Cationic Indium Alkyl Complexes Incorporating Aminotroponiminate Ligands

Fabien Delpech,[†] Ilia A. Guzei,[‡] and Richard F. Jordan*[,†]

Department of Chemistry, The University of Chicago, 5735 S. Ellis Avenue, Chicago, Illinois 60637, and Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received June 28, 2001

The synthesis and structures of indium complexes incorporating the bidentate monoanionic ligand *N*,*N*′-diisopropylaminotroponiminate (^{i}Pr$_2$-ATI) are described. The reaction of $InCl_3$ with Li[^{i}Pr$_2$-ATI] yields (^{i}Pr$_2$-ATI)$InCl_2$ (**3**), which is converted to (^{i}Pr$_2$-ATI)$InMe_2$ (**4**) by reaction with MeLi; **4** is also formed by the reaction of $InMe_3$ with (^{i}Pr$_2$-ATI)H. The reaction of **4** with $[Ph_3C][B(C_6F_5)_4]$ at 23 °C yields the diimine complex [{1,2-(N^{i}Pr)$_2$-5-CPh_3-cyclohepta-3,6-diene}$InMe_2$][$B(C_6F_5)_4$] (**5**) via addition of Ph_3C^+ to the C5 carbon of **4**. Thermolysis of **5** (75 °C) yields [(^{i}Pr$_2$-ATI)InMe][$B(C_6F_5)_4$] (**6**) and Ph_3CMe. **6** was isolated as the chlorobenzene solvate **6**·PhCl. An X-ray diffraction study shows that there are two independent cations in the asymmetric unit of **6**·PhCl. One cation (In(1)) is ion-paired with two $B(C_6F_5)_4^-$ anions, while the second cation is complexed with two PhCl molecules and is disordered between two equally occupied positions (In(2) and In(3)). Dative In−ClPh bonding and PhCl/ATI π-stacking interactions contribute to the PhCl coordination in **6**·PhCl. The reaction of **4** with $B(C_6F_5)_3$ yields [(^{i}Pr$_2$-ATI)InMe][$MeB(C_6F_5)_3$] (**7**), which decomposes slowly at 23 °C by $C_6F_5^-$ transfer reactions. The reaction of **4** with [$HNMe_2Ph$][$B(C_6F_5)_4$] yields the labile amine adduct [(^{i}Pr$_2$-ATI)In(Me)(NMe_2Ph)][$B(C_6F_5)_4$] (**10**).

Introduction

Neutral group 13 EX_3 and ER_3 complexes are widely used as Lewis acids, alkylating agents and reducing agents.[1−3] Cationic group 13 complexes are of interest for these and other applications because the charge may enhance the Lewis acidity of the metal center and influence the reactivity of the E−X or E−R groups.[4−7] Low-coordinate cations are particularly attractive for applications in catalysis.[8,9] We have described the chemistry of cationic aluminum complexes (^{i}Pr$_2$-ATI)-AlR^+ which are stabilized by the *N*,*N*′-diisopropyl-aminotroponiminate ligand (^{i}Pr$_2$-ATI) and can be isolated as the $B(C_6F_5)_4^-$ salts.[10] These formally three-coordinate species are potent Lewis acids and form complexes with amines, phosphines, acetone, CH_3CN, neutral Al alkyls (via Me bridging), and chlorobenzene, which undergo associative ligand exchange. The (^{i}Pr$_2$-ATI)AlR^+ cations catalyze the dimerization of terminal alkynes by an insertion/σ-bond metathesis mechanism and initiate the polymerization of isobutylene and propylene oxide. The dinuclear hydride cation {(^{i}Pr$_2$-

[†] University of Chicago.
[‡] Iowa State University.

(1) (a) Paquette, L. A. In *Encyclopedia of Reagents for Organic Synthesis*; Wiley & Sons: New York, 1995; p 153 and p 645. (b) Eisch, J. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier: Oxford, UK, 1995; Vol 11, Chapter 6. (c) Kennedy, J. P.; Marechal, E. *Carbocationic Polymerization*; Wiley-Interscience: New York, 1982. (d) Olah, G. A. In *Friedel−Crafts Chemistry*; Wiley & Sons: New York, 1972; p 215.

(2) Miller, J. A. In *Chemistry of Aluminium, Gallium, Indium and Thallium*; Downs, A. J., Ed.; Chapman & Hall: London, UK, 1993; p 372.

(3) (a) Loh, T. P.; Pei, J.; Cao, G. Q. *Chem. Commun.* **1996**, 1819. (b) Loh, T. P.; Pei, J.; Lin, M. *Chem. Commun.* **1996**, 2315. (c) Chan, T. H.; Yang, Y. *J. Am. Chem. Soc.* **1999**, *121*, 3228.

(4) Atwood, D. A. *Coord. Chem. Rev.* **1998**, *176*, 407.

(5) (a) Bochmann, M.; Sarsfield, M. J. *Organometallics* **1998**, *17*, 5908. (b) Dohmeier, C.; Schnöckel, H.; Robl, C.; Schneider, U.; Ahlrichs, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1655. (c) Bochmann, M.; Dawson, D. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2226. (d) Burns, C. T.; Stelck, D. S.; Shapiro, P. J.; Vij, A.; Kunz, K.; Kehr, G.; Concolino, T.; Rheingold, A. L. *Organometallics* **1999**, *18*, 5432.

(6) (a) Coslédan, F.; Hitchcock, P. B.; Lappert, M. F. *Chem. Commun.* **1999**, 705. (b) Atwood, D. A.; Jegier, J. *Inorg. Chem.* **1996**, *35*, 4277. (c) Atwood, D.; Jegier, J. *Chem. Commun.* **1996**, 1507. (d) Uhl, W.; Wagner, J.; Fenske, D.; Baum, G. *Z. Anorg. Allg. Chem.* **1992**, *612*, 25. (e) Self, M. F.; Pennington, W. T.; Laske, J. A.; Robinson, G. H. *Organometallics* **1991**, *10*, 36. (f) Kynast, U.; Kelton, B. W.; White, A. H.; Henderson, M. J.; Raston, C. L. *J. Organomet. Chem.* **1990**, *384*, C1. (g) Engelhardt, L. M.; Kynast, U.; Raston, C. L.; White, A. H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 681. (h) Bourget, L.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1999**, 2645. (i) Emig, N.; Nguyen, H.; Krautscheid, H.; Réau, R.; Cazaux, J.-B.; Bertrand, G. *Organometallics* **1998**, *17*, 3599. (j) Emig, N.; Réau, R.; Krautscheid, H.; Fenske, D.; Bertrand, G. *J. Am. Chem. Soc.* **1996**, *118*, 5822. (k) Bruce, M.; Gibson, V. C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 2523. (l) Cameron, P. A.; Gibson, V. C.; Redshaw, C.; Segal, J. A.; Bruce, M. D.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1999**, 1883. (m) Hayashi, Y.; Rohde, J. J.; Corey, E. J. *J. Am. Chem. Soc.* **1996**, *118*, 5502.

(7) (a) Atwood, D. A.; Jegier, J. A.; Rutherford, D. *J. Am. Chem. Soc.* **1995**, *117*, 6779. (b) Jegier, J. A.; Atwood, D. A. *Inorg. Chem.* **1997**, *36*, 2034. (c) Munoz-Hernandez, M.-A.; Sannigrahi, B.; Atwood, D. A. *J. Am. Chem. Soc.* **1999**, *121*, 6747. (d) Jegier, J. A.; Munoz-Hernandez, M.-A.; Atwood, D. A. *J. Chem. Soc., Dalton Trans.* **1999**, 2583.

(8) (a) Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1997**, *119*, 8125. (b) Radzewich, C. E.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 9384. (c) Radzewich, C. E.; Guzei, I. A.; Jordan, R. F. *J. Am. Chem. Soc.* **1999**, *121*, 8673. (d) Dagorne, S.; Guzei, I. A.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 274. (e) Jordan, R. F.; Aeilts, S. L.; Coles, M. P.; Dagorne, S. G.; Ihara, E. *Polym. Mater. Sci. Eng.* **1999**, *80*, 418.

(9) Krossing, I.; Nöth, H.; Schwenk-Kircher, H. *Eur. J. Inorg. Chem.* **1998**, 927.

(10) (a) Ihara, E.; Young, V. G.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 8277. (b) Korolev, A. V.; Guzei, I. A.; Jordan, R. F. *J. Am. Chem. Soc.* **1999**, *121*, 11605. (c) Korolev, A. V.; Delpech, F.; Dagorne, S.; Guzei, I. A.; Jordan, R. F. *Organometallics* **2001**, *20*, 3367. (d) Korolev, A. V.; Ihara, E.; Guzei, I. A.; Young, V. G.; Jordan, R. F. *J. Am. Chem. Soc.* **2001**, *123*, 8291.

10.1021/om010578x CCC: $22.00
Publication on Web 02/20/2002

ATI)Al}$_2H_3^+$ polymerizes methyl methacrylate. The most prominent reaction of (^{i}Pr$_2$-ATI)AlCH$_2$CH$_2$R$^+$ species with unsaturated substrates is β-H transfer to the coordinated substrate.

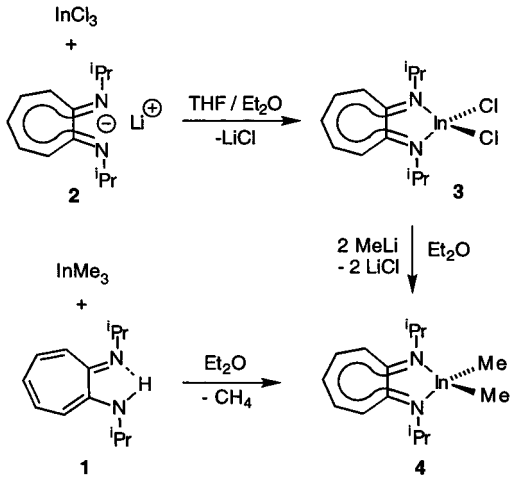
Here we describe initial studies of the analogous cationic indium aminotroponiminate species (^{i}Pr$_2$-ATI)InMe$^+$.[10c] Indium and Al differ in several key respects: In is significantly larger than Al (covalent radii 1.50 vs 1.25 Å), In−C bonds are significantly weaker (38 vs 66 kcal/mol) and less polar than Al−C bonds (Pauling χ values: In 1.78; Al 1.61), and In Lewis acids are generally weaker than the corresponding Al Lewis acids.[11] Indium alkyls are generally less reactive than Al alkyls but do undergo alkane elimination and insertion reactions. For example, InR$_3$ (R = Me, Et) complexes react with phenylacetylene to yield R$_2$In(C≡CPh) products, and In(CH$_2$CH$_2$CH$_2$CH$_2$CH=CH$_2$)$_3$ undergoes slow cyclization to In(cyclopentylmethyl)$_3$.[12,13] The long-term objective of the present work is to probe how these differences in elemental properties influence the structures and reactivity of Al and In (^{i}Pr$_2$-ATI)-ER$^+$ species. Dias has pioneered the use of the ^{i}Pr$_2$-ATI ligand in main group chemistry and has prepared the bis-aminotroponiminate complex (Me$_2$-ATI)$_2$InCl.[14] The tropolonate complex {C$_7$H$_5$O$_2$}InMe$_2$ has also been prepared.[15]

Several classes of indium cations are known, including In(H$_2$O)$_6^{3+}$ and related aquo species,[16] four-, five-, and six-coordinate InX$_2$L$_n^+$ complexes (X = halide; n = 2−4; L = O, N, or P donor),[17] and higher coordinate InX$_2$L$_n^+$ complexes incorporating crown ether or other multidentate ligands.[18] Additionally, and most relevant to the present work, several "InR$_2^+$" species have been characterized. The InMe$_2^+$ cation is stable in aqueous solution,[19] and in the solid state InR$_2^+$ cations typically exhibit tetragonal bipyramidal structures with a nearly linear InR$_2^+$ core and four weakly coordinated equatorial ligands.[20,21]

Results and Discussion

Neutral Indium Aminotroponiminate Complexes. The reaction of *N*-isopropyl-2-(isopropylamino)troponimine ((^{i}Pr$_2$-ATI)H, **1**) with BuLi (Et$_2$O, −78 °C) yields Li[^{i}Pr$_2$-ATI] (**2**), which can be isolated in high yield as an orange powder and is a convenient source of the ^{i}Pr$_2$-ATI$^-$ ligand. The reaction of **2** with 1 equiv of InCl$_3$ yields (^{i}Pr$_2$-ATI)InCl$_2$ (**3**) as a pale yellow solid in 64% yield (Scheme 1). Alkylation of **3** with 2 equiv of MeLi (Et$_2$O, −78 °C) affords (^{i}Pr$_2$-ATI)InMe$_2$ (**4**). Compound **4** is also formed by the reaction of InMe$_3$ with 1 equiv of **1**. Compound **4** is isolated as a yellow crystalline solid by crystallization from cold pentane. Compounds **3** and **4** are stable in air and in wet NMR solvents for several days. The ^{1}H and ^{13}C NMR spectra of **3** and **4** are consistent with C_{2v}-symmetric structures and symmetrical bidentate coordination of the aminotroponiminate ligand.

Scheme 1



Molecular Structures of 3 and 4. The molecular structures of **3** and **4** were determined by X-ray crystallography (Figures 1, 2 and Tables 1, 2). In both cases, there are two independent molecules in the asymmetric unit which have very similar structures; average metrical parameters for the two molecules are referred to in the following discussion. Both **3** and **4** adopt monomeric structures with distorted tetrahedral geometry at In. The ^{i}Pr$_2$-ATI ligands in both species are coordinated in a symmetrical fashion, and the ATI π-systems are delocalized. The major structural difference between **3** and **4** is that the Me−In−Me angle in **4** (128.2° av) is ca. 22° larger than the Cl−In−Cl angle in **3** (106.3° av). This difference reflects the higher p character in the In orbitals used in In−Cl bonding compared to In−Me bonding due to the higher electronegativity of Cl compared to Me (Bent's rule).[22,23] The N−In−N bite angle

(11) Downs, A. J. In *Chemistry of Aluminium, Gallium, Indium and Thallium*; Downs, A. J., Ed.; Chapman & Hall: London, UK, 1993; p 1.

(12) (a) Alcock, N. W.; Degnan, I. A.; Roe, S. M.; Wallbridge, M. G. H. *J. Organomet. Chem.* **1991**, *414*, 285. (b) Jeffery, E. A.; Mole, T. *J. Organomet. Chem.* **1968**, *11*, 393.

(13) Dolzine, T. W.; Oliver, J. P. *J. Organomet. Chem.* **1974**, *78*, 165.

(14) (a) Dias, H. V. R.; Jin, W. *Inorg. Chem.* **1996**, *35*, 6546. (b) Dias, H. V. R.; Jin, W.; Ratcliff, R. E. *Inorg. Chem.* **1995**, *34*, 6100.

(15) Waller, I.; Halder, T.; Schwarz, W.; Weidlein, J. *J. Organomet. Chem.* **1982**, *232*, 99.

(16) (a) Tuck, D. G. In *Comprehensive Coordination Chemistry*; Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, UK, 1987; Vol. 3, p 153. (b) Taylor, M. J.; Brothers, P. J. In *Chemistry of Aluminium, Gallium, Indium and Thallium*; Downs, A. J., Ed.; Chapman & Hall: London, UK, 1993; p 142. (c) Brown, P. L.; Ellis, J.; Sylva, R. N. *J. Chem. Soc., Dalton Trans.* **1982**, 1911.

(17) (a) Sigl, M.; Schier, A.; Schmidbaur, H. *Eur. J. Chem.* **1998**, 203. (b) Robinson, W. T.; Wilkins, C, J.; Zeying, Z. *J. Chem. Soc., Dalton Trans.* **1990**, 219. (c) Canty, A. J.; Titcombe, L. A.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1988**, 35.

(18) Kloo, L. A.; Taylor, M. J. *J. Chem. Soc., Dalton Trans.* **1997**, 2693. (b) Taylor, M. J.; Tuck, D. G. *J. Chem. Soc., Dalton Trans.* **1981**, 928. (c) Abram, S.; Maichle-Mössmer, C.; Abram, U. *Polyhedron* **1998**, *17*, 131.

(19) (a) Hobbs, C. W.; Tobias, R. S. *Inorg. Chem.* **1970**, *9*, 1998. (b) Olapinski, H.; Weidlein, J.; Hausen, H. D. *J. Organomet. Chem.* **1974**, *64*, 193. (c) Hausen, H. D.; Schwering, H. U. *Z. Anorg. Allg. Chem.* **1973**, *398*, 119. (d) Olapinski, H.; Weidlein, J. *J. Organomet. Chem.* **1973**, *54*, 87.

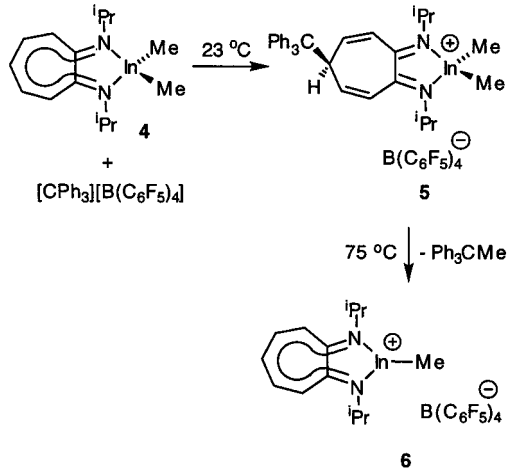
(20) (a) Me$_2$InBr: Hausen, H. D.; Mertz, K.; Weidlein, J.; Schwarz, W. *J. Organomet. Chem.* **1975**, *93*, 291. (b) [^{i}Pr$_2$In(THF)$_2$][BF$_4$]: Neumuller, B.; Gahlmann, Y. T. *J. Organomet. Chem.* **1991**, *414*, 271. (c) [(mesityl)$_2$In][BF$_4$]: Gahlmann, Y. T.; Neumuller, B. *Z. Anorg. Allg. Chem.* **1994**, *620*, 847. (d) Me$_2$In(OAc): Einstein, F. W. B.; Gilbert, M. M.; Tuck, D. G. *J. Chem. Soc., Dalton Trans.* **1973**, 248.

(21) See also: (a) Greenwood, N. N.; Thomas, B. S.; Waite, D. W. *J. Chem. Soc., Dalton Trans.* **1975**, 299. (b) Poland, J. S.; Tuck, D. G. *J. Organomet. Chem.* **1972**, *42*, 315. (c) Gynane, M. J. S.; Waterworth, L. G.; Worrall, J. *J. Organomet. Chem.* **1972**, *43*, 257. (d) Brill, T. B. *Inorg. Chem.* **1976**, *15*, 2558. (e) Schbaurmid, H.; Koth, D. *Naturwissenschaften* **1976**, *63*, 482. (f) Wilder, H. J.; Hausen, H. D.; Weidlein, J. *Z. Naturforsh.* **1975**, *30*, 645.

(22) (a) Bent, H. A. *J. Chem. Educ.* **1960**, *37*, 616. (b) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

(23) The In−Cl and In−Me cone angles are estimated to be 96° and 97°, respectively, so steric effects do not contribute to the difference in X−In−X angles in **3** and **4**.

Scheme 2



(74.10° av) and N−In−C angles (110.4° av) in **4** are correspondingly smaller than the N−In−N (78.46° av) and N−In−Cl (117.70° av) angles in **3**. The core structure of **4** is similar to that in the oxamidinate complex $Me_2In\{(MeN)_2CC(NMe)_2\}InMe_2$, in which the $InMe_2$ units are incorporated into five-membered chelate rings which are directly analogous to that in **4**.[24] The In−Cl distances in **3** (2.350 Å av) are similar to those in $InCl_3(NMe_3)_2$ (2.359 Å av)[25] and are in the range normally observed for terminal In−Cl bonds (2.31−2.43 Å).[26] The In−Me distances in **4** (2.157 Å av) are similar to those in $Me_2In\{(MeN)_2CC(NMe)_2\}InMe_2$ (2.175 Å av)[24] and $\{Me_2In(\mu\text{-}NMePh)\}_2$ (2.153 Å av).[27] The ^{i}Pr$_2$-ATI ligand in **4** is slightly twisted such that the angle between the InN_2C_2 plane and the seven-membered ring plane is 6.3° and 13.4° in the two independent molecules. The twist angle is smaller in **3** (2.7° and 1.4°). Similar twist distortions were observed in Li, Zr, Hf, and Y aminotroponiminate compounds.[28]

Electrophilic Addition of CPh_3^+ to 4. The reaction of **4** with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ in pentane (23 °C, 20 h) yields the diimine complex $[\{1,2\text{-}(N^iPr)_2\text{-}5\text{-}CPh_3\text{-}cyclohepta\text{-}3,6\text{-}diene\}InMe_2][B(C_6F_5)_4]$ (**5**, Scheme 2), which is isolated as a pale yellow solid in 90% yield. Compound **5** forms by electrophilic addition of CPh_3^+ to C5 of the ^{i}Pr$_2$-ATI ligand of **4**. The ^{1}H and ^{13}C NMR spectra for **5** each contain two In-*Me* resonances, one ^{i}Pr-*CH* resonance, and two ^{i}Pr-*Me*$_2$ resonances, consistent with C_s symmetry at In. The ^{13}C NMR resonance for C5 of **5** appears at δ 47.5 with $^1J_{CH}$ = 120 Hz, characteristic of sp^3 hybridization and indicative of addition of CPh_3^+ at this position. For comparison, the C5 resonance for **4** appears at δ 112.7 ($^1J_{CH}$ = 151), characteristic of sp^2 hybridization. Similarly, the ^{1}H NMR H5 resonance of **5** (δ 5.35; t, $^3J_{HH}$ = 6.1) is shifted upfield from the corresponding resonance of **4** (δ 6.13; t, $^3J_{HH}$ = 9.2 Hz). Analogous $\{1,2\text{-}(N^iPr)_2\text{-}5\text{-}CPh_3\text{-}cyclohepta\text{-}3,6\text{-}diene\}AlMe_2^+$ addition products were observed as intermediates in the reaction of $(^iPr_2\text{-}ATI)AlR_2$ (R = Me, Et) with $[Ph_3C][B(C_6F_5)_4]$ at low temperature, but these adducts convert to $(^iPr_2\text{-}ATI)AlR^+$ species at ca. −40 °C.[29]

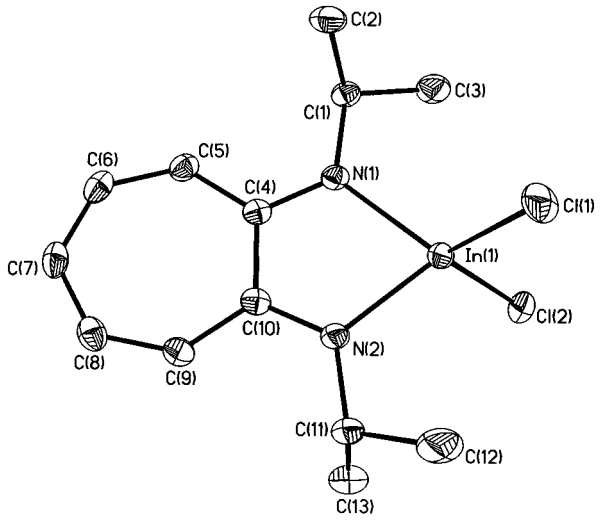


Figure 1. Molecular structure of (^{i}Pr$_2$-ATI)InCl$_2$ (**3**). Hydrogen atoms are omitted.

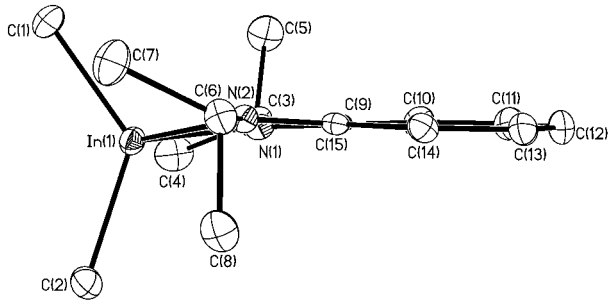


Figure 2. Molecular structure of (^{i}Pr$_2$-ATI)InMe$_2$ (**4**). Hydrogen atoms are omitted.

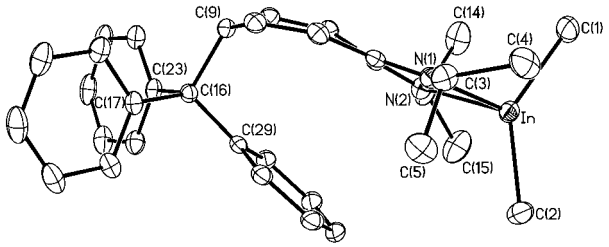


Figure 3. Molecular structure of the $\{1,2\text{-}(N^iPr)_2\text{-}5\text{-}CPh_3\text{-}cyclohepta\text{-}3,6\text{-}diene\}InMe_2^+$ cation in **5**. Hydrogen atoms are omitted.

Molecular Structure of 5. The molecular structure of **5** was confirmed by X-ray crystallography (Figure 3 and Table 3). Addition of the CPh_3 group to the C5 position results in disruption of the π-delocalization and pronounced bond length alternation within the ATI ring. The C=N^{i}Pr distances (1.286 Å av) are characteristic of C(sp^2)=N double bonds.[30] The In−C bond distances (2.130 Å av) are ca. 0.03 Å shorter than those in **4**, while the In−N distances (2.255 Å av) are ca. 0.07 Å longer than those in **4** (2.185 Å av), as expected due to

(24) Gerstner, F.; Schwarz, W.; Hausen, H. D.; Weidlein, J. *J. Organomet. Chem.* **1979**, *175*, 33.
(25) Karia, R.; Willey, G. R.; Drew, M. G. B. *Acta Crystallogr. C.* **1986**, *42*, 558.
(26) Starowieyski, K. B. In *Chemistry of Aluminium, Gallium, Indium and Thallium*; Downs, A. J., Ed.; Chapman & Hall: London, UK, 1993; p 335.
(27) Beachley, O. T.; Bueno, C.; Churchill, M. R.; Hallock, R. B.; Simmons, R. G. *Inorg. Chem.* **1981**, *20*, 2423.
(28) (a) Dias, H. V. R.; Jin, W.; Ratcliff, R. E. *Inorg. Chem.* **1996**, *35*, 6074. (b) Roesky, P. W. *Chem. Ber.* **1997**, *130*, 859. (c) Roesky, P. W. *Eur. J. Inorg. Chem.* **1998**, 593.
(29) Ihara, E.; Korolev, A. V.; Jordan, R. F. Unpublished results.
(30) Levine, I. R. *J. Chem. Phys.* **1963**, *38*, 2326.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3

In(1)−Cl(1)	2.3447(7)	In(2)−Cl(1′)	2.3466(8)
In(1)−Cl(2)	2.3515(9)	In(2)−Cl(2′)	2.3557(7)
In(1)−N(1)	2.093(2)	In(2)−N(1′)	2.103(2)
In(1)−N(2)	2.098(2)	In(2)−N(2′)	2.107(2)
N(1)−C(4)	1.346(3)	N(1′)−C(4′)	1.344(3)
N(2)−C(10)	1.342(3)	N(2′)−C(10′)	1.342(3)
Cl(1)−In(1)−Cl(2)	108.99(3)	Cl(1′)−In(2)−Cl(2′)	103.56(3)
N(1)−In(1)−N(2)	78.52(8)	N(1′)−In(2)−N(2′)	78.39(8)
N(1)−In(1)−Cl(1)	112.81(6)	N(1′)−In(2)−Cl(1′)	114.50(6)
N(2)−In(1)−Cl(1)	115.45(6)	N(2′)−In(2)−Cl(1′)	120.14(6)
N(1)−In(1)−Cl(2)	123.06(6)	N(1′)−In(2)−Cl(2′)	121.75(6)
N(2)−In(1)−Cl(2)	115.45(6)	N(2′)−In(2)−Cl(2′)	118.27(6)

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4

In(1)−C(1)	2.161(2)	In(2)−C(1′)	2.156(2)
In(1)−C(2)	2.153(2)	In(2)−C(2′)	2.157(2)
In(1)−N(1)	2.187(2)	In(2)−N(1′)	2.184(2)
In(1)−N(2)	2.187(2)	In(2)−N(2′)	2.184(2)
N(1)−C(9)	1.328(3)	N(1′)−C(9′)	1.331(3)
N(2)−C(15)	1.334(3)	N(2′)−C(15′)	1.332(3)
C(1)−In(1)−C(2)	127.2(1)	C(1′)−In(2)−C(2′)	129.2(1)
N(1)−In(1)−N(2)	73.78(6)	N(1′)−In(2)−N(2′)	74.42(6)
N(1)−In(1)−C(1)	109.59(9)	N(1′)−In(2)−C(1′)	107.84(8)
N(2)−In(1)−C(1)	113.15(9)	N(2′)−In(2)−C(1′)	111.70(8)
N(1)−In(1)−C(2)	112.16(8)	N(1′)−In(2)−C(2′)	111.78(9)
N(2)−In(1)−C(2)	108.43(8)	N(2′)−In(2)−C(2′)	108.58(8)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 5

In−C(1)	2.128(2)	In−C(2)	2.131(2)
In−N(1)	2.251(2)	In−N(2)	2.260(2)
N(1)−C(6)	1.287(3)	N(2)−C(12)	1.285(3)
C(6)−C(7)	1.462(3)	C(11)−C(12)	1.462(3)
C(7)−C(8)	1.334(3)	C(10)−C(11)	1.333(3)
C(8)−C(9)	1.483(3)	C(9)−C(10)	1.493(3)
C(9)−C(16)	1.609(2)		
C(1)−In−C(2)	139.0(1)	N(1)−In−N(2)	71.84(6)
N(1)−In−C(1)	103.40(9)	N(2)−In−C(1)	102.57(9)
N(1)−In−C(2)	109.51(9)	N(2)−In−C(2)	110.34(9)

conversion of the formally anionic $^{i}Pr_2$-ATI$^-$ ligand in **4** to a neutral diimine ligand in **5**. The In center in **5** has a highly distorted tetrahedral geometry, with a large C−In−C angle (139.0(1)°) and small N−In−N angle (71.84(6)°), reflecting the tendency of the $InMe_2^+$ unit to adopt a more linear geometry as the donor ability of the additional ligands becomes weaker.[20,21]

Synthesis of [(^{i}Pr$_2$-ATI)InMe][B(C$_6$F$_5$)$_4$]·C$_6$H$_5$Cl (6·PhCl). Thermolysis of **5** at 75 °C (12 h, C_6H_5Cl) yields a 1:1 mixture of [($^{i}Pr_2$-ATI)InMe][B(C_6F_5)$_4$] (**6**) and Ph_3CMe (Scheme 2), presumably by dissociation of CPh_3^+ to regenerate **4** and CPh_3^+, followed by Me^- abstraction. The chlorobenzene solvate **6**·PhCl was isolated as a yellow solid in 81% yield by generation of **6** in chlorobenzene, removal of the volatiles, and pentane washing; **6**·PhCl was also isolated in crystalline form by recrystallization from chlorobenzene/pentane. The ^{1}H and ^{13}C NMR spectra for **6** in C_6D_5Cl each contain one In-*Me* resonance, one ^{i}Pr-*CH* resonance, and one ^{i}Pr-*Me*$_2$ resonance indicative of C_{2v} symmetry. The ^{13}C NMR C5 resonance appears at δ 118.5 (d, $^1J_{CH}$ = 154 Hz), characteristic of sp^2 hybridization. The ^{11}B, ^{13}C, and ^{19}F NMR data for the B(C_6F_5)$_4^-$ anion in **6** are characteristic of the free anion.[31] Complex **6** is undoubtedly solvated in C_6D_5Cl solution, but rapid solvent exchange results in time-averaged C_{2v} symmetry.

Solid-State Molecular Structure of 6·PhCl. The molecular structure of **6**·PhCl in the solid state was determined by X-ray crystallography (Figures 4, 5 and Table 4). There are two independent cations in the asymmetric unit. One cation (In(1)) is ion-paired with two B(C_6F_5)$_4^-$ anions, while the second cation is complexed with two PhCl molecules and is disordered between two equally occupied positions (In(2) and In(3)). The geometry around In(1) (Figure 4) is distorted trigonal bipyramidal (*tbp*) with the two axial positions occupied by the B(C_6F_5)$_4^-$ anions (F(20)−In(1)−F(23A) = 162.3(2)°). The In(1)− F(20) (2.950(5) Å) and In(1)− F(23A) (2.711(5) Å) distances are intermediate between the sums of the In and F covalent (2.14 Å) and van der Waals (vdW) radii (3.37 Å).[32] Similar In−F distances were observed for the intramolecular In− F contacts involving the *ortho*-CF_3 groups in In$_2${2,4,6-tris(trifluoromethyl)phenyl)}$_4$ (2.80(1)−2.96(1) Å) and In{2,4,6-tris(trifluoromethyl)phenyl)}$_3$ (2.722(7)−2.798(5) Å).[33] Somewhat longer intermolecular In− F contacts were observed in In(C_6F_5)$_2$(κ^2-$CH_2CH_2CH_2NMe_2$) (3.175(5) Å).[34]

The In(2) and In(3) cations of **6**·PhCl are structurally very similar and feature *tbp* geometries with PhCl ligands in the axial positions (Figure 5). The In−Cl dative bond distances (In(3)−Cl(2) 3.061(4) Å, In(3)−Cl(3) 3.272(3) Å) are intermediate between the sums of the In and Cl covalent and vdW radii (2.49 and 3.65 Å)[32] and are comparable to the In-μCl distances in polymeric $MeInCl_2$ (3.20 Å) and {(H_2Bpz_2)InMe(μ-Cl)}$_2$ ($H_2Bpz_2^-$ = dihydrobis(pyrazolyl)borate; 3.066(1) and 3.203(1) Å).[35,36] The structure of the chlorobenzene ligand is not significantly perturbed by coordination. The C(200)−Cl(2) (1.702(6) Å) and C(300)−Cl(3) (1.729(5) Å) distances in **6**·PhCl are close to the C−Cl bond distance in free chlorobenzene (1.737(5) Å gas phase).[37] As illustrated in Figure 5, the two PhCl ligands are nearly parallel to the $^{i}Pr_2$-ATI plane (angles between planes 4.4° and 8.8°) and are shifted off-center in opposite directions, such that the electron-deficient PhCl ipso carbons are located above and below the electron-rich $^{i}Pr_2$-ATI nitrogens (C(200)−N(2B) 3.35 Å, C(300)−N(1B) 3.51 Å), and the PhCl ring centroids lie above and below the electron-deficient $^{i}Pr_2$-ATI iminato carbons (centroid(200)−C(11B) 3.41 Å, centroid(300)−C(5B) 3.47 Å). This orientation permits an attractive π-stacking interaction between PhCl and ATI rings.[38] Thus it appears that both dative In−ClPh bonding and π-stacking interactions contribute to the PhCl coordination in **6**·PhCl.

(31) These data are nearly identical to those for [CPh_3][B(C_6F_5)$_4$]. See the Supporting Information.

(32) The covalent and van der Waals radii for In (1.50 and 1.90 Å) were taken from ref 11, and those for F (0.64 and 1.47 Å) and Cl (0.99 and 1.75 Å) were taken from: Kulawiec, R. J.; Crabtree, R. H. *Coord. Chem. Rev.* **1990**, *99*, 89.

(33) Schluter, R. D.; Cowley, A. H.; Atwood, D. A.; Jones, R. A.; Bond, M. R.; Carrano, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 2070.

(34) Schumann, H.; Just, O.; Seuss, T. D.; Gorlitz, F. H.; Weimann, R. *J. Organomet. Chem.* **1994**, *466*, 5.

(35) Mertz, K.; Schwarz, W.; Zettler, F.; Hausen, H. D. *Z. Naturforsch.* **1975**, *30*, 159.

(36) Reger, D. L.; Knox, S. J.; Rheingold, A. L.; Haggerty, B. S. *Organometallics* **1990**, *9*, 2581.

(37) Penionzhkevich, N. P.; Sadova, N. I.; Vilkov, L. V. *Zh. Struct. Khim.* **1979**, *20*, 527.

(38) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 6·C_6H_5Cl

In(1)−C(1)	2.088(5)	In(2)−C(1A)	2.121(1)	In(3)−C(1B)	2.121(1)
In(1)−N(1)	2.069(4)	In(2)−N(1A)	2.100(1)	In(3)−N(1B)	2.100(1)
In(1)−N(2)	2.070(4)	In(2)−N(2A)	2.100(1)	In(3)−N(2B)	2.100(1)
N(1)−C(5)	1.340(6)	N(1A)−C(5A)	1.333(1)	N(1B)−C(5B)	1.333(1)
N(2)−C(11)	1.335(6)	N(2A)−C(11A)	1.333(1)	N(2B)−C(11B)	1.333(1)
In(1)−F(20)	2.950(5)	In(2)−Cl(1)	3.050(4)	In(3)−Cl(2)	3.061(4)
In(1)−F(23A)	2.711(5)	In(2)−Cl(4)	3.284(3)	In(3)−Cl(3)	3.272(3)
N(1)−In(1)−N(2)	79.5(2)	N(1A)−In(2)−N(2A)	78.6(2)	N(1B)−In(3)−N(2B)	79.2(2)
N(1)−In(1)−C(1)	138.1(2)	N(1A)−In(2)−C(1A)	142.5(3)	N(1B)−In(3)−C(1B)	141.2(3)
N(2)−In(1)−C(1)	142.2(2)	N(2A)−In(2)−C(1A)	138.9(3)	N(2B)−In(3)−C(1B)	139.6(3)
F(20)−In(1)−F(23A)	162.3(2)	Cl(1)−In(2)−Cl(4)	176.6(1)	Cl(2)−In(3)−Cl(3)	176.4(1)

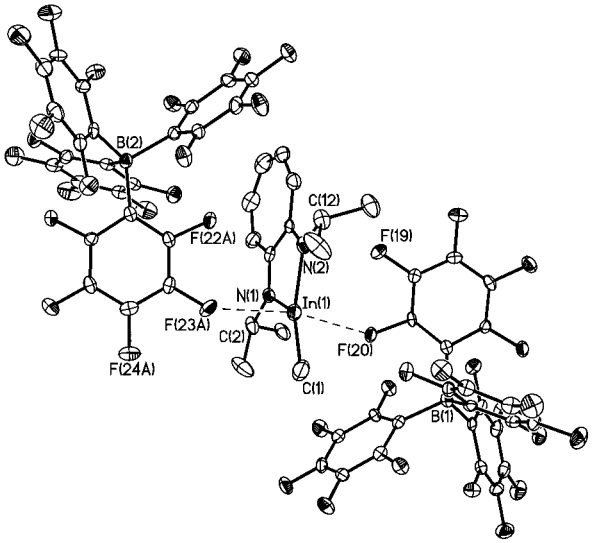


Figure 4. Molecular structure of the In(1) site in [(^{i}Pr$_2$-ATI)InMe][B(C_6F_5)$_4$]·PhCl (**6**·PhCl). Hydrogen atoms are omitted.

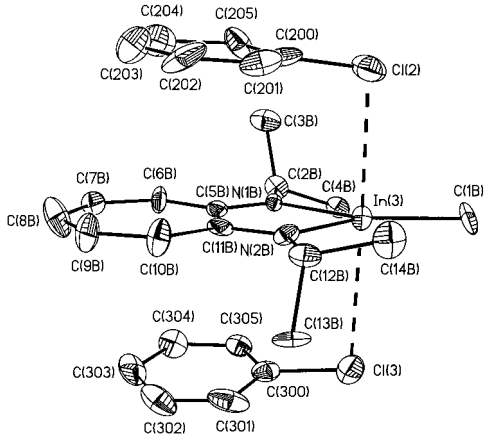
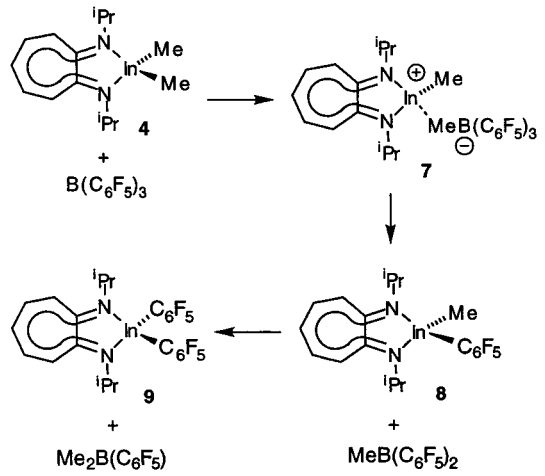


Figure 5. Molecular structure of the In(3) site in [(^{i}Pr$_2$-ATI)InMe][B(C_6F_5)$_4$]·PhCl (**6**·PhCl). Hydrogen atoms are omitted.

Reaction of 4 with B(C_6F_5)$_3$. The reaction of **4** with B(C_6F_5)$_3$ proceeds by methyl abstraction and yields [(^{i}Pr$_2$-ATI)InMe][MeB(C_6F_5)$_3$] (**7**, Scheme 3), which can be isolated as a yellow solid (77%) by simple filtration when the reaction is conducted in hexanes. Compound **7** does not react further with excess B(C_6F_5)$_3$ in C_6D_5Cl at 23 °C. The ^{1}H NMR spectrum of **7** (C_6D_5Cl, 23 °C) contains a singlet at δ 1.00 for the *Me*B(C_6F_5)$_3^-$ group, which is slightly shifted from the free anion resonance (δ 1.11).[39] Additionally, the In-*Me* and ^{i}Pr$_2$-ATI resonances of **7** are shifted slightly from the corresponding resonances of **6**. This effect is most significant for the H5 resonance, which appears at δ 6.59 for **7** versus δ 6.70 ppm for **6**. These results suggest that MeB(C_6F_5)$_3^-$ anion is ion-paired with the cation in **7** in C_6D_5Cl. The ion-pairing interaction is labile however, as **7** exhibits C_{2v} symmetry on the NMR time scale even at 185 K in CD_2Cl_2.

Scheme 3



Compound **7** undergoes ligand redistribution to form (^{i}Pr$_2$-ATI)In(Me)(C_6F_5) (**8**) and MeB(C_6F_5)$_2$ over the course of 5 h at 23 °C in C_6D_5Cl (Scheme 3). The **8**/MeB(C_6F_5)$_2$ mixture undergoes further ligand redistribution to yield (^{i}Pr$_2$-ATI)In(C_6F_5)$_2$ (**9**) and Me$_2$B(C_6F_5) after 10 days at 23 °C. Analogous $C_6F_5^-$ transfer processes were observed in the reaction of B(C_6F_5)$_3$ with Al and Ga amidinate complexes {^{t}BuC(NR)$_2$}MMe$_2$ and with {HC(CMeNAr)$_2$}AlMe$_2$ and other Al diketiminate complexes.[8d,40]

Molecular Structure of 9. The molecular structure of **9** is shown in Figure 6, and selected bond distances and angles are collected in Table 5. The In−C_6F_5 bond distances (2.178(2), 2.164(2) Å) are similar to those in In(C_6F_5)$_2$(κ^2-$CH_2CH_2CH_2NMe_2$) (2.194(9), 2.196(8) Å)[34] and [PPN][In(C_6F_5)$_4$] (2.189(3)−2.206(3) Å)[41] and are intermediate between the In−C distances in InPh$_3$ (2.11(1), 2.16(1) Å)[42] and In{2,4,6-tris(trifluoromethyl)-phenyl)}$_3$ (2.22 Å av). The C−In−C angle (118.94(8)°) in **9** is intermediate between the Me−In−Me angle in **4** and the Cl−In−Cl angle in **3**.[43]

(39) The MeB(C_6F_5)$_3^-$ anion is considered to be a free anion in [$NBu_3(CH_2Ph)$][MeB(C_6F_5)$_3$] in C_6D_5Cl solution. See: Supporting Information.

(40) Baixin, Q.; Ward, D. L.; Smith, M. R. *Organometallics* **1998**, *17*, 3070.

(41) Choi, Z.; Tyrra, W.; Adam, A. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1287.

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

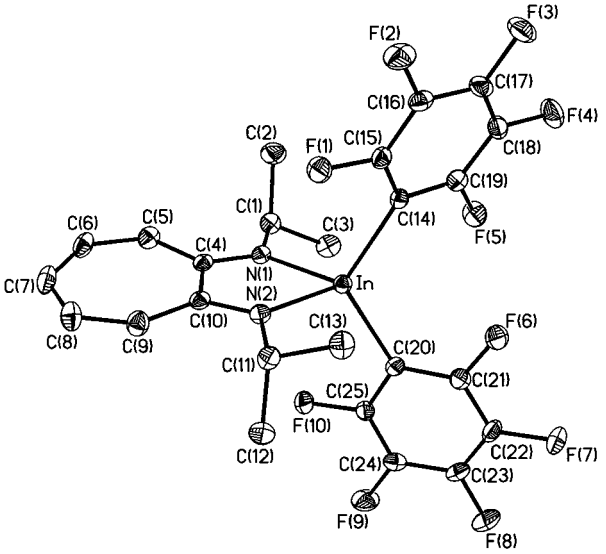
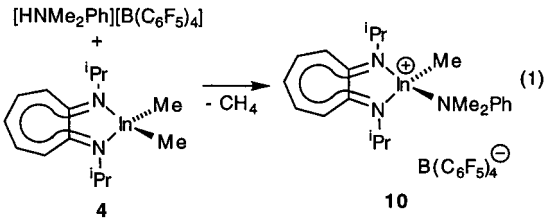


Figure 6. Molecular structure of (^{i}Pr$_2$-ATI)In(C_6F_5)$_2$ (**9**). Hydrogen atoms are omitted.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 9

In−C(14)	2.178(2)	In−C(20)	2.164(2)
In−N(1)	2.126(2)	In−N(2)	2.129(2)
N(1)−C(4)	1.330(3)	N(2)−C(10)	1.337(2)
C(14)−In−C(20)	118.94(8)	N(1)−In−N(2)	76.59(6)
N(1)−In−C(14)	110.43(7)	N(2)−In−C(14)	115.10(7)
N(1)−In−C(20)	118.09(7)	N(2)−In−C(20)	110.45(7)

Reaction of 4 with [HNMe$_2$Ph][B(C_6F_5)$_4$]. The reaction of **4** with 1 equiv of [HNMe$_2$Ph][B(C_6F_5)$_4$] in C_6D_5Cl (23 °C) generates the amine adduct [(^{i}Pr$_2$-ATI)In(Me)(NMe$_2$Ph)][B(C_6F_5)$_4$] (**10**) and methane (eq 1). The ^{1}H and ^{13}C NMR spectra of **10** contain NMe$_2$Ph resonances which are shifted from those of free NMe$_2$Ph, consistent with coordination of the amine to In.[44] However, **10** exhibits C_s symmetry on the NMR time scale at 23 °C and at low temperature (185 K in CD_2Cl_2), which indicates that intermolecular amine exchange is fast.



Molecular Structure of 10. Compound **10** crystallizes as discrete ions, and the structure of the B(C_6F_5)$_4^-$ anion is normal. The structure of the cation of **10** is illustrated in Figure 7, and selected bond distances and angles are collected in Table 6. The geometry at In is distorted trigonal pyramidal, and the NMe$_2$Ph ligand occupies the apical site. Thus the In−Me and In−NMe$_2$Ph groups are displaced from the N_{ATI}−In−N_{ATI} plane by 29.2° and 69.8°, respectively. In contrast, in each of the (^{i}Pr$_2$-ATI)InX_2 compounds **3** (X = Cl), **4** (*X* = Me), and **9** (X = C_6F_5), the two X ligands are symmetrically displaced from the N−In−N plane.[45] The difference in the coordination geometry of **10** versus **3**, **4**, and **9** is readily apparent from comparison of Figures 7 and 2. The trigonal distortion in **10** is due to the difference in the donor ability of the Me and NMe$_2$Ph ligands. As the donor ability of L in a (^{i}Pr$_2$-ATI)E(R)(L)$^+$ species decreases, the (^{i}Pr$_2$-ATI)E(R)$^+$ unit approaches the planar structure expected for the base-free species.[8c] This trend was observed previously for (^{i}Pr$_2$-ATI)Al(R)(L)$^+$ cations.[10] The ^{i}Pr$_2$-ATI ligand in **10** is slightly twisted such that the dihedral angle between the InN_2C_2 and the seven-membered ring planes is 11.2°. The In−N(amine) bond distance (2.405(2) Å) is in the range observed for other four-coordinate In(III) amine complexes (2.29−2.50 Å).[46]

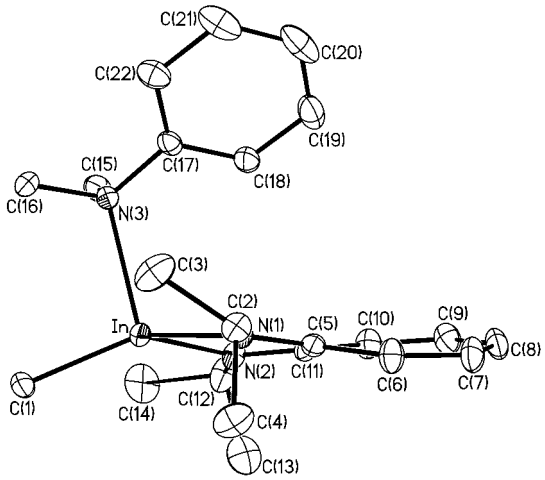


Figure 7. Molecular structure of the (^{i}Pr$_2$-ATI)In(Me)(NMe$_2$Ph)$^+$ cation in **10**. Hydrogen atoms are omitted.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for 10

In−C(1)	2.121(2)	In−N(3)	2.405(2)
In−N(1)	2.112(2)	In−N(2)	2.104(2)
N(1)−C(5)	1.333(3)	N(2)−C(11)	1.351(3)
N(1)−In−N(2)	78.18(6)	C(1)−In−N(3)	99.79(8)
C(1)−In−N(1)	133.62(9)	C(1)−In−N(2)	131.03(9)
N(1)−In−N(3)	103.79(6)	N(2)−In−N(3)	107.10(7)

Reactivity of (^{i}Pr$_2$-ATI)In(Me)$^+$. The addition of 1 equiv of the appropriate Lewis base to **6** in C_6D_5Cl yields the adducts [(^{i}Pr$_2$-ATI)In(Me)(L)][B(C_6F_5)$_4$] (L = NMe$_2$Ph (**10**), CH_3CN (**11**), Me_2CO (**12**), and PMe_3 (**13**, eq 2). Similarly, **7** reacts with Lewis bases to yield [(^{i}Pr$_2$-ATI)-In(Me)(L)][MeB(C_6F_5)$_3$] adducts (L = NMe$_2$Ph (**14**), PMe_3 (**15**), eq 2). The NMR spectra of these adducts contain resonances for the coordinated Lewis base that are shifted from the free base resonances.[44] However, in each case the NMR spectra show that the (^{i}Pr$_2$-ATI)In(Me)(L)$^+$ cation has time-averaged C_{2v} sym-

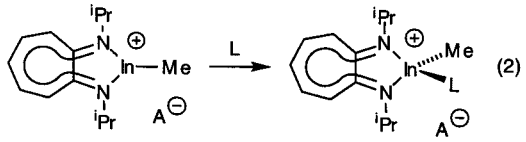
(43) The In−C_6F_5 cone angle (145.2°) is significantly larger than the In−Me or In−Cl cone angles.

(44) See Supporting Information.

(45) Displacements of X groups from N−In−N plane (deg) are as follows. **3**: molecule 1: 58.07, 50.48; molecule 2: 53.45, 49.74; **4**: molecule 1: 62.80, 64.12, molecule 2: 64.0.68, 64.19; **9**: 60.26, 57.87.

(46) (a) Atwood, D. A.; Coley, A. H.; Jones, R. A.; Atwood, J. L.; Bott, S. G. *J. Coord. Chem.* **1992**, *26*, 293. (b) Bradley, D. C.; Dawes, H.; Frigo, D. M.; Hursthouse, M. B.; Hussain, B. *J. Organomet. Chem.* **1987**, *325*, 55. (c) Schumann, H.; Hartmann, U.; Wassermann, W.; Dietrich, A.; Gorlitz, F. H.; Pohl, L.; Hostalek, M. *Chem. Ber.* **1990**, *123*, 2093. (d) Fisher, R. A.; Nlate, S.; Hoffmann, H.; Herdtweck, E.; Blumel, J. *Organometallics* **1996**, *15*, 5746. (e) Kummel, C.; Meller, A.; Noltemeyer, M. *Z. Naturforsh.* **1996**, *51*, 209. (f) Jutzi, P.; Dalhaus, J.; Neumann, B.; Stammler, H. G. *Organometallics* **1996**, *15*, 747. (g) Atwood, D. A.; Jones, R. A.; Coley, A. H.; Bott, S. G.; Atwood, J. L. *J. Organomet. Chem.* **1992**, *434*, 143.

metry at 23 °C, consistent with fast intermolecular exchange of the Lewis base. Low-temperature NMR spectra of **14** and **15** in CD_2Cl_2 show that ligand exchange is fast down to 185 K. The $MeB(C_6F_5)_3^-$ salts **14** and **15** are stable in C_6D_5Cl at 23 °C, which contrasts with the low stability of **7** under these conditions. Evidently the Lewis base prevents the reaction of the cation with the anion. Exposure of **14** to air results in hydrolysis of the anion and formation of (^{i}Pr$_2$-ATI)In(Me)(μ-OH)B(C_6F_5)$_3$.[47]



6, A^- = $B(C_6F_5)_4^-$
7, A^- = $MeB(C_6F_5)_3^-$

A^- = $B(C_6F_5)_4^-$
L = NMe_2Ph (**10**), MeCN (**11**)
Me_2CO (**12**), PMe_3 (**13**)

A^- = $MeB(C_6F_5)_3^-$
L = NMe_2Ph (**14**), PMe_3 (**15**)

Compound **6** does not react with ethylene (1 atm, 70 °C), ^{t}BuC≡CH (80 °C), H_2 (1 atm, 23 °C), or CO (1 atm, 23 °C) and shows only trace activity for isobutylene polymerization.

Conclusion

The reaction of (^{i}Pr$_2$-ATI)$InMe_2$ (**4**) with $[CPh_3][B(C_6F_5)_4]$ yields the cationic complex [(^{i}Pr$_2$-ATI)InMe][$B(C_6F_5)_4$] (**6**), which is isolated as the PhCl solvate **6**·PhCl. Two independent (^{i}Pr$_2$-ATI)$InMe^+$ cations are present in the solid-state structure of **6**·PhCl: one cation (In(1)) which is ion-paired with two $B(C_6F_5)_4^-$ anions via In−F contacts and a second disordered cation (In(2) and In(3)) which is complexed by two PhCl ligands by dative In−ClPh bonding and PhCl/ATI π-stacking interactions. Compound **4** reacts with $B(C_6F_5)_3$ to yield [(^{i}Pr$_2$-ATI)InMe][$MeB(C_6F_5)_3$], which decomposes at 23 °C by $C_6F_5^-$ transfer processes and with $[NMe_2Ph][B(C_6F_5)_4]$ to yield the labile amine complex [(^{i}Pr$_2$-ATI)In(Me)(NMe_2Ph)][$B(C_6F_5)_4$] (**10**). Thus $[CPh_3][B(C_6F_5)_4]$ is the most useful reagent for generating (^{i}Pr$_2$-ATI)InR^+ species. Several observations suggest that (^{i}Pr$_2$-ATI)InR^+ cations will be less reactive than the corresponding (^{i}Pr$_2$-ATI)AlR^+ species studied earlier.[10] Most notably (i) while the reaction of (^{i}Pr$_2$-ATI)$AlMe_2$ with 1 equiv of Ph_3C^+ yields {(^{i}Pr$_2$-ATI)Al(Me)}$_2$(μ-Me)$^+$ (and 0.5 equiv of unreacted Ph_3C^+) via trapping of the initial product (^{i}Pr$_2$-ATI)Al(Me)$^+$ by (^{i}Pr$_2$-ATI)$AlMe_2$, the analogous dinuclear In cation is not observed in the reaction of **4** with Ph_3C^+, (ii) (^{i}Pr$_2$-ATI)AlR^+ cations catalyze the dimerization of terminal alkynes by an insertion/σ-bond metathesis mechanism, whereas (^{i}Pr$_2$-ATI)$InMe^+$ does not react with ^{t}BuC≡CH, and (iii) (^{i}Pr$_2$-ATI)AlR^+ species initiate the polymerization of isobutylene, while (^{i}Pr$_2$-ATI)$InMe^+$ shows only trace activity with this substrate. These differences reflect the lower Lewis acidity and the lower E−C bond polarity in the In complexes compared to the Al complexes.

(47) Guzei, I. A.; Delpech, F.; Jordan, R. F. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2000**, *C56*, E327.

Experimental Section

General Procedures. All operations were carried out under an atmosphere of purified N_2 or under vacuum using a glovebox or a high-vacuum line. Trimethylindium was purchased from Strem and used as received. $[CPh_3][B(C_6F_5)_4]$, $[NMe_2Ph][B(C_6F_5)_4]$, and $B(C_6F_5)_3$ were obtained from Boulder Scientific and used as received. Other chemicals were purchased from Aldrich and used as received. Solvents were distilled from Na/benzophenone, except for CH_2Cl_2, which was distilled from CaH_2. Methylene chloride-d_2, chlorobenzene-d_5, and benzene-d_6 (Cambridge) were dried over CaH_2 for 24 h and degassed by freeze−pump−thaw cycles.

^{1}H, ^{13}C, ^{11}B, and ^{31}P NMR spectra were recorded on a Bruker AMX-360 spectrometer, and ^{19}F NMR spectra were recorded on a Bruker AC-300 spectrometer in flamed-sealed or Teflon-valved tubes at ambient probe temperature unless otherwise indicated. ^{1}H and ^{13}C chemical shifts are reported versus $SiMe_4$ and were determined by reference to the residual solvent peaks. ^{11}B chemical shifts are reported versus BF_3·Et_2O (0.1 M in C_6D_5Cl), ^{19}F chemical shifts are reported versus $CFCl_3$ in $CDCl_3$, and ^{31}P chemical shifts are reported versus H_3PO_4 (85% in THF-d_8). Coupling constants are reported in Hz. Elemental analyses were performed by Midwest Microlabs, Indianapolis, IN.

Li[^{i}Pr$_2$-ATI] (2). A solution of (^{i}Pr$_2$-ATI)H (1.10 g, 5.35 mmol) in Et_2O (25 mL) was cooled to 0 °C. ^{n}BuLi (3.3 mL of a 1.6 M solution in hexanes, 5.35 mmol) was added dropwise. The mixture was allowed to warm to room temperature and was stirred for 2 h. The volatiles were removed under vacuum, yielding an orange solid, which was washed with pentane and dried under vacuum (1.08 g, 95%). ^{1}H NMR (C_6D_6): δ 1.19 (d, $^3J_{HH}$ = 6.1, 12H, Me), 3.95 (sept, $^3J_{HH}$ = 6.1, 2H, C*H*Me$_2$), 6.24 (t, $^3J_{HH}$ = 9.0, 1H, H^5), 6.57 (d, $^3J_{HH}$ = 11.2, 2H, H^{3,7}), 7.05 (t, $^3J_{HH}$ = 9.7, 2H, H^{4,6}).

(^{i}Pr$_2$-ATI)$InCl_2$ (3). A solution of Li[^{i}Pr$_2$-ATI] (5.10 mmol) in Et_2O (25 mL) was generated as described above and cooled to −78 °C. A solution of $InCl_3$ (1.13 g, 5.10 mmol) in THF (50 mL) was added dropwise at −78 °C. The mixture was allowed to warm to room temperature and was stirred overnight. The volatiles were removed under vacuum, and the crude product was extracted with toluene. The extract was filtered and concentrated, and pentane was added, resulting in the precipitation of a pale yellow solid, which was isolated by filtration (1.27 g, 64%). ^{1}H NMR (CD_2Cl_2): δ 1.46 (d, $^3J_{HH}$ = 6.1, 12H, CH*Me*$_2$), 4.19 (sept, $^3J_{HH}$ = 6.1, 2H, C*H*Me$_2$), 6.70 (t, $^3J_{HH}$ = 9.2, 1H, H^5), 6.93 (d, $^3J_{HH}$ =11.5, 2H, H^{3,7}), 7.32 (dd, $^3J_{HH}$ = 9.4 and 11.5, 2H, H^{4,6}). ^{13}C NMR (CD_2Cl_2): δ 24.4 (q, $^1J_{CH}$ = 127, Me), 48.9 (d, $^1J_{CH}$ = 137, *C*HMe$_2$), 116.4 (d, $^1J_{CH}$ = 153, C^5), 122.6 (d, $^1J_{CH}$ = 161, C^{3,7}), 136.9 (d, $^1J_{CH}$ = 145, C^{4,6}), 158.0 (s, C^{1,2}). Anal. Calcd for $C_{13}H_{19}Cl_2InN_2$: C, 40.13; H, 4.92; N,7.20. Found: C, 40.15; H, 4.85; N, 7.14.

(^{i}Pr$_2$-ATI)$InMe_2$ (4). A solution of (^{i}Pr$_2$-ATI)H (0.758 g, 3.71 mmol) in pentane (20 mL) was added to a solution of $InMe_3$ (0.630 g, 3.94 mmol) in pentane (20 mL). The mixture was stirred for 30 min, concentrated to 20 mL, and cooled to −78 °C for 22 h, resulting in the formation of a yellow crystalline solid, which was isolated by filtration (1.19 g, 92%). Alternate synthesis: Excess MeLi (0.4 mL of a 1.4 M solution in Et_2O, 0.56 mmol) was added to a solution of (^{i}Pr$_2$-ATI)$InCl_2$ (0.074 g, 0.19 mmol) in Et_2O at −78 °C. The mixture was warmed to room temperature and stirred overnight. The volatiles were removed under vacuum, and the product was extracted from the LiCl with pentane. The pentane extract was concentrated and cooled to −78 °C to afford (^{i}Pr$_2$-ATI)$InMe_2$ as yellow crystals, which were isolated by filtration (0.058 g, 88%). ^{1}H NMR (CD_2Cl_2): δ −0.20 (s, 6H, In*Me*), 1.25 (d, $^3J_{HH}$ = 6.3, 12H, CH*Me*$_2$), 3.96 (sept, $^3J_{HH}$ = 6.3, 2H, C*H*Me$_2$), 6.13 (t, $^3J_{HH}$ = 9.2, 1H, H^5), 6.41 (d, $^3J_{HH}$ = 11.9, 2H, H^{3,7}), 6.90 (dd, $^3J_{HH}$ = 9.0 and 11.9, 2H, H^{4,6}). ^{1}H NMR (C_6D_5Cl): δ −0.06 (s, 6H, In*Me*), 1.09 (d, $^3J_{HH}$ = 6.3, 12H, CH*Me*$_2$), 3.70 (sept, $^3J_{HH}$ =

6.3, 2H, C*H*Me$_2$), 6.17 (t, $^3J_{HH}$ = 9.2, 1H, H^5), 6.27 (d, $^3J_{HH}$ = 11.9, 2H, H^{3,7}), 6.84 (dd, $^3J_{HH}$ = 9.0 and 11.9, 2H, H^{4,6}). ^{13}C NMR (CD_2Cl_2): δ −4.1 (q, $^1J_{CH}$ = 126, In*Me*$_2$), 23.8 (q, $^1J_{CH}$ = 128, CH*Me*$_2$), 48.7 (d, $^1J_{CH}$ = 135, *C*HMe$_2$), 112.7 (d, $^1J_{CH}$ = 151, C^5), 116.3 (d, $^1J_{CH}$ = 161, C^{3,7}) 135.3 (d, $^1J_{CH}$ = 155, C^{4,6}), 161.0 (s, C^{1,2}). ^{13}C NMR (C_6D_5Cl): δ −3.9 (In*Me*), 23.8 (CH*Me*$_2$), 48.7 (*C*HMe$_2$), 112.5 (C^5), 116.3 (C^{3,7}), 135.3 (C^{4,6}), 160.8 (C^{1,2}). Anal. Calcd for $C_{15}H_{25}InN_2$: C, 51.74; H, 7.24; N, 8.05. Found: C, 51.54; H, 7.13; N, 8.15.

[{1,2-(N^{i}Pr)$_2$-5-CPh$_3$-cyclohepta-3,6-diene}InMe$_2$][B(C$_6$F$_5$)$_4$] (5). A mixture of (^{i}Pr$_2$-ATI)InMe$_2$ (0.158 g, 0.453 mmol) and [CPh$_3$][B(C$_6$F$_5$)$_4$] (0.418 g, 0.453 mmol) in hexanes (5 mL) was stirred at 23 °C for 3 days, resulting in the formation of a yellow solid. The mixture was filtered, and the solid was washed with hexanes (3 × 5 mL) and dried under vacuum to afford a yellow solid (0.516 g, 90%). ^{1}H NMR (C_6D_5Cl): δ −0.08 (s, 3H, In*Me*), 0.00 (s, 3H, In*Me*), 0.90 (d, $^3J_{HH}$ = 4.0, 6H, CH*Me*), 0.92 (d, $^3J_{HH}$ = 4.0, 6H, CH*Me*), 3.42 (m, 2H, C*H*Me$_2$), 5.35 (t, $^3J_{HH}$ = 6.1,1H, H^5), 5.81 (d, $^3J_{HH}$ = 13.0, 2H, H^{3,7}), 6.72 (dd, $^3J_{HH}$ = 6.1 and 12.6, 2H, H^{4,6}), 7.06 (br m, 15H, C*Ph*$_3$). ^{13}C NMR (C_6D_5Cl): δ −2.9 (q, $^1J_{CH}$ =132, In*Me*), −2.1 (q, $^1J_{CH}$ = 133, In*Me*), 22.8 (q, $^1J_{CH}$ = 126, CH*Me*), 23.7 (q, $^1J_{CH}$ = 129, CH*Me*), 47.5 (d, $^1J_{CH}$ = 120, C^5) 52.8 (d, $^1J_{CH}$ = 141 *C*HMe$_2$), 64.8 (s, *C*Ph$_3$), 121.4 (d, $^1J_{CH}$ = 162, C^{3,7}), 125 (br, *ipso*-C$_6$F$_5$), 136.9 (d, $^1J_{CF}$ = 243, *C*$_6$F$_5$), 138.7 (d, $^1J_{CF}$ = 245, *C*$_6$F$_5$), 148.5 (d, $^1J_{CH}$ = 160, C^{4,6}), 148.9 (d, $^1J_{CF}$ = 241, *C*$_6$F$_5$), 161.5 (s, C^{1,2}); the remaining Ph resonances are broad due to restricted rotation. ^{11}B NMR (C_6D_5Cl): δ −16.5 (s). ^{19}F NMR (C_6D_5Cl): δ −132.0 (m, 8F, *o*-C$_6$*F*$_5$), −162.6 (t, $^3J_{FF}$ = 20, 4F, *p*-C$_6$*F*$_5$), −166.5 (m, 8F, *m*-C$_6$*F*$_5$). Anal. Calcd for $C_{58}H_{40}BF_{20}InN_2$: C, 54.83; H, 3.17; N, 2.21. Found: C, 53.84; H, 3.12; N, 2.28.

[(^{i}Pr$_2$-ATI)InMe][B(C$_6$F$_5$)$_4$]·C$_6$H$_5$Cl (6·C$_6$H$_5$Cl). A solution of [{1,2-(N^{i}Pr)$_2$-5-CPh$_3$-cyclohepta-3,6-diene}InMe$_2$][B(C$_6$F$_5$)$_4$] (0.148 g, 0.130 mmol) in C$_6$H$_5$Cl (10 mL) was heated to 75 °C for 12 h. The volatiles were removed under vacuum, leaving an oily dark yellow residue. Trituration with pentane afforded pure [(^{i}Pr$_2$-ATI)InMe][B(C$_6$F$_5$)$_4$]·C$_6$H$_5$Cl as a yellow solid (0.104 mg, 79%). ^{1}H NMR (C_6D_5Cl): δ 0.70 (s, 3H, In*Me*), 1.04 (d, $^3J_{HH}$ = 6.1, 12H, CH*Me*$_2$), 3.65 (sept, $^3J_{HH}$ = 6.1, 2H, C*H*Me$_2$), 6.69 (d, $^3J_{HH}$ = 11.9, 2H, H^{3,7}), 6.70 (t, $^3J_{HH}$ = 8.6, 1H, H^5), 7.15 (m, 2H, H^{4,6}). ^{13}C NMR (C_6D_5Cl): δ 2.6 (q, $^1J_{CH}$ = 138, In*Me*), 24.6 (q, $^1J_{CH}$ = 128, CH*Me*$_2$), 48.8 (d, $^1J_{CH}$ = 141, *C*HMe$_2$), 118.5 (d, $^1J_{CH}$ = 154, C^5), 126.8 (d, $^1J_{CH}$ = 156, C^{3,7}), 137.0 (d, $^1J_{CF}$ = 243, *C*$_6$F$_5$), 137.3 (d, $^1J_{CH}$ = 157, C^{4,6}), 138.8 (d, $^1J_{CF}$ = 245, *C*$_6$F$_5$), 149.0 (d, $^1J_{CF}$ = 241, *C*$_6$F$_5$), 158.3 (s, C^{1,2}); the *ipso*-C$_6$F$_5$ resonance was not observed. ^{11}B NMR (C_6D_5Cl): δ −16.5 (s). ^{19}F NMR (C_6D_5Cl): δ −132.0 (m, 8F, *o*-C$_6$*F*$_5$), −162.6 (t, $^3J_{FF}$ = 21, 4F, *p*-C$_6$*F*$_5$), −166.4 (m, 8F, *m*-C$_6$*F*$_5$). Anal. Calcd for $C_{38}H_{22}BF_{20}InN_2$·C_6H_5Cl: C, 46.99; H, 2.42; N, 2.49. Found: C, 46.61; H, 2.23; N, 2.64.

[(^{i}Pr$_2$-ATI)InMe][MeB(C$_6$F$_5$)$_3$] (7). A mixture of (^{i}Pr$_2$-ATI)InMe$_2$ (0.199 g, 0.572 mmol) and B(C$_6$F$_5$)$_3$ (0.293 g, 0.572 mmol) in hexanes (5 mL) was stirred at 23 °C for 2 h, resulting in the formation of a yellow solid. The solid was collected by filtration, washed with hexanes (3 × 5 mL), and dried under vacuum to afford pure [(^{i}Pr$_2$-ATI)InMe][MeB(C$_6$F$_5$)$_3$] as a yellow solid (0.378 g, 77%). ^{1}H NMR (C_6D_5Cl): δ 0.62 (s, 3H, In*Me*), 1.00 (br s, 3H, *Me*B), 1.04 (d, $^3J_{HH}$ = 6.1, 12H, CH*Me*$_2$), 3.67 (sept, $^3J_{HH}$ = 6.1, 2H, C*H*Me$_2$), 6.59 (t, $^3J_{HH}$ = 9.7, 1H, H^5), 6.64 (d, $^3J_{HH}$ = 11.5, 2H, H^{3,7}), 7.10 (t, $^3J_{HH}$= 10.3, 2H, H^{4,6}). ^{1}H NMR (CD_2Cl_2, 195 K): δ 0.36 (br s, 3H, *Me*B), 1.11 (br s, 3H, In*Me*), 1.36 (br s, 12H, CH*Me*$_2$), 4.22 (br s, 2H, C*H*Me$_2$), 7.00 (t, $^3J_{HH}$ = 9.6, 1H, H^5), 7.16 (d, $^3J_{HH}$ = 11.0, 2H, H^{3,7}), 7.52 (t, $^3J_{HH}$= 9.9, 2H, H^{4,6}). ^{13}C NMR (C_6D_5Cl): δ 3.1 (q, $^1J_{CH}$ = 137, In*Me*), 12.6 (br s, *Me*B), 24.5 (q, $^1J_{CH}$ = 127, CH*Me*$_2$), 48.8 (d, $^1J_{CH}$ = 142, *C*HMe$_2$), 118.4 (d, $^1J_{CH}$ = 153, C^5), 126.4 (d, $^1J_{CH}$ = 155, C^{3,7}), 137.1 (d, $^1J_{CF}$ = 246, *C*$_6$F$_5$), 137.1 (d, $^1J_{CH}$ = 156, C^{4,6}), 138.1 (d, $^1J_{CF}$ = 245, *C*$_6$F$_5$), 149.0 (d, $^1J_{CF}$ = 240, *C*$_6$F$_5$), 160.8 (s, C^{1,2}); the *ipso*-C$_6$F$_5$ resonance was not observed. ^{11}B NMR (C_6D_5Cl): δ −14.6 (s). ^{9}F NMR (C_6D_5Cl): δ −132.3 (m, 6F, *o*-C$_6$*F*$_5$), −163.6 (t, $^3J_{FF}$ = 20, 3F, *p*-C$_6$*F*$_5$), −166.4 (m, 6F, *m*-C$_6$*F*$_5$). Anal. Calcd for $C_{33}H_{25}BF_{15}InN_2$: C, 46.08; H, 2.93; N, 3.26. Found: C, 45.99; H, 2.99; N, 3.24.

Reaction of (^{i}Pr$_2$-ATI)In(Me)$^+$ with MeB(C$_6$F$_5$)$_3^-$. An NMR tube was charged with [(^{i}Pr$_2$-ATI)In(Me)][MeB(C$_6$F$_5$)$_3$] (0.025 g, 0.029 mmol), and C$_6$D$_5$Cl (0.5 mL) was added by vacuum transfer at −78 °C. The tube was maintained at 23 °C and monitored by ^{1}H NMR. The NMR spectra showed that complete conversion of the starting material to (^{i}Pr$_2$-ATI)In(C$_6$F$_5$)(Me) (**8**) and MeB(C$_6$F$_5$)$_2$ had occurred after 5 h and complete conversion to (^{i}Pr$_2$-ATI)In(C$_6$F$_5$)$_2$ (**9**) and MeB(C$_6$F$_5$)$_2$ had occurred after 10 days. Data for (^{i}Pr$_2$-ATI)In(C$_6$F$_5$)(Me) (**8**). ^{1}H NMR (C_6D_5Cl): δ 0.33 (s, 3H, In*Me*), 1.01 (d, $^3J_{HH}$ = 6.5, 6H, CH*Me*), 1.09 (d, $^3J_{HH}$ = 6.5, 6H, CH*Me*), 3.72 (sept, $^3J_{HH}$ = 6.5, 2H, C*H*Me$_2$), 6.29 (t, $^3J_{HH}$ = 9.2, 1H, H^5), 6.42 (d, $^3J_{HH}$ = 11.9, 2H, H^{3,7}), 6.93 (dd, $^3J_{HH}$ = 9.4 and 11.9, 2H, H^{4,6}). ^{13}C NMR (C_6D_5Cl): δ −3.8 (q, $^1J_{CH}$ = 128, In*Me*), 23.4 (q, $^1J_{CH}$ = 127, CH*Me*), 24.1 (q, $^1J_{CH}$ = 128, CH*Me*), 48.1 (d, $^1J_{CH}$ = 135, *C*HMe$_2$), 114.0 (d, $^1J_{CH}$ = 151, C^5), 118.4 (d, $^1J_{CH}$ = 160, C^{3,7}), 121.2 (br t, i*pso*-C$_6$F$_5$, $^2J_{CF}$ = 60), 135.8 (d, $^1J_{CH}$ = 156, C^{4,6}), 137.0 (d, $^1J_{CF}$ = 254, *o*-C$_6$F$_5$), 141.2 (d, $^1J_{CF}$ = 255, *p*-C$_6$F$_5$), 149.0 (d, $^1J_{CF}$ = 231, *m*-C$_6$F$_5$), 160.5 (s, C^{1,2}). ^{19}F NMR (C_6D_5Cl): δ −118.3 (m, 2F, o−C$_6$*F*$_5$), −154.3 (t, $^3J_{FF}$ = 20, 1F, *p*-C$_6$*F*$_5$), −160.5 (m, 2F, *m*-C$_6$*F*$_5$). Data for MeB(C$_6$F$_5$)$_2$. ^{1}H NMR (C_6D_5Cl): δ 1.53 (quintet, $^5J_{HF}$ = 1.8, 3H). ^{13}C NMR (C_6D_5Cl): δ 15.3 (s, br, *Me*B), 137.5 (d, $^1J_{CF}$ = 254, *C*$_6$F$_5$), 143.8 (d, $^1J_{CF}$ = 247, *C*$_6$F$_5$), 147.8 (d, $^1J_{CF}$ = 249, *C*$_6$F$_5$); the *ipso*-C$_6$F$_5$ resonance was not observed. ^{11}B NMR (C_6D_5Cl): δ 71.5 (br s). ^{19}F NMR (C_6D_5Cl): δ −129.3 (m, 4F, *o*-C$_6$*F*$_5$), −147.1 (m, 2F, *p*-C$_6$*F*$_5$), −161.1 (m, 4F, *m*-C$_6$*F*$_5$). Data for (^{i}Pr$_2$-ATI)In(C$_6$F$_5$)$_2$ (**9**). ^{1}H NMR (C_6D_5Cl): δ 1.11 (d, $^3J_{HH}$ = 6.1, 12H, CH*Me*$_2$), 3.77 (sept, $^3J_{HH}$ = 6.1, 2H, C*H*Me$_2$), 6.38 (t, $^3J_{HH}$ = 11.0, 1H, H^5), 6.54 (d, $^3J_{HH}$ = 14.4, 2H, H^{3,7}), 6.98 (dd, $^3J_{HH}$ = 11.2 and 14.4, 2H, H^{4,6}). ^{13}C NMR (C_6D_5Cl): δ 23.5 (q, $^1J_{CH}$ = 129, CH*Me*$_2$), 48.9 (d, $^1J_{CH}$ = 139, *C*HMe$_2$), 115.4 (d, $^1J_{CH}$ = 151, C^5), 117.6 (t, br, $^2J_{CF}$ = 55, *ipso*-C$_6$F$_5$), 120.3 (d, $^1J_{CH}$ = 162, C^{3,7}), 136.3 (d, $^1J_{CH}$ = 153, C^{4,6}), 139.6 (d, $^1J_{CF}$ = 255, *o* -C$_6$F$_5$), 141.9 (d, $^1J_{CF}$ = 252, *p*-C$_6$F$_5$), 147.6 (d, $^1J_{CF}$ = 234, *m*-C$_6$F$_5$), 160.2 (s, C^{1,2}). ^{19}F NMR (C_6D_5Cl): δ −117.8 (m, 4F, *o*-C$_6$*F*$_5$), −152.1 (t, $^3J_{FF}$ = 20, 2F, *p*-C$_6$*F*$_5$), −159.7 (m, 4F, *m*-C$_6$*F*$_5$). Data for Me$_2$B(C$_6$F$_5$). ^{1}H NMR (C_6D_5Cl): δ 1.09 (s, 3H, overlapped with CH*Me*$_2$ resonance of **9**). ^{13}C NMR (C_6D_5Cl): δ 16.7 (br s, *Me*B) 141.9 (d, $^1J_{CF}$ = 252, *C*$_6$F$_5$), 148.9 (d, $^1J_{CF}$ = 238, *C*$_6$F$_5$); the *meta* and *ipso*-C$_6$F$_5$ resonances are obscured. ^{11}B NMR (C_6D_5Cl): δ 80.6 (br s). ^{19}F NMR (C_6D_5Cl): δ −130.3 (m, 2F, *o*-C$_6$*F*$_5$), −151.2 (m, 1F, *p*-C$_6$*F*$_5$), −162.4 (m, 2F, *m*-C$_6$*F*$_5$).

[(^{i}Pr$_2$-ATI)In(Me)(NMe$_2$Ph)][B(C$_6$F$_5$)$_4$] (10). An NMR tube was charged with (^{i}Pr$_2$-ATI)InMe$_2$ (0.029 g, 0.083 mmol) and [NMe$_2$Ph][B(C$_6$F$_5$)$_4$] (0.066 g, 0.083 mmol), and C$_6$D$_5$Cl (0.5 mL) was added by vacuum transfer at −78 °C. The tube was warmed to room temperature, and NMR spectra were recorded which showed the formation of [(^{i}Pr$_2$-ATI)In(Me)(NMe$_2$Ph)][B(C$_6$F$_5$)$_4$] (**10**, 85%). ^{1}H NMR (C_6D_5Cl): δ 0.40 (s, 3H, In*Me*), 0.81 (d, $^3J_{HH}$ = 6.1, 12H, CH*Me*$_2$), 2.35 (s, 6H, N*Me*$_2$), 3.51 (sept, $^3J_{HH}$ = 6.1, 2H, C*H*Me$_2$), 6.59−6.64 (m, 5H, H^{3,7} and H^5 overlapped with NMe$_2$*Ph*), 6.94 (t, 1H, $^3J_{HH}$ = 7.9, Ph), 7.10 (m, 4H, H^{4,6} overlapped with NMe$_2$*Ph*). ^{1}H NMR (CD_2Cl_2): δ 0.73 (br s, 3H, In*Me*), 1.01 (br s, 12H, CH*Me*$_2$), 2.77 (s, 6H, N*Me*$_2$), 3.89 (br s, 2H, C*H*Me$_2$), 6.83 (br s, 1H, H^5), 6.98 (d, $^3J_{HH}$ = 11.6, 2H, H^{3,7}), 7.09 (d, $^3J_{HH}$ = 7.6, 2H, Ph), 7.26 (t, 1H, $^3J_{HH}$ = 7.0, Ph), 7.39 (m, 4H, H^{4,6} overlapped with NMe$_2$*Ph*). ^{13}C NMR (C_6D_5Cl): δ −2.9 (q, $^1J_{CH}$ = 135, In*Me*), 24.9 (q, $^1J_{CH}$ = 127, CH*Me*$_2$), 44.9 (q, $^1J_{CH}$ = 139, N*Me*$_2$), 48.7 (d, $^1J_{CH}$ = 137, *C*HMe$_2$), 117.6 (d, $^1J_{CH}$ = 156, Ph), 118.2 (d, $^1J_{CH}$ = 152, C^5), 124.1 (d, $^1J_{CH}$ = 163, C^{3,7}), 125.6 (d, $^1J_{CH}$ = 162, Ph, 130.2 (d, $^1J_{CH}$ = 161, Ph), 136.9 (d, $^1J_{CF}$ = 243, *C*$_6$F$_5$), 136.9 (d, $^1J_{CH}$ = 156, C^{4,6}), 138.7 (d, $^1J_{CF}$ = 245, *C*$_6$F$_5$), 147.8 (s, *ipso*-Ph), 148.9 (d, $^1J_{CF}$ = 241, *C*$_6$F$_5$), 160.1 (s, C^{1,2}); the *ipso*-C$_6$F$_5$ resonance was not observed. ^{11}B NMR (C_6D_5Cl): δ −16.5

Table 7. Summary of Crystal Data for Compounds 3, 4, 5, 6·C_6H_5Cl, 9, and 10

	3	4	5	6·C_6H_5Cl	9	10
formula	$C_{13}H_{19}Cl_2InN_2$	$C_{15}H_{25}InN_2$	$C_{58}H_{40}BF_{20}InN_2$	$C_{44}H_{27}BClF_{20}InN_2$	$C_{25}H_{19}F_{10}InN_2$	$C_{46}H_{33}BF_{20}InN_3$
fw	389.02	348.19	1270.55	1124.76	652.24	1133.38
cryst size (mm)	0.45 × 0.42 × 0.31	0.46 × 0.25 × 0.15	0.40 × 0.35 × 0.35	0.20 × 0.15 × 0.10	0.45 × 0.43 × 0.27	0.41 × 0.39 × 0.39
d(calc), Mg/m^3	1.617	1.429	1.625	1.745	1.745	1.683
cryst syst	monoclinic	orthorhombic	triclinic	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	*Pbca*	$P\bar{1}$	$P2_1/c$	$Pna2_1$	$P2_1/c$
a (Å)	13.8228(1)	20.796(1)	11.3595(6)	17.4035(9)	16.330(1)	12.1883(9)
b (Å)	16.594(1)	9.2365(5)	14.2584(7)	10.8193(6)	17.700(1)	20.925(2)
c (Å)	15.534(1)	33.711(2)	17.0182(8)	45.479(2)	8.5897(5)	17.570(1)
α (deg)			89.939(1)			
β (deg)	116.231(1)		88.532(1)	90.708(1)		93.187(1)
γ (deg)			70.431(1)			
V (Å^3)	3195.9(4)	6475.1(6)	2596.3(2)	8562.7(8)	2482.7(3)	4473.9(6)
Z	8	16	2	8	4	4
T (K)	183(2)	183(2)	183(2)	183(2)	173(2)	183(2)
diffractometer	Bruker CCD-1000	Bruker CCD-1000	Bruker CCD-1000	Bruker CCD-1000	Bruker CCD-1000	Bruker CCD-1000
radiation, *λ* (Å)	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73
θ range (deg)	1.64 < *θ* < 26.37	1.21 < *θ* < 26.37	1.52 < *θ* < 26.37	1.46 < *θ* < 26.37	1.70 < *θ* < 26.37	1.95 < *θ* < 26.37
data collected: *h*;*k*;*l*	−17,15; 0,20; 0,19	0,25; 0,11; 0,42	−13,14; ±17; 0,21	±21; 0,13; 0,56	−19,20; −13,26; ±10	±15; 0,26; 0,21
no. of reflns collected	18 844	44 343	14 924	56 135	11 469	33 129
no. of indpt reflns	6472	6623	9641	17295	4577	9111
R_{int}	0.0230	0.0372	0.0119	0.0803	0.0176	0.0162
μ (mm^{-1})	1.799	1.447	0.570	0.739	1.045	0.650
max/min transmn	0.6055 and 0.4982	0.8122 and 0.5557	0.8255 and 0.8041	0.9298 and 0.8663	0.7657 and 0.6507	0.7855 and 0.7763
structure solution	direct methods[a]	direct methods[a]	direct methods[a]	direct methods[a]	direct methods[a]	direct methods[a]
no. of data/retrains/ params	6472/0/333	6623/0/337	9641/0/745	17295/55/1194	4577/1/347	9111/24/670
GOF on F^2	1.020	1.021	1.017	0.984	0.988	1.024
R indices ($I > 2\sigma(I)$)[b]	R1 = 0.0260, wR2 = 0.0517	R1 = 0.0224, wR2 = 0.0436	R1 = 0.0280, wR2 = 0.0729	R1 = 0.0600, wR2 = 0.1081	R1 = 0.0169, wR2 = 0.0376	R1 = 0.0253, wR2 = 0.0622
R indices (all data)[b]	R1 = 0.0412, wR2 = 0.0550	R1 = 0.0414, wR2 = 0.0470	R1 = 0.0358, wR2 = 0.0765	R1 = 0.1303, wR2 = 0.1275	R1 = 0.0199, wR2 = 0.0384	R1 = 0.0341, wR2 = 0.0665
max diff peak/hole (e/Å^3)	0.598 −0.498	0.305 −0.302	0.393 −0.356	0.790 −0.633	0.242 −0.357	0.739 −0.762

[a] *SHELXTL-Version 5.1*; Bruker Analytical X-ray systems, Madison, WI. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$.

(s). ^{19}F NMR (C_6D_5Cl): *δ* −132.0 (m, 8F, *o*-C_6F_5), −162.7 (t, $^3J_{FF}$ = 20, 4F, *p*-C_6F_5), −166.5 (m, 8F, *m*-C_6F_5).

Reaction of [(^{i}Pr$_2$-ATI)InMe][B(C_6F_5)$_4$]·C_6H_5Cl (6·PhCl) or [(^{i}Pr$_2$-ATI)InMe][MeB(C_6F_5)$_3$] (7) with Lewis Bases. Solutions of **6**·PhCl or **7** and 1 equiv of the appropriate Lewis base were prepared and warmed to room temperature, and NMR spectra were recorded. In all cases reactions were complete within the time required to obtain NMR spectra (minutes). Data for **10** are given above; data for other cases are listed below.

[(^{i}Pr$_2$-ATI)In(Me)(MeCN)][B(C_6F_5)$_4$] (11). ^{1}H NMR (C_6D_5Cl): *δ* 0.50 (s, 3H, In*Me*), 1.10 (d, $^3J_{HH}$ = 6.1, 12H, CH*Me*$_2$), 1.37 (br s, 3H, *Me*CN), 3.74 (sept, $^3J_{HH}$ = 6.1, 2H, C*H*Me$_2$), 6.54 (t, $^3J_{HH}$ = 9.0, 1H, H^5), 6.65 (d, $^3J_{HH}$ = 11.4, 2H, H^{3,7}), 7.09 (m, 2H, H^{4,6}). ^{13}C NMR (C_6D_5Cl): *δ* −1.4 (q, $^1J_{CH}$ = 139, In*Me*), 0.4 (q, $^1J_{CH}$ = 138, *Me*CN), 24.2 (q, $^1J_{CH}$ = 127, CH*Me*$_2$), 48.5 (d, $^1J_{CH}$ = 137, *C*HMe$_2$), 116.8 (d, $^1J_{CH}$ = 152, C^5), 118.8 (br s, Me*C*N), 123.8 (d, $^1J_{CH}$ = 162, C^{3,7}), 136.9 (d, $^1J_{CF}$ = 243, *C*$_6$F$_5$), 137.0 (d, $^1J_{CH}$ = 155, C^{4,6}), 138.7 (d, $^1J_{CF}$ = 245, *C*$_6$F$_5$), 148.9 (d, $^1J_{CF}$ = 241, *C*$_6$F$_5$), 158.3 (s, C^{1,2}); the *ipso*-C_6F_5 resonance was not observed. ^{11}B NMR (C_6D_5Cl): *δ* −16.5 (s). ^{19}F NMR (C_6D_5Cl): *δ* −132.1 (m, 8F, *o*-C_6F_5), −162.4 (t, $^3J_{FF}$ = 20, 4F, *p*-C_6F_5), −166.5 (m, 8F, *m*-C_6F_5).

[(^{i}Pr$_2$-ATI)In(Me)(Me$_2$CO)][B(C_6F_5)$_4$] (12). ^{1}H NMR (C_6D_5Cl): *δ* 0.73 (s, 3H, In*Me*), 1.18 (d, $^3J_{HH}$ = 5.8, 12H, CH*Me*$_2$), 1.87 (br s, 6H, *Me*$_2$CO), 3.87 (sept, $^3J_{HH}$ = 5.8, 2H, C*H*Me$_2$), 6.71 (t, $^3J_{HH}$ = 9.4, 1H, H^5), 6.81 (d, $^3J_{HH}$ = 11.3, 2H, H^{3,7}), 6.87 (m, 2H, H^{4,6}). ^{13}C NMR (C_6D_5Cl): *δ* −1.0 (q, $^1J_{CH}$ = 135, In*Me*), 24.3 (q, $^1J_{CH}$ = 127, CH*Me*$_2$), 31.0 (q, $^1J_{CH}$ = 128, *Me*$_2$CO), 48.4 (d, $^1J_{CH}$ = 137, *C*HMe$_2$), 117.0 (d, $^1J_{CH}$ = 152, C^5), 124.4 (d, $^1J_{CH}$ = 161, C^{3,7}), 136.8 (d, $^1J_{CF}$ = 243, *C*$_6$F$_5$), 137.1 (d, $^1J_{CH}$ = 156, C^{4,6}), 138.7 (d, $^1J_{CF}$ = 245, *C*$_6$F$_5$), 148.9 (d, $^1J_{CF}$ = 241, *C*$_6$F$_5$), 158.7 (s, C^{1,2}), 221.1 (s, *C*═O); the *ipso*-C_6F_5 resonance was not observed. ^{11}B NMR (C_6D_5Cl): *δ* −16.5 (s). ^{19}F NMR (C_6D_5Cl): *δ* −132.0 (m, 8F, *o*-C_6F_5), −162.7 (t, $^3J_{FF}$ = 20, 4F, *p*-C_6F_5), −166.5 (m, 8F, *m*-C_6F_5).

[(^{i}Pr$_2$-ATI)In(Me)(PMe$_3$)][B(C_6F_5)$_4$] (13). ^{1}H NMR (C_6D_5Cl): *δ* 0.25 (s, 3H, In*Me*), 0.89 (d, $^3J_{HH}$ = 7.9, 9H, P*Me*$_3$), 0.94 (d, $^3J_{HH}$ = 6.1, 12H, CH*Me*$_2$), 3.63 (sept, $^3J_{HH}$ = 6.1, 2H, C*H*Me$_2$), 6.47 (t, $^3J_{HH}$ = 9.6, 1H, H^5), 6.51 (d, $^3J_{HH}$ = 11.3, 2H, H^{3,7}), 7.03 (m, H^{4,6}). ^{13}C NMR (C_6D_5Cl): *δ* −4.2 (q, $^1J_{CH}$ = 132, In*Me*), 10.1 (q, $^1J_{CH}$ = 125, P*Me*$_3$), 24.4 (q, $^1J_{CH}$ = 126, CH*Me*$_2$), 48.2 (d, $^1J_{CH}$ = 133, *C*HMe$_2$), 116.7 (d, $^1J_{CH}$ = 152, C^5), 122.9 (d, $^1J_{CH}$ = 161, C^{3,7}), 136.9 (d, $^1J_{CF}$ = 243, *C*$_6$F$_5$), 137.0 (d, $^1J_{CH}$ = 155, C^{4,6}), 138.7 (d, $^1J_{CF}$ = 245, *C*$_6$F$_5$), 148.9 (d, $^1J_{CF}$ = 241, *C*$_6$F$_5$), 161.3 (s, C^{1,2}); the *ipso*-C_6F_5 resonance was not observed. ^{11}B NMR (C_6D_5Cl): *δ* −16.5 (s). ^{19}F NMR (C_6D_5Cl): *δ* −132.0 (m, 8F, *o*-C_6F_5), −162.5 (t, $^3J_{FF}$ = 20, 4F, *p*-C_6F_5), −166.4 (m, 8F, *m*-C_6F_5). ^{31}P NMR (C_6D_5Cl): *δ* −46.3 (br s).

[(^{i}Pr$_2$-ATI)In(Me)(NMe$_2$Ph)][MeB(C_6F_5)$_3$] (14) and [(^{i}Pr$_2$-ATI)In(Me)(PMe$_3$)][MeB(C_6F_5)$_3$] (15). NMR data for **14** and **15** are identical to data for **10** and **13**, respectively, except for the anion resonances.

X-ray Structural Determinations. Crystal data, data collection details, and solution and refinement procedures are collected in Table 7, and full details are provided in the Supporting Information. The ORTEP diagrams were drawn with 30% probability ellipsoids. All non-hydrogen atoms were refined with anisotropic displacement coefficients unless otherwise indicated. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative anisotropic displacement coefficients. Additional comments specific to each structure follow.

(^{i}Pr$_2$-ATI)InCl$_2$ (3) and (^{i}Pr$_2$-ATI)InMe$_2$ (4). Crystals were grown from a saturated pentane solution to −78 °C.

[{1,2-(N^{i}Pr)$_2$-5-CPh$_3$-cyclohepta-3,6-diene}InMe$_2$][B(C$_6$F$_5$)$_4$] (5). Crystals were grown by slow evaporation of chlorobenzene solution of at 23 °C.

[(^{i}Pr$_2$-ATI)InMe][B(C$_6$F$_5$)$_4$]·C$_6$H$_5$Cl (6·C$_6$H$_5$Cl). The complex was dissolved in chlorobenzene, and pentane was slowly layered on top (chlorobenzene/pentane = 1:2) resulting in slow crystal growth. All non-hydrogen atoms except C(104) and C(105) were refined with anisotropic displacement coefficients. There are two symmetry-independent molecules in the asymmetric unit; one molecule is equally disordered over two positions and was refined with an idealized geometry. There are also two C_6H_5Cl molecules equally disordered over two positions.

(^{i}Pr$_2$-ATI)In(C$_6$F$_5$)$_2$ (9). Crystals were grown from pentane at 23 °C.

[(^{i}Pr$_2$-ATI)In(Me)(NMe$_2$Ph)][B(C$_6$F$_5$)$_4$] (10). The complex was dissolved in chlorobenzene and pentane was slowly layered on top (chlorobenzene/pentane = 1:2), resulting in slow crystal growth. The isopropyl group on N(2) is equally disordered over two positions and was refined with an idealized geometry.

Acknowledgment. This work was supported by DOE grant DE-FG02-88ER13935.

Supporting Information Available: NMR data for anions and Lewis bases in C_6D_5Cl and details of X-ray crystallographic analyses of **3**, **4**, **5**, **6**·PhCl, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010578X