Main-Group-Metal Chlorobenzene Complexes

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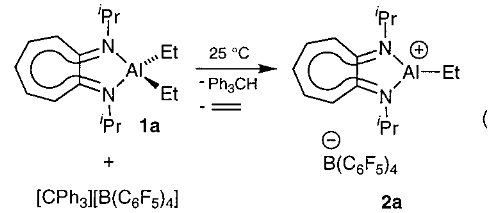
Summary: Stable group 13 metal chlorobenzene complexes of general type [(^{i}Pr$_2$-ATI)MR][B(C$_6$F$_5$)$_4$](ClPh) (M = Al, Ga, In; ^{i}Pr$_2$-ATI = N,N′-diisopropylaminotroponiminate) have been isolated. X-ray crystallographic studies show that the PhCl ligands in these compounds are coordinated by dative M−ClPh bonding and suggest that π-stacking interactions between the PhCl phenyl ring and the ^{i}Pr$_2$-ATI ligand may also contribute to the PhCl coordination.

The coordination of halocarbons to d- and p-block metals plays an important role in metal-mediated carbon−halogen bond activation reactions and Friedel−Crafts alkylations[1,2] and can strongly influence the speciation, stability, and reactivity of unsaturated metal complexes in solution.[3] Halocarbon coordination to d-block metals has been extensively investigated,[3] and η^1 and η^2 chlorocarbon complexes of Mn, Re, Ru, Ir, Pt, and Ag have been crystallographically characterized.[4,5] However, little is known about p-block metal chlorocarbon complexes. Weak bidentate coordination of 1,2-dichloroethane to Tl(I) was observed in the solid-state structure of [Tl(ClCH$_2$CH$_2$Cl)][B(OTeF$_5$)$_4$]; in this case, the C−Cl distance and $\nu_{\mathrm{C-Cl}}$ values are only slightly perturbed upon coordination.[6,7] Vapor pressure measurements of AlX$_3$ and GaX$_3$ solutions in CH$_3$X (X = Cl, Br, I) established the formation of 1:1 MX$_3$(XCH$_3$) adducts,[8] and NMR and UV data support the formation of AlCl$_3$(ClCH$_3$) and AlCl$_3$(Cl$_2$CH$_2$) adducts in solution.[9,10] Here we describe the synthesis and solid-state structures of cationic group 13 metal chlorobenzene complexes of general type [(^{i}Pr$_2$-ATI)MR][B(C$_6$F$_5$)$_4$](ClPh) (M = Al, Ga, In; ^{i}Pr$_2$-ATI = *N*,*N*′-diisopropylaminotroponiminate).

The reaction of (^{i}Pr$_2$-ATI)AlEt$_2$ (**1a**) and 1 equiv of [CPh$_3$][B(C$_6$F$_5$)$_4$] in toluene or pentane/hexanes proceeds by net β-H abstraction and yields [(^{i}Pr$_2$-ATI)AlEt][B(C$_6$F$_5$)$_4$] (**2a**) which can be isolated as a base-free yellow powder (eq 1).[11] Recrystallization of **2a** from chlorobenzene at −40 °C yields yellow crystals of the PhCl complex [(^{i}Pr$_2$-ATI)AlEt(ClPh)][B(C$_6$F$_5$)$_4$] (**2a**(ClPh)) which also contain 0.5 equiv of noncoordinated PhCl of crystallization. This material readily loses PhCl and is converted to base-free **2a** upon exposure to vacuum. The structure of the **2a**(ClPh) unit (Figure 1) consists of a distorted-tetrahedral (^{i}Pr$_2$-ATI)AlEt(ClPh)$^+$ cation which is weakly ion-paired to the B(C$_6$F$_5$)$_4$$^-$ anion.[12] The Al−Cl distance (2.540(3) Å) is somewhat longer than the Al−(μ-Cl) distances in Cl-bridged dialuminum complexes (2.2−2.5 Å)[13] or the sum of the Al and Cl covalent radii (2.24 Å) but is far shorter than the sum of Al and Cl van der Waals (vdW) radii (3.8 Å),[14] consistent with a dative Al−ClPh bond. The Al−ClPh interaction does not significantly perturb the C−Cl bond distance (1.774-



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† The University of Chicago.

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(1) (a) Kulawiec, R. J.; Faller, J. W.; Crabtree, R. H. *Organometallics* **1990**, *9*, 745. (b) Winter, C. H.; Veal, W. R.; Garner, C. M.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 4766. (c) Tjaden, E. B.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1995**, *14*, 371. (d) Poignant, G.; Sinbandhit, S.; Toupet, L.; Guerchais, V. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 963. (e) Grushin, V. V.; Alper, H. *Chem. Rev.* **1994**, *94*, 1047.

(2) (a) Olah, G. A. *Friedel−Crafts Chemistry*; Wiley: New York, 1973; p 311. (b) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 479.

(3) (a) Kulawiec, R. J.; Crabtree, R. H. *Coord. Chem. Rev.* **1990**, *99*, 89. (b) Plenio, H. *Chem. Rev.* **1997**, *97*, 3363.

(4) (a) Fang, X.; Huhmann-Vincent, J.; Scott, B. L.; Kubas, G. J. *J. Organomet. Chem.* **2000**, *609*, 95. (b) Huhmann-Vincent, J.; Scott, B. L.; Kubas, G. J. *Inorg. Chem.* **1999**, *38*, 115. (c) Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970. (d) Butts, M. D.; Scott, B. L.; Kubas, G. J. *J. Am. Chem. Soc.* **1996**, *118*, 11831. (e) Huhmann-Vincent, J.; Scott, B. L.; Kubas, G. J. *J. Am. Chem. Soc.* **1998**, *120*, 6808. (f) Fornies, J.; Martinez, F.; Navarro, R.; Urriolabeitia, E. P. *Organometallics* **1996**, *15*, 1813. (g) Van Seggen, D. M.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1992**, *31*, 2987.

(5) (a) Huang, D.; Bollinger, J. C.; Streib, W. E.; Folting, K.; Young, V., Jr.; Eisenstein, O.; Caulton, K. G. *Organometallics* **2000**, *19*, 2281. (b) Huang, D.; Huffman, J. C.; Bollinger, J. C.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1997**, *119*, 7398. (c) Van Seggen, D. M.; Hurlburt, P. K.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1995**, *34*, 3453.

(6) Hurlburt, P. K.; Anderson, O. P.; Strauss, S. H. *Can. J. Chem.* **1992**, *70*, 726.

(7) Bidentate coordination of 1,2-dichloroethane to Cs$^+$ was reported recently: Levitskaia, T. G.; Bryan, J. C.; Sachleben, R. A.; Lamb, J. D.; Moyer, B. A. *J. Am. Chem. Soc.* **2000**, *122*, 554.

(8) (a) Brown, H. C.; Eddy, L. P.; Wong, R. *J. Am. Chem. Soc.* **1953**, *75*, 6275. (b) Brown, H. C.; Wallace, W. J. *J. Am. Chem. Soc.* **1953**, *75*, 6279.

(9) Kennedy, J. P.; Thomas, R. M. *J. Polym. Sci.* **1960**, *45*, 227.

(10) Toman, L.; Spevacek, J.; Pokorny, S. *J. Polym. Sci., A: Polym. Chem.* **1989**, *27*, 785.

(11) (a) Ihara, E.; Young, V. G., Jr.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 8277. (b) The synthesis of (^{i}Pr$_2$-ATI)AlMe$_2$ compounds by reaction of (^{i}Pr$_2$-ATI)H and AlMe$_3$ is described in: Dias, H. V. R.; Jin, W.; Ratcliff, R. E. *Inorg. Chem.* **1995**, *34*, 6100. Similar methods were used for the synthesis of **1a**−**c**.

(12) (a) X-ray data for **2a**(ClPh)·0.5ClPh: monoclinic, $P2_1/c$, a = 14.2338(9) Å, b = 20.026(1) Å, c = 16.546(1) Å, β = 98.450(1)°, V = 4665.1(5) Å^3, Z = 4, T = 173(2) K, D_{calcd} = 1.576 g/cm^3, R1 = 0.0879, wR2 = 0.1855 ($I \geq 2\sigma(I)$). (b) X-ray data for **2c**(ClPh): monoclinic, $P2_1/c$, a = 17.4035(9) Å, b = 10.8193(6) Å, c = 45.479(2) Å, β = 90.708(1)°, V = 8562.7(8) Å^3, Z = 8, T = 183(2) K, D_{calcd} = 1.745 g/cm^3, R1 = 0.0600, wR2 = 0.1081 ($I \geq 2\sigma(I)$). (c) Further details concerning the synthesis, characterization, and crystallographic analysis of **2a**(ClPh)·0.5ClPh and **2c**(ClPh) are given in the Supporting Information.

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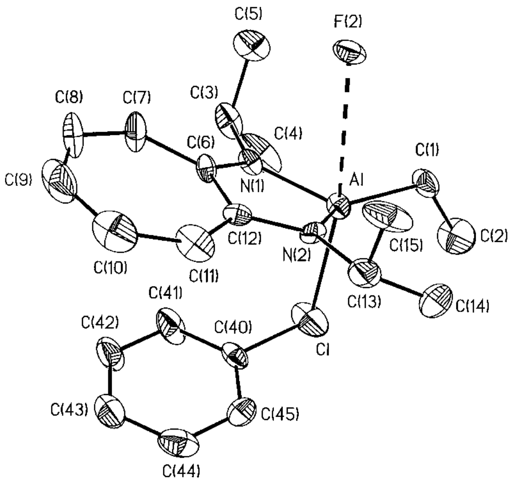


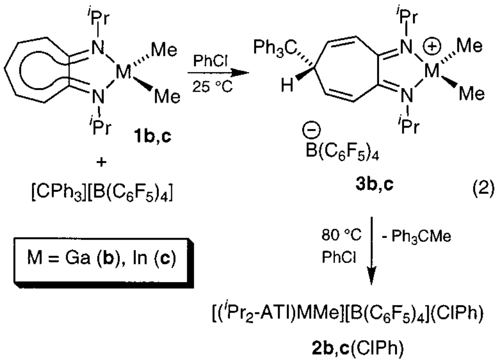
Figure 1. Structure of the [(^{i}Pr$_2$-ATI)AlEt(ClC$_6$H$_5$)][B(C$_6$F$_5$)$_4$] unit in **2a**(ClC$_6$H$_5$)·0.5C$_6$H$_5$Cl. Only the B(C$_6$F$_5$)$_4^-$ fluorine atom that is closest to Al (F(2)) is shown. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg) not given in the text: Al−N(1) = 1.827(6), Al−N(2) = 1.850(5), Al−C(1) = 1.919(7); Al−C(1)−C(2) = 119.4(6), N(1)−Al−N(2) = 87.8(2), N(1)−Al−C(1) = 129.3(3), N(1)−Al−Cl = 99.4(2), N(2)−Al−C(1) = 133.8(3), N(2)−Al−Cl = 99.3(2), C(1)−Al−Cl = 99.9(2). Hydrogen atoms are omitted.

(7) Å vs 1.737(5) Å in free PhCl in the gas phase)[15] but does induce a 0.31 Å displacement of the Al atom out of the N(1)−N(2)−C(1) plane (sum of angles at Al 350.9°). Additionally, the PhCl phenyl ring is positioned close to the ^{i}Pr$_2$-ATI ligand in an orientation that permits an attractive π-stacking interaction.[16] The distances between PhCl carbon atoms and the plane of the ^{i}Pr$_2$-ATI ligand are between 3.3 and 4.0 Å, and the PhCl ring is shifted to one side of the ^{i}Pr$_2$-ATI ligand such that the electron-deficient PhCl ipso carbon lies under the electron-rich N(2) atom (C(40)- - -N(2) = 3.39 Å), and the centroid of the PhCl phenyl ring lies under the electron-deficient ^{i}Pr$_2$-ATI iminato carbon atom (centroid- - -C(12) = 3.66 Å). The Al−Cl−Ph angle is 102.7(2)°, and the angle between the PhCl and ^{i}Pr$_2$-ATI planes is 17.1°. The closest Al−F contact to the anion (Al- - -F(2) = 3.23 Å) is close to the sum of the Al and F vdW radii (3.52 Å),[14] indicating that the cation−anion interaction is extremely weak.[17]

The Al−ClPh coordination in **2a**(ClPh) is similar to the Al−F ion-pairing interactions in the β-diketiminate complexes [{HC(CMeNAr)$_2$}AlMe][B(C$_6$F$_5$)$_4$] and [{HC(CMeNAr)$_2$}AlMe][MeB(C$_6$F$_5$)$_3$] (Ar = 2,6-diisopropylphenyl) in the solid state.[18] In these complexes, the Al−FC distances (2.151(1) and 2.275(1) Å, respectively) are much closer to the sum of the Al and F covalent radii (1.89 Å) than to the sum of the vdW radii (3.52 Å), and the Al is displaced from the N$_2$C plane toward the anion by 0.28 and 0.24 Å, respectively. The Al−ClPh distance in **2a**(ClPh) is similar to the Al−F distances in these β-diketiminate complexes after the difference in the Cl and F radii is taken into account.

Variable-temperature multinuclear NMR spectra of **2a** in C$_6$D$_5$Cl (to −40 °C) and CD$_2$Cl$_2$ (to −90 °C) establish that the (^{i}Pr$_2$-ATI)AlEt$^+$ cation retains effective C_{2v} symmetry and that ion-pairing interactions are not significant enough to perturb the spectra of the B(C$_6$F$_5$)$_4^-$ anion in these chlorocarbon solvents. It is likely that **2a** forms **2a**(ClR) adducts and that intermolecular RCl exchange is rapid in chlorocarbon solution.

The reaction of (^{i}Pr$_2$-ATI)MMe$_2$ (M = Ga, **1b**; M = In, **1c**)[11b] with 1 equiv of [CPh$_3$][B(C$_6$F$_5$)$_4$] in PhCl at 25 °C yields the diimine complexes [{Ph$_3$CCH(CH=CHC=N^{i}Pr)$_2$}MMe$_2$][B(C$_6$F$_5$)$_4$] (**3b**,**c**) via electrophilic addition of CPh$_3^+$ to the ATI ring (eq 2).[19]



(2)

Compounds **3b**,**c** are stable at 25 °C but undergo Ph$_3$CMe elimination within minutes (Ga) or hours (In) at 80 °C to afford [(^{i}Pr$_2$-ATI)MMe][B(C$_6$F$_5$)$_4$](ClPh) (**2b**,**c**(ClPh)), probably by dissociation of CPh$_3^+$ and subsequent Me$^-$ abstraction.

Compounds **2b**,**c** crystallize from PhCl/hexane or PhCl/pentane as **2b**(ClPh) and **2c**(ClPh) solvates which have been characterized by X-ray diffraction. For the In complex **2c**(ClPh), there are two independent cations in the asymmetric unit. One cation (In(1)) is ion-paired with two B(C$_6$F$_5$)$_4^-$ 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 2) is distorted trigonal bipyramidal (tbp) with the two axial positions occupied by the B(C$_6$F$_5$)$_4^-$ 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) contacts are intermediate between the sums of the In and F covalent (2.14 Å) and vdW radii (3.37 Å). Similar In−F distances were ob-

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(13) Representative examples are as follows. (a) [(BHT)AlMe(μ-Cl)]$_2$ (BHT = 2,6-bis-*tert*-butyl, 4-methylphenoxide; Al−Cl = 2.277(3) and 2.291(3) Å): Healy, M. D.; Ziller, J. W.; Barron, A. R. *Organometallics* **1992**, *11*, 3041. (b) [(ArO)AlMe(μ-Cl)]$_2$ (Ar = 2,6-bis-*tert*-butylphenyl; Al−Cl 2.298(2) Å): Jegier, J. A.; Atwood, D. A. *Bull. Soc. Chim. Fr.* **1996**, *133*, 965. (c) Starowieyski, K. B. In *Chemistry of Aluminium, Gallium, Indium and Thallium*; Downs, A. J., Ed.; Chapman & Hall: London, 1993; pp 322−371.

(14) The covalent and van der Waals radii for Al (1.25 and 2.05 Å) and In (1.50 and 1.90 Å) were taken from ref 13c, p 2, and those for F (0.64 and 1.47 Å) and Cl (0.99 and 1.75 Å) were taken from ref 3a.

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

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

(17) The Re PhCl complexes [(C$_5$R$_5$)Re(NO)(PPh$_3$)(ClPh)][BF$_4$] (C$_5$R$_5$ = C$_5$H$_5$, C$_5$Me$_5$) have been characterized in C$_6$H$_5$Cl/C$_6$D$_5$Cl solution by multinuclear NMR. These species exist predominantly as Cl-ligated isomers at −45 °C, but other isomers are also observed at higher temperatures: (a) Peng, T.-S.; Winter, C. H.; Gladysz, J. A. *Inorg. Chem.* **1994**, *33*, 2534. (b) Kowalczyk, J. J.; Agbossou, S. K.; Gladysz, J. A. *J. Organomet. Chem.* **1990**, *397*, 333.

(18) Radzewich, C. E.; Guzei, I. A.; Jordan, R. F. *J. Am. Chem. Soc.* **1999**, *121*, 8673.

(19) (a) Compounds **3b**,**c** were characterized by X-ray diffraction: Dagorne, S.; Delpech, F.; Guzei, I. A.; Jordan, R. F. Unpublished results. (b) The reaction of **1a** and [CPh$_3$][B(C$_6$F$_5$)$_4$] in CD$_2$Cl$_2$ at −90 °C yields the analogous intermediate **3a**, which is converted to **2a** at −40 °C.

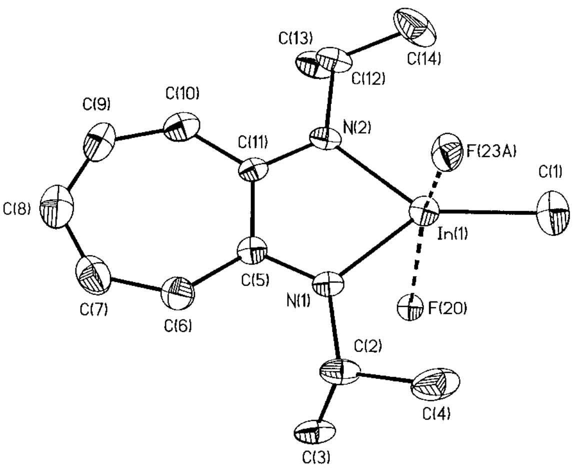

Figure 2. Structure of the In(1) site in **2c**(C_6H_5Cl). Only the coordinated F atoms of the two axial $B(C_6F_5)_4^-$ anions (F(23A), F(20)) are shown. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg) not given in text: In(1)−N(1) = 2.069(4), In(1)−N(2) = 2.070(4), In(1)−C(1) = 2.088(5); N(1)−In(1)−N(2) = 79.5(2), N(1)−In(1)−C(1) = 138.1(2), N(2)−In(1)−C(1) = 142.2(2). Hydrogen atoms are omitted.

served for the intramolecular In−F contacts in $In_2(R^F)_4$ and $In(R^F)_3$ (R^F = 2,4,6-tris(trifluoromethyl)phenyl).[20]

The In(2) and In(3) cations of **2c**(ClPh) are structurally very similar and feature tbp geometries with PhCl ligands in the axial positions (Figure 3a). The In−Cl 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).[14] The ca. 0.23 Å difference in In−Cl distances indicates that one PhCl molecule is more strongly coordinated than the other. The In−ClPh dative bond distances in **2c**(ClPh) are comparable to the In−Cl−In distances in polymeric $MeInCl_2$ (3.20 Å) and $\{(H_2Bpz_2)InMe(\mu\text{-}Cl)\}_2$ ($H_2Bpz_2^-$ = dihydrobis(pyrazolyl)borate; 3.066(1) and 3.203(1) Å).[21,22] The C(200)−Cl(2) (1.702(6) Å) and C(300)−Cl(3) (1.729(5) Å) bond distances in **2c**(ClPh) are close to the C−Cl bond distance in free chlorobenzene.[15] As illustrated in Figure 3b, the two PhCl ligands are π-stacked with the ^{i}Pr$_2$-ATI$^-$ ligand in an arrangement similar to that in **2a**(ClPh). The PhCl rings 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 PhCl ipso carbons are located above and below the ^{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 ^{i}Pr$_2$-ATI iminato carbons (centroid(200)- - -C(11B) = 3.41 Å, centroid(300)- - -C(5B) = 3.47 Å). The structure of the Ga complex **2b**(ClPh) is similar to that of **2c**(ClPh).[12c] However, in this case the PhCl molecules are severely disordered, which precludes a detailed comparison of **2b**(ClPh) and **2c**(ClPh).

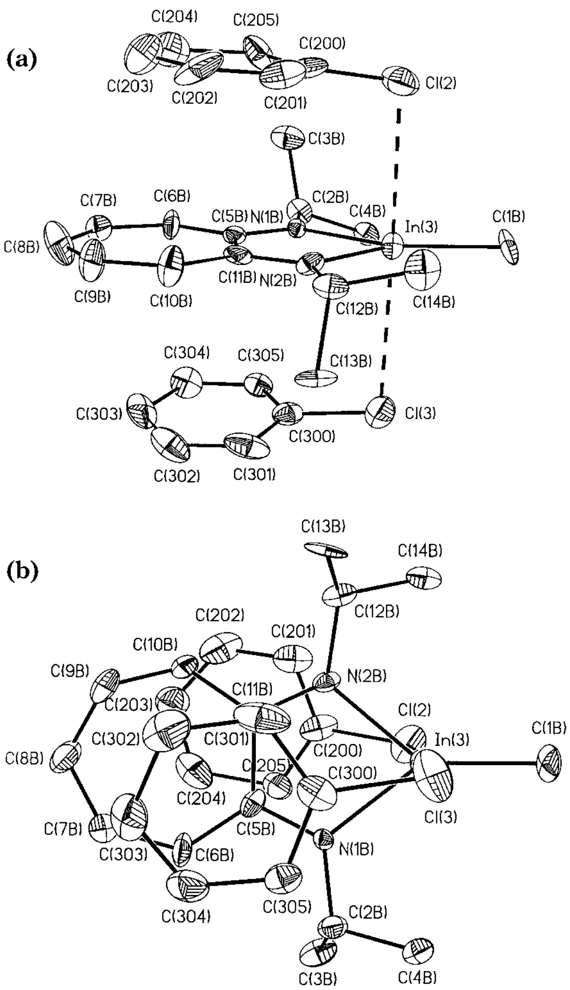

Figure 3. Two views (a, b) of the In(3) site in **2c**(C_6H_5Cl). Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg) not given in text: In(3)−N(1B) = 2.100(1), In(3)−N(2B) = 2.100(1), In(3)−C(1B) = 2.121(1); N(1B)−In(3)−N(2B) = 79.2(2), N(1B)−In(3)−C(1B) = 141.2(4), N(2B)−In(3)−C(1B) = 139.6(4), In(3)−Cl(2)−C(200) = 99.8(2), In(3)−Cl(3)−C(300) = 96.1(2). Hydrogen atoms are omitted. The In(2) site is very similar.

This work shows that cationic group 13 alkyl species (^{i}Pr$_2$-ATI)MR$^+$ (M = Al, Ga, In) coordinate chlorobenzene through dative M−ClPh bonding and suggests that attractive PhCl/(^{i}Pr$_2$-ATI) π-stacking interactions may also contribute to the overall PhCl complexation in the solid state. Similar solvent interactions probably stabilize these and related cationic main-group complexes in solution. Further studies of the bonding and reactivity of these main-group halocarbon complexes will be reported in due course.

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

Supporting Information Available: Text giving details of the syntheses of all new compounds and text and tables giving details of the X-ray crystal structures of **2a**(ClPh)·0.5PhCl, **2b**(ClPh), and **2c**(ClPh). This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) 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.

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

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