)-N(1)	3.204(6)
In(1)-N(2)	2.311(6)	In(1)-N(3)	2.428(7)
In(1)-N(4)	2.250(7)	In(1)-N(5)	2.351(7)
N(1)-N(12)	1.31(1)	N(1)-C(11)	1.41(1)
N(2)-N(12)	1.31(1)	N(2)-C(21)	1.36(1)
N(3)-N(34)	1.29(1)	N(3)-C(31)	1.42(1)
N(4)-N(34)	1.29(1)	N(4)-C(41)	1.41(1)
C(1)-In(1)-N(1)	105.8(3)	C(1)-In(1)-N(2)	101.4(3)
C(1)-In(1)-N(3)	164.0(3)	C(1)-In(1)-N(4)	111.1(3)
C(1)-In(1)-N(5)	95.3(3)	N(1)-In(1)-N(2)	55.2(2)
N(1)-In(1)-N(3)	90.2(2)	N(1)-In(1)-N(4)	138.7(2)
N(1)-In(1)-N(5)	99.2(2)	N(2)-In(1)-N(3)	87.5(2)
N(2)-In(1)-N(4)	98.9(2)	N(2)-In(1)-N(5)	152.3(2)
N(3)-In(1)-N(4)	53.8(2)	N(3)-In(1)-N(5)	82.0(2)
N(4)-In(1)-N(5)	95.3(2)	In(1)-N(1)-N(12)	98.0(5)
In(1)-N(1)-C(11)	146.7(5)	In(1)-N(2)-N(12)	97.8(5)
In(1)-N(2)-C(21)	144.1(5)	In(1)-N(3)-N(34)	93.7(5)
In(1)-N(3)-C(31)	149.9(6)	In(1)-N(4)-N(34)	102.4(5)
In(1)-N(4)-C(41)	139.7(6)	N(1)-N(12)-N(2)	108.9(6)
N(3)-N(34)-N(4)	110.2(7)		

and 3,5-Me$_2$py ligands are mutually *cis*, and the two triazenides act as bidentate chelating ligands, consistent with the IR spectra (vide supra). As was observed for the aluminum analog of **2**, the In–N distance *trans* to the methyl substituent [In(1)–N(3) = 2.428(7) Å] is significantly longer than those *cis* to the methyl [2.250(7)–2.351(7) Å]. The lengthening in the present compound is undoubtedly due to the large *trans* influence of the methyl group.[12] We have previously observed the larger *trans* influence of chloride versus a nitrogen donor ligand for six-coordinate indium complexes.[7]

The molecular structure of **4** is shown in Figure 3; selected bond lengths and angles are given in Table III. The indium is in a trigonally distorted octahedral coordination environment (N–In–N$_{av}$ = 148°), with the triazenido ligands in a pseudo-C_3 propeller arrangement. As a consequence of the increased radii of In^{3+} versus Al^{3+} (0.81 versus 0.51 Å), the trigonal distortion in **4** is significantly larger than that found in Al(dpt)$_3$ (N–Al–N$_{av}$ = 161°). The difference in calculated radii between Al^{3+} and In^{3+} (0.30 Å) is comparable to the difference in the average M–N distances (0.26 Å).

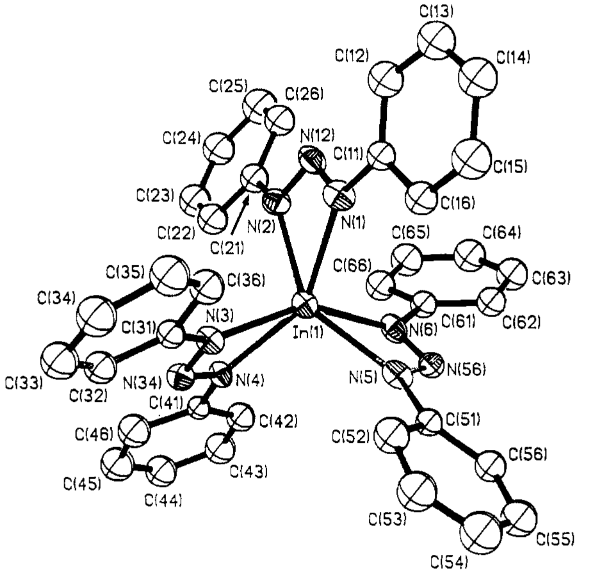

Figure 3. Molecular structure of In(dpt)$_3$ (**4**). Thermal ellipsoids show 30% probability levels. Hydrogen atoms have been omitted for clarity.

Table III. Selected Bond Lengths (Å) and Angles (deg) in In(dpt)$_3$ (4)

In(1)-N(1)	2.259(9)	In(1)-N(2)	2.26(1)
In(1)-N(3)	2.22(1)	In(1)-N(4)	2.231(9)
In(1)-N(5)	2.24(1)	In(1)-N(6)	2.21(1)
N(1)-N(12)	1.28(1)	N(1)-C(11)	1.39(1)
N(2)-N(12)	1.29(1)	N(2)-C(21)	1.41(1)
N(3)-N(34)	1.29(1)	N(3)-C(31)	1.41(1)
N(4)-N(34)	1.30(1)	N(4)-C(41)	1.41(1)
N(5)-N(56)	1.29(1)	N(5)-C(51)	1.37(1)
N(6)-N(56)	1.30(1)	N(6)-C(61)	1.41(1)
N(1)-In(1)-N(2)	55.2(4)	N(1)-In(1)-N(3)	105.6(4)
N(1)-In(1)-N(4)	148.9(4)	N(1)-In(1)-N(5)	102.0(3)
N(1)-In(1)-N(6)	99.7(4)	N(2)-In(1)-N(3)	107.8(4)
N(2)-In(1)-N(4)	102.9(4)	N(2)-In(1)-N(5)	144.1(4)
N(2)-In(1)-N(6)	97.2(4)	N(3)-In(1)-N(4)	56.5(3)
N(3)-In(1)-N(5)	105.0(4)	N(3)-In(1)-N(6)	151.5(4)
N(4)-In(1)-N(5)	107.1(3)	N(4)-In(1)-N(6)	105.4(3)
N(5)-In(1)-N(6)	56.3(4)	In(1)-N(1)-N(12)	97.9(7)
In(1)-N(1)-C(11)	143.6(9)	N(12)-N(1)-C(11)	118(1)
In(1)-N(2)-N(12)	97.4(7)	In(1)-N(2)-C(21)	140.7(8)
N(12)-N(2)-C(21)	118(1)	In(1)-N(3)-N(34)	97.6(7)
In(1)-N(3)-C(31)	145.9(8)	N(34)-N(3)-C(31)	116.5(9)
In(1)-N(4)-N(34)	97.2(6)	In(1)-N(4)-C(41)	143.2(8)
N(34)-N(4)-C(41)	119.5(9)	In(1)-N(5)-N(56)	97.0(8)
In(1)-N(5)-C(51)	145(1)	N(56)-N(5)-C(51)	117(1)
In(1)-N(6)-N(56)	98.3(8)	In(1)-N(6)-C(61)	141.4(9)
N(56)-N(6)-C(61)	117(1)	N(1)-N(12)-N(2)	109(1)
N(3)-N(34)-N(4)	108.8(9)	N(5)-N(56)-N(6)	108(1)

Experimental Section

Elemental analyses were performed by Oneida Research Services, Whitesborough, NY. Melting points were determined in sealed capillaries and are uncorrected. IR spectra (4000–400 cm^{-1}) were recorded on a Nicolet DX-5 FTIR spectrometer in KBr pellets. ^{1}H and ^{13}C NMR spectra, in C$_6$D$_6$, were recorded on Bruker AM-250 (^{1}H) and AM-500 (^{13}C) spectrometers, and chemical shifts are reported versus external SiMe$_4$. All manipulations were carried out under nitrogen. Solvents were dried, distilled, and degassed prior to use.

InMe$_3$, InCl$_3$ (Morton International), and MeLi (1.4 M solution in Et$_2$O, Aldrich) were used as supplied. The syntheses of Hdpt[13] and InCl$_2$(dpt)(3,5-Me$_2$py)$_2$[7] were carried out according to literature methods.

InMe$_3$(3,5-Me$_2$py) (1). A solution of InMe$_3$ (0.70 g, 4.40 mmol) in hexane (30 mL) was treated with 3,5-Me$_2$py (0.50 mL, 0.47 g, 4.40 mmol). After 1 h of stirring, the solvent was slowly removed

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[12] For a review of the theoretical treatments of the *trans* influence see: Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

[13] Hartman, W. W.; Dickey, J. B. *Org. Synth.* **1943**, *2*, 163.

Table IV. Summary of X-ray Diffraction Data

compd	$InMe_2(dpt)(3,5\text{-}Me_2py)$ (**2**)	$InMe(dpt)_2(3,5\text{-}Me_2py)$ (**3**)	$In(dpt)_3$ (**4**)
empir formula	$C_{21}H_{25}InN_4$	$C_{32}H_{32}InN_5$	$C_{36}H_{30}InN_9$
cryst size, mm	0.73 × 0.55 × 0.54	0.42 × 0.45 × 0.61	0.43 × 0.44 × 0.42
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_1/c$	$Pna2_1$
a, Å	9.475(3)	9.932(3)	18.591(5)
b, Å	11.135(2)	17.027(5)	10.043(4)
c, Å	19.814(4)	18.436(5)	18.365(8)
β, deg	101.92(2)	94.94(2)	
V, Å^3	2045.5(8)	3106(1)	3429(3)
Z	4	4	4
d(calcd), g cm^{-3}	1.136	1.346	1.363
abs coeff, mm^{-1}	6.125	0.793	0.728
λ(Mo Kα), Å (graphite monochromator)	0.710 73	0.710 73	0.710 73
temp, K	193	298	298
2θ range, deg	4.0–40.0	4.0–40.0	4.0–40.0
index range	$0 \le h \le 9, 0 \le k \le 10, -18 \le l \le 18$	$0 \le h \le 9, 0 \le k \le 16, -17 \le l \le 17$	$-17 \le h \le 17, -9 \le k \le 9, 0 \le l \le 17$
no. of rflns collected	2265	3355	6718
no. of ind rflns	1907	2876	1680
no. of obsd rflns ($F > 4.0\sigma(F)$)	1704	2234	1494
weight scheme	$w^{-1} = \sigma^2(\lvert F_o\rvert) + 0.0002(\lvert F_o\rvert)^2$	$w^{-1} = \sigma^2(\lvert F_o\rvert) + 0.0058(\lvert F_o\rvert)^2$	$w^{-1} = \sigma^2(\lvert F_o\rvert) + 0.014(\lvert F_o\rvert)^2$
final R, R_w	0.049, 0.059	0.042, 0.067	0.040, 0.054
largest diff peak, e Å^{-3}	0.42	0.56	0.44

Table V. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 $\times$ 10^{13}) for $InMe_2(dpt)(3,5\text{-}Me_2py)$ (2)

	x	y	z	U(eq)[a]
In(1)	8833(1)	872(1)	7097(1)	24(1)
C(1)	7831(6)	−824(5)	7212(3)	41(2)
C(2)	10069(6)	1651(5)	6410(3)	32(2)
N(1)	7811(4)	2354(4)	7641(2)	23(2)
N(12)	6642(4)	2597(4)	7168(2)	23(2)
N(2)	6621(4)	1950(4)	6625(2)	22(2)
C(11)	7927(6)	3031(4)	8250(3)	21(2)
C(12)	9173(6)	2899(5)	8760(3)	25(2)
C(13)	9338(6)	3521(5)	9375(3)	29(2)
C(14)	8290(6)	4297(5)	9497(3)	27(2)
C(15)	7052(6)	4451(5)	8988(3)	30(2)
C(16)	6870(6)	3821(5)	8371(3)	27(2)
C(21)	5414(6)	2125(4)	6088(3)	23(2)
C(22)	4139(6)	2660(5)	6165(3)	28(2)
C(23)	3020(6)	2797(5)	5596(3)	34(2)
C(24)	3167(6)	2413(5)	4952(3)	36(2)
C(25)	4424(6)	1865(5)	4870(3)	36(2)
C(26)	5537(6)	1717(5)	5441(3)	29(2)
N(3)	10873(4)	522(4)	8039(2)	25(2)
C(31)	10769(6)	−12(5)	8630(3)	27(2)
C(32)	11939(6)	−305(4)	9144(3)	26(2)
C(33)	13287(6)	−20(5)	9024(3)	27(2)
C(34)	13444(6)	532(5)	8429(3)	26(2)
C(35)	12202(6)	791(5)	7943(3)	26(2)
C(36)	11749(7)	−902(5)	9802(3)	41(2)
C(37)	14891(6)	878(6)	8289(3)	45(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

under vaccum until *ca.* 5 mL of solution remained. Cooling to −24 °C resulted in the crystallization of a colorless solid. Yield: 0.49 g, 1.84 mmol, 41%. Mp: 49–50 °C. Anal. Calcd for $C_{10}H_{18}InN$: C, 53.09; H, 7.96; N, 6.19. Found: C, 53.12; H, 7.99; N, 6.10. NMR (ppm): ^1H, 7.99 (2H, s, *o*-C*H*), 6.45 (1H, s, *p*-C*H*), 1.56 (6H, s, CH_3), 0.20 (9H, s, In–CH_3); ^{13}C, 146.1 (*o*-C*H*), 139.1 (*m*-CH), 134.1 (*p*-CH), 17.6 (CH_3), −7.1 (In-CH_3).

$InMe_2(dpt)(3,5\text{-}Me_2py)$ (2). $InMe_3$ (0.477 g, 2.98 mmol) was dissolved in pentane (20 mL), and 3,5-Me_2py (0.34 mL, 0.32 g, 2.98 mmol) was added via syringe. After the mixture was cooled to 0 °C in an ice bath, a solution of Hdpt (0.588 g, 2.98 mmol) in pentane/toluene (20 mL/5 mL) was added dropwise over 30 min. The ice bath was removed and the clear orange solution allowed to warm to room temperature. After 12 h of stirring, the solvent was removed in vacuo, to give an orange oil. Trituration with cold pentane (20 mL, −20 °C) gave an orange powder, which was filtered off, washed with pentane (20 mL), and dried under vacuum. Yield: 0.845 g, 1.87 mmol, 63%. Mp: 123–124 °C. Anal. Calcd for $C_{21}H_{25}InN_4$: C, 56.27; H, 5.62; N, 12.50. Found: C, 55.98; H, 5.56; N, 12.44. IR: 3000 (w), 1545 (s), 1480 (s), 1459 (m), 1327 (s), 1302 (s), 1280 (s), 1227 (s), 1142 (m), 1169 (m), 1072 (w), 1036 (w), 854 (m), 761 (s), 746 (w), 709 (m), 695 (s), 659 (m), 521 (m), 474 (w) cm^{-1}. NMR (ppm): ^1H, 7.97 (2H, s, *o*-C*H*), 7.38 [4H, d, J = 7.4 Hz, *o*-C*H*, Ph], 7.14 [4H, dd, J = 7.4 Hz, *m*-C*H*, Ph], 6.92 [2H, t, J = 7.4 Hz, *p*-C*H*, Ph], 6.50 (1H, s, *p*-C*H*), 1.56 (6H, s, CH_3), 0.33 (6H, s, In–CH_3); ^{13}C, 148.8 (*o*-CH), 146.2 (N–*C*, Ph), 139.3 (*p*-CH), 134.4 (*m*-CH), 129.1 (*m*-CH, Ph), 123.5 (*p*-CH, Ph), 119.4 (*o*-CH, Ph), 17.6 (CH_3), −5.6 (In-CH_3).

$InMe(dpt)_2(3,5\text{-}Me_2py)$ (3). Method 1. $InMe_3$ (0.49 g, 3.1 mmol) was dissolved in pentane (30 mL), and 3,5-Me_2py (0.35 mL, 0.33 g, 3.1 mmol) was added via syringe. After the mixture was cooled to 0 °C in an ice bath, a solution of Hdpt (1.209 g, 6.13 mmol) in pentane/toluene (30 mL/10 mL) was added dropwise over 30 min, and an orange precipitate formed within 5 min of adding the last of the reactants. The ice bath was removed, and the mixture was allowed to warm to room temperature. After 12 h of stirring, the flask was cooled to −24 °C, after which the solid was isolated and dried under vacuum. Yield: 1.55 g, 2.48 mmol, 80%.

Method 2. $InMe_2(dpt)(3,5\text{-}Me_2py)$ (0.931 g, 2.08 mmol) was dissolved in hexane (30 mL), and a solution of Hdpt (0.41 g, 2.08 mmol) in hexane (20 mL) added slowly from a dropping funnel. After addition was complete, the mixture was refluxed for 1 h. A fine pale yellow-orange precipitate formed during this time. Cooling to −24 °C gave further solid. Crystals suitable for X-ray crystallography were grown by slow solvent diffusion of a pentane overlayer into a solution of **3** in toluene. Yield: 0.75 g, 1.18 mmol, 57%. Mp: 169–170 °C. Anal. Calcd for $C_{32}H_{32}InN_7$: C, 61.06; H, 5.12; N, 15.58. Found: C, 60.59; H, 5.18; N, 15.06. IR: 1593 (s), 1482 (s), 1331 (m), 1305 (s), 1277 (s), 1229 (s), 1165 (w), 1146 (w), 763 (m), 694 (s), 659 (m), 517 (w) cm^{-1}. NMR (ppm): ^1H, 8.18 (2H, s, *o*-C*H*), 7.56 [8H, d, J = 7.5 Hz, *o*-C*H*, Ph], 7.10 [8H, dd, J = 8.0 Hz, *m*-C*H*, Ph], 6.87 [4H, t, J = 7.3 Hz, *p*-C*H*, Ph], 6.42 (1H, s, *p*-C*H*), 1.50 (6H, s, CH_3), 0.54 (3H, s, In–CH_3); ^{13}C, 149.5 (*o*-CH), 146.4 (N–*C*, Ph), 139.4 (*p*-CH), 134.3 (*m*-CH), 129.4 (*m*-CH, Ph), 124.2 (*p*-CH, Ph), 119.3 (*o*-CH, Ph), 17.6 (CH_3), −3.2 (In-CH_3).

Reaction of $InCl_2(dpt)(3,5\text{-}Me_2py)_2$ with MeLi. $InCl_2(dpt)(3,5\text{-}Me_2py)_2$ (5.00 g, 8.40 mmol) was suspended in hexane (150 mL), the mixture was cooled to −78 °C, and MeLi (12 mL, 1.4 M, Et_2O, 16.8 mmol) was added from a dropping funnel over a period of 30 min. The reaction mixture was stirred for 2 h at −78 °C, warmed to room temperature, and stirred for a further 2 h. During this time, the original orange slurry became a deep red solution with a white precipitate (LiCl). The deep red color faded to orange within 10 min after reaching room temperature. The reaction mixture was then refluxed to give a paler orange solution, which was filtered while hot. Approximately 20 mL of the solvent

Table VI. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å$^2 \times 10^3$) for InMe(dpt)$_2$(3,5-Me$_2$py) (3)

	x	*y*	*z*	*U*(eq)[a]
In(1)	2247(1)	1132(1)	3041(1)	54(1)
N(1)	1611(6)	518(4)	1951(3)	53(3)
N(2)	1598(6)	1773(4)	1962(3)	53(3)
N(12)	1318(7)	1150(4)	1559(4)	56(3)
N(3)	4558(7)	1219(4)	2712(4)	55(3)
N(4)	3832(7)	1982(4)	3501(4)	63(3)
N(34)	4866(7)	1793(4)	3158(4)	56(3)
N(5)	3130(7)	43(4)	3707(4)	62(3)
C(1)	418(9)	1220(5)	3508(5)	64(3)
C(11)	1403(8)	−205(5)	1577(5)	52(3)
C(12)	1259(9)	−860(6)	1987(5)	72(4)
C(13)	1004(11)	−1585(6)	1648(6)	87(5)
C(14)	938(10)	−1650(6)	917(6)	85(5)
C(15)	1100(12)	−982(6)	514(6)	91(5)
C(16)	1325(10)	−264(5)	822(5)	73(4)
C(21)	1208(9)	2479(5)	1666(4)	59(4)
C(22)	324(10)	2588(6)	1033(5)	80(4)
C(23)	−71(13)	3302(7)	767(6)	96(5)
C(24)	450(14)	3975(7)	1103(7)	109(6)
C(25)	1314(12)	3902(6)	1737(7)	94(5)
C(26)	1666(10)	3169(6)	2005(5)	76(4)
C(31)	5627(9)	921(5)	2324(4)	57(4)
C(32)	5339(10)	294(6)	1870(5)	70(4)
C(33)	6350(13)	−31(6)	1497(5)	84(5)
C(34)	7599(14)	278(9)	1520(6)	102(6)
C(35)	7859(11)	892(11)	1951(7)	108(6)
C(36)	6895(10)	1249(6)	2354(6)	81(4)
C(41)	4013(10)	2567(5)	4046(5)	59(3)
C(42)	5232(10)	2960(6)	4209(6)	80(4)
C(43)	5305(15)	3480(8)	4771(7)	112(6)
C(44)	4255(18)	3655(8)	5159(7)	118(7)
C(45)	3053(13)	3269(7)	4986(6)	102(5)
C(46)	2943(11)	2753(6)	4425(6)	85(4)
C(51)	3739(9)	−565(6)	3418(5)	68(4)
C(52)	4176(11)	−1205(6)	3803(7)	85(5)
C(53)	3999(10)	−1198(6)	4546(7)	82(5)
C(54)	3397(9)	−585(7)	4861(5)	72(4)
C(55)	2998(9)	30(5)	4414(5)	64(4)
C(56)	4797(16)	−1889(8)	3441(7)	156(8)
C(57)	3208(12)	−584(8)	5652(5)	108(6)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table VII. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å$^2 \times 10^3$) for In(dpt)$_3$ (4)

	x	*y*	*z*	*U*(eq)[a]
In(1)	6299(1)	675(1)	2104	51(1)
N(1)	5136(4)	40(11)	2020(7)	57(3)
N(2)	5903(6)	−1109(10)	1468(6)	57(4)
N(12)	5222(6)	−920(10)	1568(7)	61(4)
N(3)	6674(5)	−45(10)	3187(5)	49(3)
N(4)	7440(5)	146(9)	2345(5)	48(4)
N(34)	7344(6)	−210(9)	3020(5)	52(4)
N(5)	6200(4)	2888(10)	2225(7)	49(4)
N(6)	6349(5)	2084(12)	1181(6)	55(4)
N(56)	6223(5)	3176(12)	1539(7)	59(4)
C(11)	4438(6)	369(10)	2232(8)	62(4)
C(12)	3841(6)	−353(12)	2045(13)	78(4)
C(13)	3173(10)	86(17)	2273(11)	112(6)
C(14)	3091(10)	1195(17)	2646(10)	100(5)
C(15)	3679(7)	1930(18)	2845(10)	94(5)
C(16)	4363(7)	1533(13)	2636(8)	70(4)
C(21)	6125(6)	−1989(13)	913(7)	62(3)
C(22)	6835(8)	−2302(13)	860(8)	83(4)
C(23)	7088(9)	−3134(14)	326(9)	98(5)
C(24)	6624(9)	−3540(16)	−231(10)	95(5)
C(25)	5926(9)	−3218(16)	−195(11)	105(5)
C(26)	5660(8)	−2429(14)	374(8)	79(4)
C(31)	6470(6)	−403(11)	3901(7)	48(3)
C(32)	6938(8)	−901(12)	4400(8)	71(4)
C(33)	6682(8)	−1198(15)	5102(9)	86(4)
C(34)	5982(9)	−981(15)	5257(10)	92(5)
C(35)	5499(9)	−529(14)	4767(9)	86(5)
C(36)	5756(7)	−227(14)	4058(8)	75(4)
C(41)	8130(5)	30(9)	2029(7)	45(3)
C(42)	8288(8)	635(12)	1394(8)	71(4)
C(43)	8969(9)	550(13)	1087(10)	87(4)
C(44)	9496(9)	−138(15)	1427(10)	92(5)
C(45)	9364(9)	−721(14)	2094(16)	106(4)
C(46)	8668(7)	−661(13)	2381(8)	78(5)
C(51)	6143(7)	3933(13)	2709(8)	51(4)
C(52)	6101(7)	3652(16)	3418(9)	74(4)
C(53)	6064(9)	4623(15)	3972(11)	94(5)
C(54)	6100(10)	5925(20)	3762(12)	108(6)
C(55)	6147(7)	6245(18)	3052(9)	80(4)
C(56)	6189(7)	5276(13)	2525(9)	66(4)
C(61)	6288(6)	2130(14)	413(8)	62(4)
C(62)	5920(7)	3158(13)	40(8)	70(4)
C(63)	5853(8)	3000(16)	−718(9)	87(4)
C(64)	6135(8)	1989(18)	−1075(11)	104(5)
C(65)	6498(9)	1038(17)	−724(10)	100(5)
C(66)	6588(8)	1081(14)	42(8)	75(4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

was removed (under vaccum) from the filtrate, and the solution was cooled to −24 °C, whereupon a small quantity of fine pale yellow-orange crystals of **3** was deposited. These were isolated by removing the solvent via cannula (see below), washing with pentane (10 mL), and vacuum-drying. Yield: 0.64 g, 1.00 mmol, 12%. The supernatant above was reduced in volume by 80 mL under vacuum until crystallization was imminent. Cooling to −25 °C gave bright orange needles of **2**. Crystals suitable for X-ray crystallography were grown from hexane. Yield: 2.2 g, 5.04 mmol, 60%.

X-ray Crystallographic Studies. A crystal data summary is given in Table IV; fractional atomic coordinates are listed in Tables V–VII.

Crystals of **2** and **4** were mounted directly onto a fiber which was mounted on the goniometer *via* a glass pin with silicone grease. A crystal of **3** was mounted in a sealed glass capillary which was mounted onto the goniometer. Unit-cell parameters and intensity data were obtained by following previously detailed procedures,[14] using a Nicolet R3m/V diffractometer operating in either the 2θ–θ (**2**) or ω (**3** and **4**) scan mode. Data collection was controlled by using the Nicolet P3 program.[15] Empirical absorption corrections were applied to the data for compound **2** using the program PSICOR. Further experimental data are given in Table IV. The structures were solved using the direct-methods program XS, which in each case revealed the positions of most of the heavy atoms. Not all of the hydrogen atoms were visible in the final difference maps, and all hydrogens were therefore included as fixed-atom contributors in the final cycles: d(C–H) = 0.96 Å and U(iso) = 0.08 Å.^{2} All non-hydrogen atoms (except the phenyl carbons in **4**) were refined anisotropically. Details of the refinement are given in Table IV. Atomic scattering factors and anomalous scattering factors were as given in the literature.[16]

Acknowledgment. Financial support of this work is provided in part by the National Science Foundation and the donors of the Petroleum Research Fund (administered by the American Chemical Society). We acknowledge Morton International for the generous gifts of InMe$_3$ and InCl$_3$.

Supplementary Material Available: Tables of bond lengths and angles and anisotropic thermal parameters (11 pages). Ordering information is given on any current masthead page.

OM930031L

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