

nors (i.e., phosphites) which do not react with $[\text{HB}(\text{pz})_3](\text{CO})_2\text{W}\equiv\text{C}-\text{SMe}$.

Acknowledgment. We appreciate the support of this work by the National Science Foundation (Grant No. CHE-8719744).

Registry No. 1, 121866-67-9; 2-BF₄, 121866-90-8; 2-PF₆,

121866-69-1; 3-2BF₄, 121866-71-5; 4-BF₄, 121866-73-7; 5-BF₄, 121866-75-9; 6-BF₄, 121866-77-1; 7-BF₄, 121866-81-7; 9-2BF₄, 121866-96-4; 10-2BF₄, 121866-98-6; 11-2BF₄, 121867-00-3; 12-BF₄, 121866-83-9; 13-BF₄, 121866-85-1; 14-BF₄, 121866-87-3; 15-BF₄, 121866-89-5; Bu₄N[IW(CO)₄(CS)], 56031-00-6; {[HC(pz)₃(CO)P-(O-*i*-Pr)₃W[C(O)CSMe]}BF₄, 121866-92-0; {[HC(pz)₃(CO)-(PPh₂Me)W[C(O)CSMe]}BF₄, 121866-94-2.

Mesitylindium(III) Compounds. X-ray Crystal Structures of InMes₃, [NMe₄][InClMes₃], and [InClMes₂]₂

John T. Leman and Andrew R. Barron*

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

Received March 17, 1989

The reaction of InCl₃ with 3 equiv of MesMgBr (Mes = mesityl, 2,4,6-Me₃C₆H₂) yields InMes₃ (1). The molecular structure of 1 consists of discrete monomeric units in which the three mesityl groups are crystallographically inequivalent. The possibility of an agostic C-H→In interaction is discussed. The addition of 1 equiv of Me₄NCl to 1 results in the formation of [Me₄N][InClMes₃] (2). The compounds InClMes₂ (3) and InCl₂Mes (4) were prepared from InMes₃ by means of exchange reactions with InCl₃. The reaction of InMes₃ with 2 equiv of Me₃NHCl yields InCl₂Mes(NMe₃) (5), which slowly redistributes to give a mixture of 4 and InCl₂Mes(NMe₃)₂ (6). The structures of 1, 2, and 3 have been confirmed by X-ray crystallography. InMes₃: monoclinic *P*2₁/*n*, *a* = 8.704 (2) Å, *b* = 21.888 (6) Å, *c* = 12.492 (4) Å, β = 95.06 (2)°, *Z* = 4, observed data 2542, *R* = 0.0348, *R*_w = 0.0391. [Me₄N][InClMes₃]-MeCN: monoclinic *P*2₁/*n*, *a* = 16.938 (5) Å, *b* = 9.154 (5) Å, *c* = 20.895 (5) Å, β = 94.49 (2)°, *Z* = 4, observed data 3400, *R* = 0.0783, *R*_w = 0.1040. [InClMes₂]₂: monoclinic, *P*2₁/*a*, *a* = 9.113 (2) Å, *b* = 16.083 (4) Å, *c* = 12.360 (3) Å, β = 109.90 (2)°, *Z* = 2, observed data 1824, *R* = 0.0449, *R*_w = 0.0658.

Introduction

Notwithstanding the renewed interest in the chemistry of the heavier group 13 (Ölander numbering) elements aluminum, gallium, and indium, the relative importance of steric and electronic effects in determining the structure and reactivity of their compounds is still poorly understood. A study of phosphine adducts of trimethylaluminum showed that the steric bulk of the phosphine predominates in defining the geometry around both aluminum and phosphorus,^{1,2} while the presence of π-bonding between aluminum and oxygen accounts for the short Al-O distances and large Al-O-C angles in monomeric four-coordinate aluminum alkoxide compounds.³

The use of sterically demanding ligands should increase the steric control over the structure of group 13 compounds. The compounds AlMes₃^{4a} and GaMes₃^{4b} (Mes = mesityl; 2,4,6-Me₃C₆H₂) were found to be monomeric, and their low Lewis acidities were proposed to be due to the steric bulk of the mesityl ligands. We report here that electronic effects, however, appear to influence the structure of the indium analogue InMes₃, whereas steric factors dominate the structures of [Me₄N][InClMes₃] and [InClMes₂]₂.

Table I. Selected Bond Lengths (Å) and Bond Angles (deg) in InMes₃

In-C(11)	2.170 (5)	In-C(21)	2.163 (5)
In-C(31)	2.170 (5)		
C(11)-In-C(21)	116.8 (2)	C(11)-In-C(31)	122.3 (2)
C(21)-In-C(31)	120.8 (2)	In-C(11)-C(12)	120.8 (3)
In-C(11)-C(16)	120.8 (3)	In-C(21)-C(22)	121.6 (3)
In-C(21)-C(26)	120.2 (4)	In-C(31)-C(32)	120.6 (4)
In-C(31)-C(36)	120.6 (3)		

Table II. Selected Intramolecular Nonbonded Distances (Å) in InMes₃

In...C(17)	3.340 (5)	In...C(19)	3.348 (5)
In...C(27)	3.338 (6)	In...C(29)	3.297 (6)
In...C(37)	3.363 (6)	In...C(39)	3.363 (6)
C(17)...C(27)	4.825 (8)	C(17)...C(37)	5.278 (8)
C(17)...C(39)	3.810 (8)	C(19)...C(27)	4.850 (8)
C(19)...C(29)	3.983 (8)	C(19)...C(39)	5.057 (9)
C(27)...C(37)	4.182 (9)	C(29)...C(37)	4.528 (8)
C(29)...C(39)	5.096 (8)		

Results and Discussion

The interaction of InCl₃ with 3 equiv of MesMgBr in Et₂O allows the formation of InMes₃ (1), the structure of which has been confirmed by X-ray crystallography (see below). Compound 1 is a colorless, crystalline solid that can be handled in air for several minutes without appreciable decomposition. InMes₃ is soluble in both Et₂O and THF, but it does not form a stable (i.e. isolable) adduct with either donor.

The molecular structure of InMes₃ is shown in Figure 1; selected bond lengths and angles are given in Table I.

(1) Barron, A. R. *J. Chem. Soc., Dalton Trans.* 1988, 3047.

(2) Wierda, D. A.; Barron, A. R. *Polyhedron* 1989, 8, 831.

(3) Healy, M. D.; Wierda, D. A.; Barron, A. R. *Organometallics* 1988, 7, 2543.

(4) (a) Jerius, J. J.; Hahn, J. M.; Rahman, A. F. M.; Mols, O.; Ilsley, W. H.; Oliver, J. P. *Organometallics* 1986, 5, 1812. (b) Beachley, O. T., Jr.; Churchill, M. R.; Pazik, J. C.; Ziller, J. W. *Organometallics* 1986, 5, 1814.

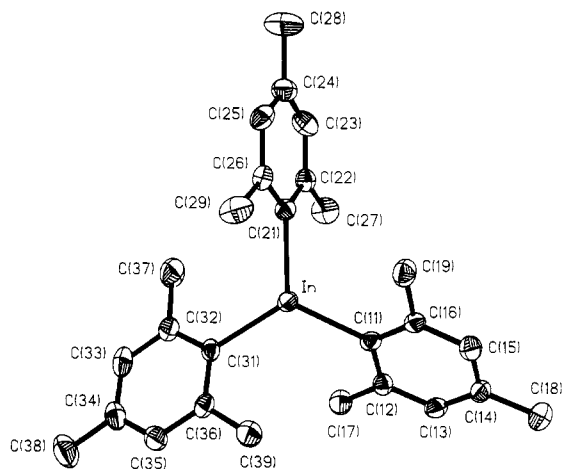


Figure 1. The structure of InMe_3 (1) viewed approximately perpendicular to the InC_3 -core plane. Thermal ellipsoids are drawn at the 50% level, and hydrogens are omitted for clarity.

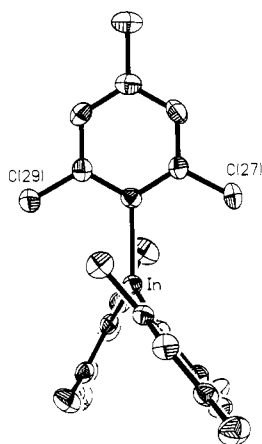


Figure 2. InMe_3 viewed perpendicular to ring 2 [C(21)–C(26)] showing the position of the ortho methyl groups on either side of the InC_3 -core plane.

The structure consists of discrete monomeric units, and there are no abnormally close intermolecular contacts. The In–C distances [2.163 (5)–2.170 (5) Å] are within the range reported for terminal In–C distances [2.093 (6)–2.26 (2) Å],⁵ and are within experimental error of those reported for InPh_3 [2.111 (14)–2.155 (14) Å].⁶ The geometry around the indium in 1 is planar, with the sum of the interligand angles (C–In–C) = 360.0 (2)°, a similar geometry is found in InPh_3 .⁶ Whereas the mesityl groups in AlMe_3 and GaMe_3 are arranged in a “propeller”-like fashion⁴ with each ring related by a crystallographic C_3 axis, the three rings in InMe_3 are inequivalent crystallographically with each mesityl ring angled differently with respect to the InC_3 -core plane: ring 1, [C(11)–C(16)] = 43.1°, ring 2, [C(21)–C(26)] = 70.2°; and ring 3, [C(31)–C(36)] = 33.6°. When compared to the angle observed in AlMe_3 and GaMe_3 (56°), it is clear that ring 2 is twisted away from and ring 1 and ring 3 are twisted in the direction of the InC_3 plane. This results in ring 2 being nearly perpendicular to the InC_3 plane as can be clearly seen in Figure 2.

As a consequence of this conformation, there is a wide range in the intramolecular C...C distances (see Table II) between adjacent ortho methyl groups in InMe_3 . It is particularly noteworthy that three of these C...C distances

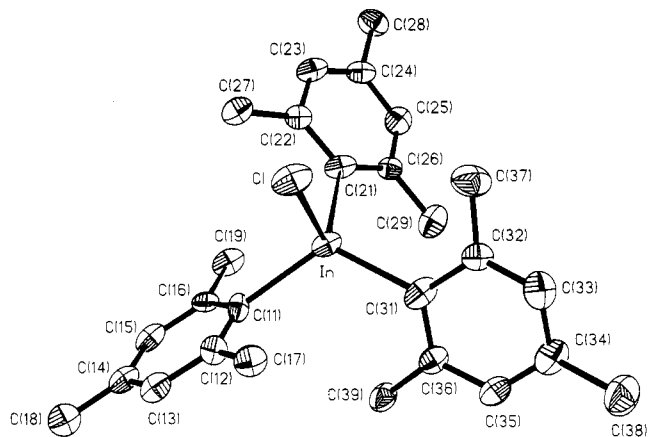


Figure 3. The structure of the $[\text{InClMe}_3]^-$ anion in 2. Thermal ellipsoids are drawn at the 50% level, and hydrogen atoms are omitted for clarity.

[C(19)–C(29) = 3.983 (8) Å, C(27)–C(37) = 4.182 (9) Å, C(17)–C(39) = 3.810 (8) Å] are shorter or close to the sum of the methyl group van der Waals radii (4.0 Å).⁷ In contrast, AlMe_3 and GaMe_3 do not have close ortho methyl contacts. Thus it is clear that the structure found in InMe_3 is sterically unfavorable as compared to a C_3 geometry. The distortions from a C_3 geometry can be accounted for by noting that an increase in the In–C distance, over the M–C distances in the related aluminum and gallium mesityl derivatives [Al–C = 1.995 (8) Å, Ga–C = 1.968 (4) Å],⁴ allows the rings to adopt a new conformation, the driving force for which could be either steric (crystal packing forces) or electronic. The latter may possibly be an agostic interaction (see below) involving the vacant In 5p orbital, in that the ortho methyl groups on ring 2 are located above and below the InC_3 plane which positions them favorably for such an interaction.

Unfortunately, the ortho methyl hydrogen atoms could not be located in the final difference map (see Experimental Section), thus precluding a crystallographic confirmation of the C–H...In interaction. It is interesting to note, however, that the In...C(27) and In...C(29) distances, 3.338 (6) and 3.297 (6) Å, respectively, are significantly shorter than those for the intertetrameric bridge bond found in InMe_3 (3.59 Å).⁸ Although all the intramolecular distances between In and the ortho methyl groups (Table II) are within the sum of the van der Waals radii (3.6 Å),^{7,9} only C(27) and C(29) are positioned suitably for any possible interaction.

The ^1H and ^{13}C NMR shift and coupling constant $J(^{13}\text{C}-^1\text{H})$ are often characteristic of agostic interactions.¹⁰ In the present case the mesityl hydrogens are equivalent on the ^1H NMR time scale even at –90 °C, although broadening of the ortho methyl resonance is observed. In the low-temperature ^{13}C NMR, however, two resonances for the ortho methyl carbons are observed [27.1 ($J(^{13}\text{C}-^1\text{H})$) = 102.0 Hz), 25.1 ppm ($J(^{13}\text{C}-^1\text{H})$) = 124.0 Hz)]. The $J(^{13}\text{C}-^1\text{H})$ coupling constant for the more downfield of the two resonances is in the region previously observed for species containing a C–H...M interaction.¹⁰ The two lines broaden and merge to a single line at room temperature. In addition the IR spectrum contains a band at 2710 cm^{-1}

(7) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960; Chapter 7.

(8) Carty, A. J.; Gynane, M. J. S.; Lappert, M. F.; Miles, S. J.; Singh, A.; Taylor, N. J. *Inorg. Chem.* 1980, 19, 3637.

(9) Amma, E. L.; Rundle, R. E. *J. Am. Chem. Soc.* 1958, 80, 4141.

(10) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* 1983, 250, 395.

(5) Tuck, D. G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 1, Chapter 7.

(6) Malone, J. F.; McDonald, W. S. *J. Chem. Soc. A* 1970, 3362.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) in $[\text{Me}_4\text{N}][\text{InClMes}_2] \cdot \text{MeCN}$

In-C	2.540 (3)	In-C(11)	2.239 (11)
In-C(21)	2.236 (11)	In-C(31)	2.209 (12)
Cl-In-C(11)	98.6 (3)	Cl-In-C(21)	105.5 (3)
C(11)-In-C(21)	118.2 (4)	Cl-In-C(31)	102.3 (3)
In-C(11)-C(12)	120.8 (8)	In-C(11)-C(16)	119.9 (8)
In-C(21)-C(22)	120.1 (8)	In-C(21)-C(16)	121.1 (8)
In-C(31)-C(32)	121.7 (8)	In-C(31)-C(36)	122.2 (9)

Table IV. Selected Intramolecular Nonbonded Distances (Å) in $[\text{Me}_4\text{N}][\text{InClMes}_2] \cdot \text{MeCN}$

In...C(17)	3.371 (12)	In...C(19)	3.421 (13)
In...C(27)	3.430 (13)	In...C(29)	3.439 (14)
In...C(37)	3.410 (16)	In...C(39)	3.404 (13)
Cl...C(17)	3.509 (14)	Cl...C(27)	3.461 (13)
Cl...C(37)	3.522 (16)	C(17)...C(27)	5.743 (18)
C(17)...C(37)	5.485 (18)	C(17)...C(39)	3.797 (20)
C(19)...C(27)	3.720 (19)	C(19)...C(29)	4.628 (20)
C(19)...C(39)	4.838 (18)	C(27)...C(37)	5.413 (18)
C(29)...C(37)	4.045 (20)	C(29)...C(39)	4.319 (20)

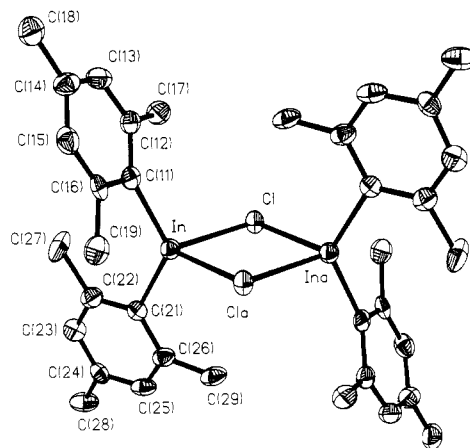
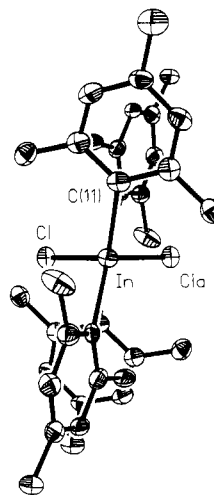
which may be associated with an agostic C-H bond.¹⁰

The spectroscopic evidence is therefore supportive of a C-H...In interaction in solution; despite this it is not possible to exclude the possibility that the distortions present in the solid state are due to crystal packing forces.

Addition of 1 equiv of Me_4NCl to an CH_2Cl_2 solution of 1 yields the ionic complex $[\text{Me}_4\text{N}][\text{InClMes}_2]$ (2), the structure of which has been confirmed by X-ray crystallography. Compound 2 is insoluble in nonpolar organic solvents but is soluble in and can be recrystallized from MeCN. The reaction of 1 and Me_4NCl in 2:1 molar ratio does not yield the chloride-bridged dimer $[\text{R}_3\text{MClMR}_3]$, found for GaMe_3 ,¹¹ but instead gives a mixture of 1 and 2.

The structure of the complex anion of 2 is shown in Figure 3; selected bond lengths and angles are given in Table III. The structure consists of discrete monomeric units with one molecule of acetonitrile per indium present in the crystal lattice. The geometry around indium is distorted tetrahedral, with the angles associated with the chloride being the most acute. The In-C bonds in 2 [2.209 (12)–2.239 (11) Å] are longer than those found for 1 [2.163 (5)–2.170 (5) Å]. This change is in the direction predicted on the basis of increased p character in the In-C bonds on changing from a planar to tetrahedral geometry. The three mesityl rings are arranged in a propeller-like fashion with the plane of the mesityl rings pitched with respect to the In-Cl vector: ring 1, [C(11)–C(16)] = 52.9°; ring 2, [C(21)–C(26)] = 42.6°; ring 3, [C(31)–C(26)] = 51.0°. The intramolecular C...C distances between adjacent ortho methyl groups (see Table IV) are divided into three groups: those between the methyls below the C_3 plane, C(19), C(29), and C(39), 4.319 (20)–4.838 (18) Å; those between the methyls above the C_3 plane, C(17), C(27), and C(37), 5.413 (19)–5.743 (18) Å; and those between the methyl above and below the plane, 3.720 (19)–4.045 (20) Å.

The In-Cl bond [2.540 (3) Å] is long compared to other terminal In-Cl bond lengths reported for MeInCl_2 [2.384 (1) Å],¹² $[\text{MeInCl}_3]^-$ [2.394 (3), 2.397 (4), and 2.409 (3) Å],¹³ and $[\text{In}(\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2))_2\text{Cl}]$ [2.465 (1) Å].¹⁴ The longer In-Cl bond found in 2 as compared to the MeInCl_3^- anion

**Figure 4.** The structure of $[\text{InClMes}_2]_2$ (3). Thermal ellipsoids are drawn at the 50% level, and hydrogen atoms are omitted for clarity.**Figure 5.** $[\text{InClMes}_2]_2$ viewed along the In...In(a) vector.**Table V. Selected Bond Lengths (Å) and Bond Angles (deg) in $[\text{InClMes}_2]_2$**

In-C	2.585 (3)	In-C(11)	2.146 (9)
In-C(21)	2.174 (10)	In-Cl(a)	2.584 (3)
Cl-In(a)	2.584 (3)		
Cl-In-C(11)	112.3 (3)	Cl-In-C(21)	101.8 (3)
C(11)-In-Cl(a)	101.3 (3)	C(21)-In-Cl(a)	117.0 (2)
In-Cl-In(a)	96.5 (1)	In-C(11)-C(12)	124.7 (7)
In-C(11)-C(16)	116.9 (6)	In-C(21)-C(22)	116.7 (6)
In-C(21)-C(26)	122.8 (8)		

Table VI. Selected Intramolecular Nonbonded Distances (Å) in $[\text{InClMes}_2]_2$

In...C(17)	3.470 (10)	In...C(19)	3.181 (9)
In...C(27)	3.269 (9)	In...C(29)	3.419 (9)
Cl...C(17)	3.636 (10)	Cl...C(29)	5.557 (9)
Cl...C(29)	3.980 (10)	Cl(a)...C(29)	3.591 (10)
C(27)...C(17)	4.237 (18)	C(27)...C(19)	4.561 (17)

suggests that the lengthening is presumably not due to electronic effects but due to steric interaction between the chloride and the ortho methyl groups; $\text{Cl}\cdots\text{C}_{\text{av}} = 3.5$ Å as compared to the sum of the van der Waals radii 3.8 Å.⁷

Although compound 2 is not the first example of a $[\text{R}_3\text{MX}]^-$ anion (M = Ga, In; X = halide) to be reported,⁵ it is the first to be crystallographically characterized.

The reaction of InMes_3 with InCl_3 in a 2:1 molar ratio yields InClMes_2 (3). Compound 3 is a colorless, crystalline solid that is soluble in nonpolar organic solvents in which its existence as a dimer has been shown by molecular

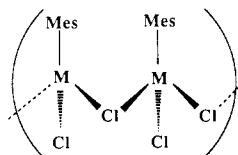
(11) Wilson, I. L.; Dehnicke, K. *J. Organomet. Chem.* 1974, 67, 229.(12) Mertz, K.; Schwartz, W.; Zettler, F.; Hausen, H. D. *Z. Naturforsch. B* 1975, 30, 159.(13) Guder, H. J.; Schwartz, W.; Weidlein, J.; Widler, H. J.; Hausen, H. D. *Z. Naturforsch. B* 1976, 31, 1185.(14) Hausen, H. D.; Mertz, K.; Weidlein, J.; Schwartz, W. *J. Organomet. Chem.* 1975, 93, 291.

weight determination. The dimeric nature of **3** in the solid state has been confirmed by X-ray crystallography.

The molecular structure of InClMes_2 is shown in Figure 4; selected bond lengths and angles are given in Table V. The structure consists of a centrosymmetric dimer with two bridging chloride ligands. The In–C distances [2.146 (9) and 2.174 (10) Å] are within the range reported for terminal In–C bonds [2.093 (6)–2.26 (2) Å].⁵ The mesityl rings are oriented almost perpendicularly (86.5°) with respect to each other, presumably in order to reduce steric interactions between the ortho methyl groups. The indium atoms are in a highly distorted tetrahedral geometry with the C(11)–In–C(21) plane pitched 99.5° with respect to the Cl–In–Cl(a) plane. This distortion can be clearly seen in Figure 5 and is undoubtedly due to the steric interaction between the ortho methyl groups and the bridging chloride atoms. The intramolecular C...C and C...Cl distances are given in Table VI.

The In–Cl distance [2.574 (3) Å] is within the range of values found in other $\text{In}(\mu\text{-Cl})_2\text{In}$ units [2.400 (1)–2.673 (9) Å].⁵ Unlike the $\text{In}(\mu\text{-Cl})_2\text{In}$ units previously reported,⁵ the chloride bridges in **3** are symmetrical. It should be noted, however, that InClMe_2 and InCl_2Me , for example, are infinite chains in the solid state,⁵ with a trigonal-bipyramidal geometry around In, as compared to the distorted tetrahedral geometry in **3**. To our knowledge this is the first report on the structural determination of a purely dimeric organoindium halide, the lack of interdimer chloride bridges being due to the steric bulk of the mesityl ligands.

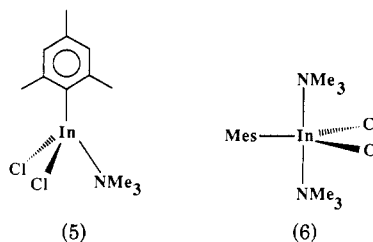
The reaction of InMe_3 with 2 equiv of InCl_3 yields InCl_2Mes (**4**) as a white solid. Although insoluble in noncoordinating solvents, **4** dissolves readily in Et_2O and THF in which it forms the adducts $\text{InCl}_2\text{Mes}\cdot\text{L}$ (L = Et_2O , THF). The insolubility in nonpolar solvents suggests that **4** is polymeric in nature, most probably isostructural to the gallium analogue reported by Beachley, Churchill, and co-workers.¹⁵



We have previously shown that the reaction of Me_3NHCl with group 13 alkyls results in the formation of the chlorides in high yield, both with and without coordination of the amine.^{3,16} We have been unable to isolate a monochloro compound, $\text{InClMes}_2(\text{NMe}_3)$, by this route. The reaction of InMe_3 with 2 equiv of Me_3NHCl , however, yields the amine adduct $\text{InCl}_2\text{Mes}(\text{NMe}_3)$ (**5**). The amine ligand does not exchange in Et_2O or THF solution.

The ^1H NMR spectrum of **5** contains two resonances for each of the meta hydrogens and ortho methyl groups suggesting that the mesityl group is rigid on the NMR time scale. The trimethylamine ligand is rotationally fluxional and remains so down to -60°C . From the NMR spectrum we propose that **5** adopts a conformation such that one ortho methyl is eclipsed with respect to the amine, with the other ortho methyl situated between the two chlorides.

Compound **5** decomposes over a period of several weeks, both in solution and in the solid state, to give **3** and a benzene-soluble compound whose ^1H NMR is consistent with $\text{InCl}_2\text{Mes}(\text{NMe}_3)_2$ (**6**). The second NMe_3 ligand is not easily displaced even on removal of the solvent under



vacuum, so it is therefore unlikely that **6** is the result of an exchange equilibrium between free and coordinated NMe_3 . Bradley et al. have reported¹⁷ and structurally characterized $\{\text{InMe}_3[\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}]\}_x$, which consists of a polymeric chain having the amine coordinated axially about a trigonal-bipyramidal indium. It is therefore reasonable to propose that a similar geometry is present in **6**, though we have been unable to confirm this because of the inability to isolate **6** free from impurities of **4** and **5**.

Experimental Section

Microanalyses were performed by Oneida Research Services Inc., Whitesboro, NY. Melting points were determined in sealed capillaries and are uncorrected. IR spectra ($4000\text{--}600\text{ cm}^{-1}$) were recorded on a Perkin-Elmer 137 grating spectrometer as Nujol mulls. NMR spectra were recorded on Bruker AM-250 (room temperature) and Bruker AM-500 (-90°C) spectrometers (δ in ppm relative to SiMe_4). Molecular weight measurements were made in benzene, using an instrument similar to that described by Clark.¹⁸ All manipulations were carried out under nitrogen. Solvents were dried, distilled, and degassed before use. InCl_3 , Me_4NCl , and Me_3NHCl were used as supplied. MesMgBr was prepared according to standard procedures.

InMe₃ (1). To a suspension of InCl_3 (4.00 g, 18.0 mmol) in Et_2O (100 mL) at 0°C was added MesMgBr (80.9 mL of 0.7 M solution in Et_2O , 56.6 mmol) dropwise in the dark. After the addition was complete, the reaction mixture was refluxed for 2 h. Removal of the solvent and drying under vacuum gave a white solid, which was extracted with boiling pentane ($2 \times 50\text{ mL}$). The extracts were reduced in volume and cooled to -20°C , affording colorless crystals: yield 6.80 g, 80%; mp $178\text{--}179^\circ\text{C}$. Anal. Calcd for $\text{C}_{27}\text{H}_{33}\text{In}$: C, 68.6; H, 6.99. Found: C, 68.7; H, 7.00. Mol wt calcd for InMe_3 : 472. Found: 480.

IR: 2710 (w), 1750 (w), 1715 (w), 1595 (m), 1540 (s), 1400 (m), 1285 (m), 1260 (m), 1080 (br), 1015 (s), 850 (s), 795 (m), 700 (w) cm^{-1} . NMR (toluene- d_6): ^1H , 6.81 (2 H, s, C_6H_2), 2.34 (6 H, s, $o\text{-CH}_3$), 2.17 (3 H, s, $p\text{-CH}_3$); ^{13}C , 150.4, 140.6, 136.2, 127.8 (C_6H_2), 25.2 [$\text{J}(\text{C}\text{--}\text{H}) = 124.1\text{ Hz}$, $o\text{-CH}_3$], 21.3 [$\text{J}(\text{C}\text{--}\text{H}) = 126.0\text{ Hz}$, $p\text{-CH}_3$].

[Me₄N][InClMes₃] (2). To a solution of InMe_3 (0.83 g, 1.76 mmol) in CH_2Cl_2 (30 mL) was added Me_4NCl (0.19 g, 1.74 mmol) as a solid. After the solution was stirred for 6 h, a white precipitate was formed. Filtration followed by washing with CH_2Cl_2 ($2 \times 10\text{ mL}$) and drying under vacuum afforded a white powder: yield 0.92 g, 91%; mp 280°C dec. Anal. Calcd for $\text{C}_{31}\text{H}_{45}\text{ClInN}$: C, 68.9; H, 7.74; N, 2.41. Found: C, 68.9; H, 7.76; N, 2.39.

IR: 1740 (w), 1700 (w), 1590 (m), 1530 (m), 1280 (w), 1265 (w), 1220 (w), 1005 (s), 940 (s), 855 (s), 715 (m) cm^{-1} . NMR ($\text{MeCN}\text{-}d_3$): ^1H , 7.70 (6 H, s, C_6H_2), 2.82 (12 H, s, NCH_3), 2.72 (18 H, s, $o\text{-CH}_3$), 2.67 (9 H, s, $p\text{-CH}_3$); ^{13}C , 151.3, 140.7, 134.9, 126.9 (C_6H_2), 40.1 (NCH_3), 22.1 ($o\text{-CH}_3$), 21.9 ($p\text{-CH}_3$). Crystals suitable for X-ray diffraction were obtained by crystallization from MeCN. Anal. Calcd for $\text{C}_{33}\text{H}_{48}\text{ClInN}_2$: C, 63.6; H, 7.71; N, 4.49. Found: C, 63.8; H, 7.72; N, 4.44.

InClMes₂ (3). To a mixture of InCl_3 (0.22 g, 1.00 mmol) and InMe_3 (0.93 g, 1.97 mmol) was added benzene (20 mL). The reaction mixture immediately gave a bright orange precipitate, which slowly dissolved on stirring for 12 h to give a colorless solution. Removal of the solvent followed by extraction with boiling pentane (50 mL) and cooling to -20°C resulted in the

(15) Beachley, O. T., Jr.; Churchill, M. R.; Pazik, J. C.; Ziller, J. W. *Organometallics* 1987, 6, 2088.

(16) Barron, A. R. *J. Chem. Soc., Dalton Trans.* 1989, 1625.

(17) Bradley, D. C.; Dawes, H.; Frigo, D. M.; Hursthouse, M. B.; Hussain, B. *J. Organomet. Chem.* 1987, 325, 55.

(18) Clark, E. P. *Ind. Eng. Chem. Anal. Ed.* 1941, 13, 820.

Table VII. Summary of X-ray Diffraction Data

	[Me ₂ N]- [InClMes ₃]		
	InMes ₃	MeCN	InClMes ₂
formula	C ₂₇ H ₃₃ In	C ₃₃ H ₄₈ ClInN ₂	C ₁₈ H ₂₂ ClIn
space group	P2 ₁ 0n	P2 ₁ /n	P2 ₁ /a
a, Å	8.704 (2)	16.938 (5)	9.113 (2)
b, Å	21.888 (6)	9.154 (5)	16.083 (4)
c, Å	12.492 (4)	20.859 (5)	12.360 (3)
β, deg	95.06 (2)	94.49 (2)	109.90 (2)
V, Å ³	2370 (1)	3224 (2)	1703.3 (7)
Z	4	4	2
D(calcd), g cm ⁻³	1.323	1.283	1.515
cryst size, mm	0.38 × 0.35 × 0.22	0.41 × 0.29 × 0.32	0.15 × 0.28 × 0.20
temp, °C	-85	-88	-82
radiant	Mo Kα (0.710 73 Å, graphite monochromator)		
2θ limits, deg	4.0–50.0	4.0–55.0	4.0–45.0
index range	-9 ≤ h ≤ 9 0 ≤ k ≤ 23 0 ≤ l ≤ 13	-18 ≤ h ≤ 18 0 ≤ k ≤ 9 0 ≤ l ≤ 22	-9 ≤ h ≤ 9 0 ≤ k ≤ 23 0 ≤ l ≤ 22
no. of collected	7024	4666	3044
no. of unique	3130	4172	2210
R(int)	0.0511	0.1131	0.0632
obsd data	2542	3400	1824
R	0.0348	0.0783	0.0449
R _w	0.0391	0.1040	0.0658
GOF	1.55	2.98	3.09
final residual, e Å ⁻³	0.69	2.25	0.77

Table VIII. Fractional Coordinates (×10⁴) and Equivalent Isotropic Thermal Parameters (×10³ Å²) of the Non-Hydrogen Atoms in InMes₃

	x	y	z	U(eq) ^a
In	2596 (1)	1378 (1)	6676 (1)	25 (1)
C(11)	2179 (5)	612 (2)	7715 (4)	25 (2)
C(12)	661 (5)	406 (2)	7827 (4)	27 (2)
C(13)	425 (6)	-98 (2)	8472 (4)	31 (2)
C(14)	1631 (6)	-413 (2)	9014 (4)	30 (2)
C(15)	3119 (6)	-204 (2)	8912 (4)	33 (2)
C(16)	3408 (5)	303 (2)	8278 (4)	25 (2)
C(17)	-697 (6)	712 (2)	7224 (5)	37 (2)
C(18)	1353 (7)	-974 (3)	9676 (5)	45 (2)
C(19)	5072 (6)	511 (3)	8216 (5)	36 (2)
C(21)	4453 (5)	1279 (2)	5647 (4)	27 (2)
C(22)	4356 (6)	870 (2)	4787 (4)	29 (2)
C(23)	5599 (6)	797 (3)	4167 (4)	37 (2)
C(24)	6930 (6)	1132 (3)	4364 (4)	36 (2)
C(25)	7025 (6)	1545 (2)	5215 (4)	32 (2)
C(26)	5812 (6)	1620 (2)	5848 (4)	29 (2)
C(27)	2881 (6)	507 (3)	4508 (5)	42 (2)
C(28)	8259 (7)	1056 (3)	3665 (5)	62 (3)
C(29)	5962 (7)	2076 (3)	6764 (5)	46 (2)
C(31)	1221 (5)	2206 (2)	6644 (4)	26 (2)
C(32)	867 (6)	2522 (2)	5682 (4)	34 (2)
C(33)	-118 (6)	3031 (2)	5663 (5)	40 (2)
C(34)	-747 (6)	3234 (2)	6581 (5)	38 (2)
C(35)	-345 (6)	2931 (2)	7538 (5)	38 (2)
C(36)	620 (6)	2420 (2)	7583 (4)	29 (2)
C(37)	1522 (8)	2336 (3)	4643 (5)	55 (2)
C(38)	-1846 (7)	3774 (3)	6526 (6)	61 (3)
C(39)	1016 (7)	2123 (3)	8662 (4)	43 (2)

^a Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized *U_{ij}* tensor.

formation of colorless crystals: yield 0.84 g, 73%; mp 178–179 °C. Anal. Calcd for C₁₈H₂₂ClIn: C, 55.6; H, 5.71. Found: C, 55.5; H, 5.74. Mol wt calcd for [InClMes₂]₂: 776. Found: 768.

IR: 1730 (w), 1725 (w), 1595 (m), 1545 (m), 1400 (m), 1290 (m), 1255 (s), 1100 (vs), 1020 (vs), 840 (m), 795 (s), 695 (m) cm⁻¹. NMR (benzene-*d*₆): ¹H, 6.68 (2 H, s, C₆H₂), 2.47 (6 H, s, *o*-CH₃), 2.11 (3 H, s, *p*-CH₃); ¹³C, 148.5, 144.4, 139.0, 128.3 (C₆H₂), 26.2 (*o*-CH₃), 21.2 (*p*-CH₃).

InCl₂Mes (4). A mixture of InCl₃ (0.26 g, 1.17 mmol) and InMes₃ (0.28 g, 0.59 mmol) in benzene (50 mL) was heated at reflux for 12 h, resulting in the formation of a white precipitate.

Table IX. Fractional Coordinates (×10⁴) and Equivalent Isotropic Thermal Parameters (×10³ Å²) of the Non-Hydrogen Atoms in [Me₂N][InClMes₃]•MeCN

	x	y	z	U(eq) ^a
In	7867 (1)	2278 (1)	4331 (1)	28 (1)
Cl	7465 (2)	4538 (3)	3678 (2)	43 (1)
C(11)	8973 (6)	1723 (12)	3862 (6)	27 (4)
C(12)	8963 (7)	1272 (13)	3204 (5)	29 (4)
C(13)	9660 (7)	1302 (12)	2915 (6)	32 (4)
C(14)	10394 (7)	1200 (13)	3275 (6)	34 (4)
C(15)	10398 (7)	1359 (12)	3925 (6)	34 (4)
C(16)	9705 (7)	1629 (12)	4237 (5)	25 (4)
C(17)	8198 (7)	1663 (15)	2779 (5)	36 (4)
C(18)	11144 (7)	881 (15)	2953 (6)	42 (5)
C(19)	9769 (7)	1739 (14)	4969 (6)	37 (4)
C(21)	7986 (7)	3101 (12)	5343 (5)	30 (4)
C(22)	8358 (7)	4447 (12)	5486 (5)	27 (4)
C(23)	8355 (7)	5011 (13)	6118 (6)	36 (4)
C(24)	8022 (7)	4289 (13)	6598 (5)	31 (4)
C(25)	7695 (7)	2935 (14)	6457 (6)	38 (4)
C(26)	7674 (7)	2312 (12)	5843 (5)	27 (4)
C(27)	8758 (8)	5348 (13)	4999 (6)	38 (4)
C(28)	7991 (8)	4977 (16)	7261 (6)	43 (5)
C(29)	7333 (8)	795 (14)	5749 (6)	41 (5)
C(31)	6831 (7)	834 (13)	4135 (6)	35 (4)
C(32)	6041 (7)	1328 (13)	4211 (5)	30 (4)
C(33)	5417 (8)	374 (15)	4101 (6)	42 (5)
C(34)	5484 (8)	-1059 (16)	3939 (6)	43 (5)
C(35)	6254 (8)	-1555 (14)	3866 (6)	37 (4)
C(36)	6910 (7)	-656 (13)	3977 (5)	32 (4)
C(37)	5891 (9)	2880 (16)	4412 (7)	53 (5)
C(38)	4784 (9)	-2094 (19)	3806 (8)	64 (6)
C(39)	7711 (7)	-1333 (13)	3948 (7)	41 (5)
N(1)	5458 (6)	1666 (11)	2129 (5)	32 (3)
C(1)	5430 (8)	38 (14)	2109 (7)	46 (5)
C(2)	6258 (8)	2141 (18)	2429 (6)	55 (5)
C(3)	5343 (8)	2265 (14)	1468 (5)	41 (4)
C(4)	4832 (7)	2218 (15)	2528 (6)	43 (5)
N(2)	1402 (10)	8005 (22)	1511 (8)	105 (8)
C(5)	1464 (9)	8255 (19)	986 (8)	62 (6)
C(6)	1569 (11)	8492 (24)	331 (8)	96 (9)

^a Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized *U_{ij}* tensor.

Filtration, followed by washing with benzene (2 × 10 mL) and pentane (10 mL), gave an off-white precipitate: yield 0.47 g, 87%; mp >300 °C. Anal. Calcd for C₉H₁₁Cl₂In: C, 35.5; H, 3.63. Found: C, 35.4; H, 3.63.

IR: 1705 (w), 1600 (m), 1280 (w), 1250 (m), 1100 (vs), 1020 (vs), 895 (w), 845 (w), 795 (m) 720 (m) cm⁻¹.

InCl₂Mes(NMe₃) (5). To a solution of InMes₃ (0.49 g, 1.04 mmol) in benzene (20 mL) was added Me₃NHCl (0.20 g, 2.09 mmol) as a solid. On stirring for 8 h all the solid dissolved. Removal of the solvent followed by extraction with pentane (20 mL) and cooling to -20 °C resulted in the formation of a colorless, microcrystalline powder: yield 0.13 g, 34%; mp 154 °C dec. Anal. Calcd for C₁₂H₂₀Cl₂InN: C, 39.6; H, 5.54; N, 3.85. Found: C, 39.5; H, 5.53; N, 3.84. Mol wt calcd for InCl₂Mes(NMe₃): 200. Found: 213.

IR: 1720 (w), 1600 (w), 1360 (m), 1265 (s), 1095 (s), 1010 (s), 980 (sh), 845 (w), 800 (s), 725 (m), 660 (w). NMR (benzene-*d*₆): ¹H, 6.76, 6.70 (2 H, s, s, C₆H₂), 2.69 (3 H, s, *o*-CH₃), 2.47 (3 H, s, *o*-CH₃), 2.12 (3 H, s, *p*-CH₃), 1.98 (9 H, s, NCH₃). ¹³C, 145.5, 144.3, 138.8, 128.2 (C₆H₂), 47.1 (NCH₃), 27.4, 26.4 (*o*-C₃), 21.2 (*p*-CH₃).

InCl₂Mes(NMe₃)₂ (6). NMR (benzene-*d*₆): ¹H, 6.78 (2 H, s, C₆H₂), 2.65 (6 H, s, *o*-CH₃), 2.13 (3 H, s, *p*-CH₃), 2.01 (18 H, s, NCH₃). ¹³C, 148.1, 144.2, 139.1, 128.2 (C₆H₂), 49.3 (NCH₃), 27.0 (*o*-CH₃), 21.0 (*p*-CH₃).

Crystallography. A crystal data summary is given in Table VII; fractional atomic coordinates are listed in Tables VIII–X. X-ray data were collected on a Nicolet R3m/v four-circle diffractometer equipped with a LT-1 low-temperature device. Data collection was controlled by using the Nicolet P3 program.¹⁹ Unit

Table X. Fractional Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\times 10^3 \text{ \AA}^2$) of the Non-Hydrogen Atoms in $[\text{InClMes}_2]_2$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
In	622 (1)	9818 (1)	3676 (1)	25 (1)
Cl	-942 (3)	10900 (2)	4387 (2)	28 (1)
C(11)	-869 (11)	8953 (6)	2477 (7)	28 (3)
C(12)	-2374 (12)	9156 (7)	1649 (8)	30 (3)
C(13)	-3157 (13)	8531 (7)	887 (8)	35 (4)
C(14)	-2582 (12)	7734 (7)	883 (8)	33 (4)
C(15)	-1145 (13)	7558 (7)	1693 (9)	35 (4)
C(16)	-280 (12)	8138 (6)	2470 (8)	29 (4)
C(17)	-3039 (13)	10008 (6)	1582 (9)	38 (4)
C(18)	-3506 (14)	7100 (7)	42 (9)	44 (4)
C(19)	1330 (12)	7923 (7)	3306 (8)	37 (4)
C(21)	2577 (11)	10557 (6)	3590 (7)	23 (3)
C(22)	2625 (12)	10720 (6)	2514 (8)	32 (4)
C(23)	3731 (12)	11278 (6)	2386 (9)	34 (4)
C(24)	4779 (12)	11684 (6)	3291 (9)	29 (3)
C(25)	4725 (12)	11498 (6)	4379 (9)	32 (4)
C(26)	3636 (12)	10937 (6)	4547 (8)	31 (3)
C(27)	1489 (14)	10334 (7)	1407 (9)	47 (5)
C(28)	5861 (13)	12315 (7)	3151 (10)	42 (4)
C(29)	3683 (12)	10736 (7)	5756 (8)	36 (4)

^a Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

cell symmetry was checked with the program XDISK. An empirical absorption correction was performed with the program PSICOR. The structure was solved by use of the SHELXTL-PLUS package of programs.²⁰ Drawings were produced using the Nicolet program XP. For each compound the unit cell was indexed by using 20 reflections obtained from a rotation photograph. The lattice was determined by using the P3 program and XCELL and confirmed by an examination of the axial photographs. The space group was determined from systematic absences. The final unit cell parameters were obtained by a least-squares refinement of 50 selected reflections, including 10 Friedel pairs, in the range $15^\circ < 2\theta < 30^\circ$.

The intensities of three check reflections were measured after every 60 reflections; the intensities did not vary significantly during the data collection for any of the compounds.

A semiempirical absorption correction based on Ψ scans from six reflections, in the range $5^\circ < 2\theta < 25^\circ$, and Lorentz and polarization corrections were applied to the data.

InMes₃. Use of direct methods readily revealed the positions of In and the aromatic rings. Standard difference map techniques were used to find the remaining non-hydrogen atoms. After all

(20) SHELXTL-PLUS Users Manual; Nicolet Instruments Corp.: Madison, WI, 1988.

of the non-hydrogen atoms were located and refined anisotropically, a difference map revealed some but not all of the hydrogen atom positions. Therefore, all of the hydrogens were placed in calculated positions [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$; $d(\text{C-H}) = 0.96 \text{ \AA}$] for refinement. The ortho methyl groups were refined as rigid bodies with free rotation about the $\text{C}_{\text{ring}}\text{-C}_{\text{methyl}}$ bond. Refinement was performed to convergence [$\Delta/\delta(\text{max}) < 0.001$] with this model. An extinction correction was applied for the final refinement. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0003F^2$. The final difference map was essentially featureless with all peaks less than 0.69 e \AA^{-3} .

[Me₄N][InClMes₃] \cdot MeCN. Use of direct methods readily revealed the positions of the In and Cl atoms. Standard difference map techniques were used to find the remaining non-hydrogen atoms including a MeCN molecule of crystallization. A difference map phased on the non-hydrogen atoms revealed most, but not all, of the hydrogen atom positions. Therefore, all hydrogen atoms were placed in calculated positions [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$; $d(\text{C-H}) = 0.96 \text{ \AA}$] for refinement. The ortho methyl groups were refined as rigid bodies with free rotation about the $\text{C}_{\text{ring}}\text{-C}_{\text{methyl}}$ bond. Refinement was performed to convergence [$\Delta/\delta(\text{max}) < 0.001$] with this model. An extinction correction was applied for the final refinement. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0004F^2$. The final difference map was essentially featureless, the only significant peak being 2.25 e \AA^{-3} near In.

[InClMes₂]₂. The positions of the unique In and Cl atoms were found by the use of direct methods. Standard difference map techniques were used to find the remaining non-hydrogen atoms. After all the non-hydrogen atoms were located and refined anisotropically, a difference map revealed some, but not all, of the hydrogen atoms; therefore, all the hydrogen atoms were placed in calculated positions [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$; $d(\text{C-H}) = 0.96 \text{ \AA}$] for refinement. The methyl groups were refined as rigid bodies with free rotation about the $\text{C}_{\text{ring}}\text{-C}_{\text{methyl}}$ bond. Refinement was performed to convergence ($\Delta/\delta(\text{max}) < 0.001$) with this model. An extinction correction was applied for the final refinement. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0001F^2$. The final difference map was essentially featureless with all peaks less than 0.771 e \AA^{-3} .

Acknowledgment. Financial support of this work was provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We wish to thank Professor David Hoffman and Dr. Joseph Ziller for useful discussions.

Registry No. 1, 121866-59-9; 2, 121866-63-5; 2-MeCN, 121866-66-8; 3, 121866-60-2; 4, 121866-61-3; 5, 121866-64-6; 6, 121866-65-7; InCl₃, 10025-82-8; MesMgBr, 2633-66-1.

Supplementary Material Available: Tables of anisotropic thermal parameters and hydrogen atom parameters (7 pages); listings of calculated and observed structure factors (35 pages). Ordering information is given on any current masthead page.