Neutral and Cationic Group 13 Alkyl and Hydride Complexes of a Phosphinimine−Amide Ligand

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The phosphinimine−amine ligand **1** reacts with MR_3 (M = Al, Ga; R = Me, H) with loss of RH to form the complexes (i-$Pr_2C_6H_3N$)C(Me)CHPPh_2(NC_6H_3-i-Pr_2)MMe_2 (M = Al (**2**), Ga (**3**)) and (i-$Pr_2C_6H_3N$)C(Me)CHPPh_2(NC_6H_3-i-Pr_2)AlH_2 (**4**). Subsequent reactions of **2** and **3** with $[Ph_3C][B(C_6F_5)_4]$ afforded $[(i\text{-}Pr_2C_6H_3N)C(Me)CHPPh_2(NC_6H_3\text{-}i\text{-}Pr_2)MMe][B(C_6F_5)_4]$ (M = Al (**5**), Ga (**6**)), while similar reactions of **2** and **3** with $B(C_6F_5)_3$ gave $[(i\text{-}Pr_2C_6H_3N)C(Me)CHPPh_2(NC_6H_3\text{-}i\text{-}Pr_2)MMe][B(C_6F_5)_3Me]$ (M = Al (**8**), Ga (**9**)). The analogous reactions of **4** with $[Ph_3C][B(C_6F_5)_4]$ and $B(C_6F_5)_3$ resulted in the formation of $[(i\text{-}Pr_2C_6H_3N)C(Me)CHPPh_2(NC_6H_3\text{-}i\text{-}Pr_2)AlH][B(C_6F_5)_4]$ (**10**) and $[(i\text{-}Pr_2C_6H_3N)C(Me)CHPPh_2(NC_6H_3\text{-}i\text{-}Pr_2)AlH][B(C_6F_5)_3H]$ (**11**), respectively. Crystallographic studies of **1**, **2**, **4**, and $[(i\text{-}Pr_2C_6H_3N)C(Me)CHPPh_2(NC_6H_3\text{-}i\text{-}Pr_2)AlMe(OEt_2)][B(C_6F_5)_4]$ (**7**) are reported.

Introduction

A recent review has summarized the use of β-diketimine ligands in the synthesis of metal complexes.[1] Jordan and co-workers have employed a bulky β-diketiminine ligand with 2,6-diisopropylphenyl substituents (NacNac) on the N atoms to prepare base-free monomeric aluminum cations.[2,3] The groups of Roesky and Power have also utilized this ligand to isolate unique Al(I)[4] and Ga(I)[5] complexes as well as Al(III) dihydroxide,[6] dithiol,[7] and diselinide[8] complexes. In targeting related ligands that provide thermal stability, additional sites for modification, and a spectroscopic handle, we have recently focused attention on the mixed-donor ligands incorporating phosphinimine donors and other N- or C-based donors.[9,10] We have also shown that, in late-transition-metal complexes, phosphinimine−imido ligands are stronger donors than their β-diketimide analogues.[9] Our previous studies also showed that, in the absence of other sterically demanding ligands, phosphinimine−amide ligands provide significantly increased steric congestion about the metal center as a result of the inclusion of the R_2PNR' fragment. In an effort to exploit such steric crowding, we sought to prepare group 13 complexes where the steric bulk would preclude dimerization or higher aggregation. Thus, in this paper, we describe the preparation and characterization of a series of monometallic neutral and cationic group 13 alkyl and hydride complexes incorporating a phosphinimine−amide ligand. Structural data are presented, and the implications are considered. Related systems are described in the preceding paper by Piers and co-workers.[11]

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2, employing both Schlenk line techniques and a Vacuum Atmospheres inert-atmosphere glovebox. Solvents were purified employing a Grubbs-type solvent purification system manufactured by Innovative Technology. Deuterated solvents were purified using the appropriate techniques. All organic reagents were purified by conventional methods. ^1H, $^{31}P\{^1H\}$, $^{11}B\{^1H\}$, $^{19}F\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker Avance-300 and -500 spectrometers. All spectra were recorded in C_6D_6 at 25 °C unless otherwise noted. Trace amounts of protonated solvents were used as references, and chemical shifts (in ppm) are reported relative to $SiMe_4$. $^{31}P\{^1H\}$, $^{11}B\{^1H\}$, and $^{19}F\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4, $BF_3{\cdot}Et_2O$, and $CFCl_3$, respectively. Combustion analyses were done in house employing a Perkin-Elmer CHN analyzer. The ligand (i-$Pr_2C_6H_3NH$)C(Me)CHPPh_2(NC_6H_3-i-Pr_2) (**1**) was prepared by literature methods.[10] Single crystals of **1** were grown over several weeks by the slow evaporation of a toluene solution. The deuterated alane $(Et_2O)AlD_3$ was prepared in situ by the method outlined by Carey et al. for $(Et_2O)AlH_3$.[12]

Synthesis of (i-$Pr_2C_6H_3N$)C(Me)CHPPh_2(NC_6H_3-i-Pr_2)MMe_2 (M = Al (2), Ga (3)) and (i-$Pr_2C_6H_3N$)C(Me)CHPPh_2(NC_6H_3-i-Pr_2)AlH_2 (4). These compounds were prepared in a similar fashion using $AlMe_3$, $GaMe_3$, and $AlH_3{\cdot}NEt_2Me$, re-

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spectively, and thus only one preparation is detailed. To a solution of **1** (0.321 g, 0.556 mmol) in 5 mL of *n*-pentane was added $AlMe_3$ (0.042 g) in 5 mL of *n*-pentane. A white precipitate formed over several minutes, and the mixture was stirred overnight. Volatiles were removed in vacuo, yielding a white powder. The material was purified by dissolving in a minimum of hot *n*-heptane and cooling the solution to room temperature, affording large colorless blocks of **2** (210 mg) in 60% yield. **2**: ^{1}H NMR 7.50−7.57 (m, 4H, *o*-PPh_2), 6.94−7.12 (m, 12H, *m*, *p*-PPh_2, *m*, *p*-Dip), 3.73 (sept, $|J_{H-H}| = 7$ Hz, 2H, CH), 3.58 (sept, $|J_{H-H}| = 7$ Hz, 2H, CH), 3.27(d, $|^2J_{P-H}| = 19$ Hz, 1H, C*H*P), 1.73 (d, $|^4J_{P-H}| = 2$ Hz, 3H, Me), 1.38 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 1.28 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 1.13 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*$^-$Pr), 0.25 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), −0.24 (s, AlMe, 6H); ^{13}C{^{1}H} NMR 173.8 (NC), 148.5 (d, $|J_{P-C}| = 5$ Hz), 145.8, 143.3, 137.9 (d, $|J_{P-C}| = 9$ Hz) 134.2 (d, $|J_{P-C}| = 10$ Hz), 132.2, 131.6, 130.9, 127.7−128.3 (m, obscured by C_6D_6), 126.3, 125.9, 124.8, 124.2, 64.4 (d, $|J_{P-C}| = 129$ Hz), 30.2, 28.8, 28.4, 26.2 (d, $|^2J_{P-C}| = 16$ Hz), 25.7, 25.1, 14.2, −6.9; ^{31}P{^{1}H} NMR 24.2. Anal. Calcd for $C_{41}H_{54}AlN_2P$: C, 77.81; H, 8.60; N, 4.43. Found: C: 77.22; H, 8.98; N, 4.40 **3**: yield 85%; ^{1}H NMR 7.67−7.74 (m, 4H, *o*-PPh_2), 7.15−7.25 (m, 12H, *m*, *p*-PPh_2, *m*, *p*-Dip), 3.82 (sept, $|J_{H-H}| = 7$ Hz, 2H, CH), 3.70 (sept, $|J_{H-H}| = 7$ Hz, 2H, CH), 3.32 (d, $|^2J_{P-H}| = 19$ Hz, 1H, C*H*P), 1.89 (d, $|^4J_{P-H}| = 2$ Hz, 3H, Me), 1.45 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 1.40 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 1.22 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 0.44 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 0.16 (s, GaMe, 6H); ^{13}C{^{1}H} NMR 173.0 (NC), 148.5 (d, $|J_{P-C}| = 6$ Hz), 145.6, 144.1, 139.1 (d, $|J_{P-C}| = 9$ Hz), 133.9 (d, $|J_{P-C}| = 9$ Hz), 133.3, 131.2, 127.7−128.3 (m, obscured by C_6D_6), 126.1, 125.4, 124.6, 124.1, 62.9 (d, $|^1J_{P-C}| = 134$ Hz), 28.6, 28.3, 27.8, 26.2 (d, $|^2J_{P-C}| = 16$ Hz), 25.6, 25.0, 22.2, −4.7; ^{31}P{^{1}H} NMR 22.8. Anal. Calcd for $C_{41}H_{54}GaN_2P$: C, 72.89; H, 8.06; N, 4.15. Found: C, 72.46; H, 8.09; N, 4.11. **4**: 337 mg, colorless needles; yield 60%; ^{1}H NMR (major isomer) 7.55−7.61 (m, 4H, *o*-PPh_2), 6.70−7.29 (m, 12H, *m*, *p*-PPh_2, *m*, *p*-Dip), 4.59 (vbr s, 2H, AlH), 3.78 (sept, $|J_{H-H}| = 7$ Hz, 2H, CH), 3.65 (sept, $|J_{H-H}| = 7$ Hz, 2H, CH), 3.44 (d, $|^2J_{P-H}| = 22$ Hz, 1H, C*H*P), 1.69 (d, $|^4J_{P-H}| = 1$ Hz, 3H, Me), 1.47 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 1.28 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 1.26 (d, $J_{H-H} = 7$ Hz, 6H, *i*-Pr), 0.37 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr); ^{13}C{^{1}H} NMR (major isomer) 171.3 (NC), 148.7 (d, $|J_{P-C}| = 5$ Hz), 147.0, 141.7, 133.9 (d, $|J_{P-C}| = 9$ Hz), 132.1, 131.1, 130.9, 127.7−129.1 (m, obscured by C_6D_6), 127.3, 126.6, 124.8, 124.4, 63.7 (d, $|J_{P-C}| = 127$ Hz), 29.5, 28.9, 27.7, 26.3 (d, $|^2J_{P-C}| = 17$ Hz), 26.3 (s), 25.2, 22.9; ^{31}P{^{1}H} NMR 30.0 (major isomer), 24.3 (minor isomer); IR (KBr pellet) 1828 (asym Al−H), 1770 (sym Al−H) cm^{-1}. Anal. Calcd for $C_{39}H_{50}AlN_2P$: C, 77.45; H, 8.33; N, 4.63. Found: 76.95; H, 8.64; N, 4.65.

Synthesis of (*i*-$Pr_2C_6H_3N$)C(Me)CHPPh_2(NC_6H_3-*i*-Pr_2)-AlD_2 (4_d). To a suspension of $LiAlD_4$ (9 mg, 0.214 mmol) in 5 mL of diethyl ether cooled to −30 °C was added $AlCl_3$ (27 mg, 0.202 mmol) in 5 mL of diethyl ether cooled to the same temperature. The mixture was placed in the freezer and periodically shaken over a 10 min period. The gray $LiAlD_4$ was slowly replaced with a white precipitate of LiCl. To this suspension was added **1** (100 mg, 0.173 mmol) in 5 mL of diethyl ether, and the mixture was warmed to 25 °C overnight with stirring. The mixture was filtered through Celite and diethyl ether removed from the filtrate under vacuum. The resulting white powder was dissolved in 10 mL of hot *n*-heptane and filtered through Celite to remove any remaining $LiAlD_4$. Cooling of the solution overnight gave 63 mg of colorless needles (yield 60%). ^{2}D NMR (toluene): 4.55 (br s, Al−D). IR (KBr pellet): 1324 (asym Al−D), 1286 (sym Al−D) cm^{-1}.

Generation of [(*i*-$Pr_2C_6H_3N$)C(Me)CHPPh_2(NC_6H_3-*i*-Pr_2)MMe][$B(C_6F_5)_4$] (M = Al (5), Ga (6)), [(*i*-$Pr_2C_6H_3N$)C-(Me)CHPPh_2(NC_6H_3-*i*-Pr_2)MMe][$B(C_6F_5)_3$Me] (M = Al (8), Ga (9)), and [(*i*-$Pr_2C_6H_3N$)C(Me)CHPPh_2(NC_6H_3*i*-Pr_2)AlH]-[$B(C_6F_5)_3$H] (11). These compounds were prepared in a similar fashion, and thus only one preparation is detailed. In a NMR tube, 30 mg (0.047 mmol) of **4** and 1 equiv of [Ph_3C][$B(C_6F_5)_4$] (44 mg) were combined in approximately 0.6 mL of C_6D_5Cl. The contents were shaken until completely dissolved, and NMR experiments showed quantitative formation of **5**. **5**: ^{1}H NMR (C_6D_5Cl) 7.03−7.46 (m, 16H, *o*-, *m*-, *p*-PPh_2, *m*-, *p*-Dip), 4.32 (d, $|^2J_{P-H}| = 21$ Hz, 1H, C*H*P), 3.14 (sept, $|J_{H-H}| = 7$ Hz, 2H, CH), 2.82 (sept, $|J_{H-H}| = 7$ Hz, 2H, CH), 1.81 (s, 3H, Me), 1.31 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 1.25 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 0.92 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 0.37 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), −0.70 (s, 3H, AlMe); ^{13}C{^{1}H} NMR (C_6D_5Cl) 170.7, 149.8 (br), 149.2, 147.8 (br), 146.3 (d, $|J_{P-C}| = 4$ Hz), 144.9, 139.5 (br), 137.7 (br), 135.7 (br), 135.0, 134.4, 134.1, 132.4 (d, $|J_{P-C}| = 10$ Hz), 127.9−129.6 (m, obscured by C_6D_5Cl), 125.6−126.3 (m, obscured by C_6D_5Cl), 125.4, 124.9, 124.0, 72.2 (d, $|J_{P-C}| = 113$ Hz), 52.5, 30.4, 29.6, 29.3, 25.5, 24.9 (d, $|^2J_{P-C}| = 16$ Hz), 24.5, 23.1, 21.6; ^{31}P{^{1}H} NMR (C_6D_5Cl) 31.0; ^{11}B{^{1}H} NMR (C_6D_5Cl) −16.4; ^{19}F{^{1}H} NMR (C_6D_5Cl) 132.2 (d, $|^3J_{F-F}| = 6$ Hz), −163.0 (d of d, $|^3J_{F-F}| = 20$ Hz), −166.8 (d of d, $|^3J_{F-F}| = 17$ Hz). **6**: ^{1}H NMR (C_6D_5Cl) 7.15−7.55 (m, 16H, *o*-, *m*-, *p*-PPh_2, *m*-, *p*-Dip), 4.38 (d, $|J_{P-H}| = 21$ Hz, 1H, C*H*P), 3.22 (sept, $|J_{H-H}| = 7$ Hz, 2H, CH), 2.95 (sept, $|J_{H-H}| = 7$ Hz, 2H, CH), 1.84 (s, 3H, Me), 1.40 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 1.29 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 1.03 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 0.49(d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), −0.08 (s, 3H, GaMe); ^{31}P{^{1}H} NMR (C_6D_5Cl) 32.1; ^{13}C{^{1}H} NMR (C_6D_5Cl) 169.7, 150.6 (br), 149.3, 147.3 (br), 146.2 (d, $|J_{P-C}| = 4$ Hz), 144.6, 140.3 (br), 138.4 (br), 135.4, 135.2 (br), 134.4, 132.3 (d, $|J_{P-C}| = 10$ Hz), 127.9−129.6 (m, obscured by C_6D_5Cl), 125.6−126.3 (m, obscured by C_6D_5Cl), 125.3, 124.9, 124.5, 71.4 (d, $|^1J_{P-C} = 115$ Hz, PCH), 52.7, 30.5, 29.6, 29.0, 25.4, 25.1 (d, $|^2J_{P-C}| = 16$ Hz), 24.5, 23.2, 22.1, 21.7; ^{11}B{^{1}H} NMR (C_6D_5Cl) −16.5; ^{19}F{^{1}H} NMR (C_6D_5Cl) −132.1 (s), −163.0 (d of d, $|^3J_{F-F}| = 21$ Hz), −166.8 (s). **8**: ^{1}H NMR (C_6D_5Cl) 7.07−7.42 (m, 16H, *o*-, *m*-, *p*-PPh_2, *m*-, *p*-Dip), 4.32 (d, $|^2J_{P-H}| = 21$ Hz, 1H, C*H*P), 3.12 (sept, $|J_{H-H}| = 7$ Hz, 2H, CH), 2.80 (sept, $|J_{H-H}| = 7$ Hz, 2H, CH), 1.72 (s, 3H, Me), 1.29 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 1.23 (s, 3H, AlMeB), 1.32 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 0.96 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 0.35 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), −0.73 (s, 3H, AlMe); ^{13}C{^{1}H} NMR (C_6D_5Cl) 169.9 (NC), 150.2 (br), 148.2 (br), 146.5, 145.1, 138.9 (br), 137.8 (br), 136.9 (br), 135.8 (br), 135.0, 134.4, 132.4 (d, $|J_{P-C}| = 9$ Hz), 129.0−129.5 (m, obscured by C_6D_5Cl), 128.0−128.5 (m, obscured by C_6D_5Cl), 125.8−126.3 (m, obscured by C_6D_5Cl), 125.4, 124.9, 124.1, 71.4 (d, $|J_{P-C}| = 114$ Hz), 29.6, 29.3, 25.6, 25.0 (d, $|^2J_{P-C}| = 17$ Hz), 23.2, 21.7, −14.2 (vbr); ^{31}P{^{1}H} NMR (C_6D_5Cl) 31.4; ^{11}B{^{1}H} NMR (C_6D_5Cl) −14.6; ^{19}F{^{1}H} NMR (C_6D_5Cl) −132.2 (d, $|^3J_{F-F}| = 22$ Hz), −164.9 (d of d, $|^3J_{F-F}| = 21$ Hz), −167.3 (d of d, $|^3J_{F-F}| = 21$ Hz). **9**: ^{1}H NMR (C_6D_5Cl) 7.18−7.46 (m, 16H, *o*-, *m*-, *p*-PPh_2, *m*-, *p*-Dip), 4.31 (d, $|^2J_{P-H}| = 20$ Hz, 1H, C*H*P), 3.12 (sept, $|J_{H-H}| = 7$ Hz, 2H, CH), 2.85 (sept, $|J_{H-H}| = 7$ Hz, 2H, CH), 1.76 (s, 3H, Me), 1.30 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 1.25 (br s, 3H, GaMeB), 1.20 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 0.94 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 0.39 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), −0.14 (s, 3H, GaMe); ^{13}C{^{1}H} NMR (C_6D_5Cl) 169.6, 150.8 (br), 147.5 (br), 146.2 (d, $|J_{P-C}| = 4$ Hz), 144.6, 138.4 (m), 136.8, 135.3, 134.4, 134.1, 132.3 (d, $|J_{P-C}| = 10$ Hz), 127.9−129.6 (m, obscured by C_6D_5Cl), 125.6−126.3 (m, obscured by C_6D_5Cl), 125.3, 124.9, 124.5, 70.9 (d, $|^1J_{P-C}| = 114$ Hz, P−C−H), 29.3, 28.9, 25.4, 25.1 (d, $|^2J_{P-C}| = 16$ Hz), 24.5, 23.1, 21.7, −9.1; ^{31}P{^{1}H} NMR (C_6D_5Cl) 32.1; ^{11}B{^{1}H} NMR (C_6D_5Cl) −14.7; ^{19}F{^{1}H} NMR (C_6D_5Cl) −132.1 (d, $|^3J_{F-F}| = 20$ Hz), −164.9 (d of d, $|^3J_{F-F}| = 21$ Hz), −167.3 (d of d, $|^3J_{F-F}| = 17$ Hz). **11**: ^{1}H NMR (C_6D_5Cl) 7.30−7.55 (m, 16H, *o*-, *m*-, *p*-PPh_2, *m*-, *p*-Dip), 4.77 (d, $|^2J_{P-H}| = 22$ Hz, 1H, C*H*P), 4.42 (vbr s, 1H, AlH), 3.96 (vbr s, 1H, AlH), 3.12 (sept, $|J_{H-H}| = 7$ Hz, 2H, CH), 2.80 (sept, $|J_{H-H}| = 7$ Hz, 2H, CH), 1.80 (s, 3H, Me), 1.17 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 1.12 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 0.96 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 0.82 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr); ^{1}H NMR (C_6D_5Cl, −40 °C) 7.13−7.57 (m, 16H, *o*-, *m*-, *p*-PPh_2, *m*-, *p*-Dip), 4.76 (d, $|^2J_{P-H}| = 23$ Hz, 1H, C*H*P), 4.75 (vbr s, 1H, AlH), 3.89 (vbr s, 1H, AlH), 3.17 (br s, $|J_{H-H}| = 7$ Hz, 2H, CH), 2.66 (br

s, $|J_{H-H}| = 7$ Hz, 2H, CH), 1.74 (s, 3H, Me), 1.27 (br s, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 1.11 (br s, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 0.96 (br s, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 0.90 (br s, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr); $^{13}C\{^1H\}$ NMR (C_6D_5Cl) 172.0, 149.7 (br m), 147.8 (br m), 146.4, 146.0, 137.8 (br m), 136.1, 135.4 (br m), 134.3, 132.6 (d, $|J_{P-C}| = 10$ Hz), 127.9−129.6 (m, obscured by C_6D_5Cl), 125.6−126.3 (m, obscured by C_6D_5Cl), 125.4, 125.2, 124.2, 75.6 (d, $|^1J_{P-C}| = 109$ Hz, P−C−H), 29.8, 28.6, 25.8, 25.1, 24.7 (d, $|^2J_{P-C}| = 16$ Hz), 24.4, 24.0, 22.4; $^{31}P\{^1H\}$ NMR (C_6D_5Cl) 30.7; $^{11}B\{^1H\}$ NMR (C_6D_5Cl) −23.6 (br); $^{19}F\{^1H\}$ NMR (C_6D_5Cl) −132.6 (br s), −163.8 (vbr s), −166.4 (br s).

Synthesis of [(*i*-Pr$_2$C$_6$H$_3$N)C(Me)CHPPh$_2$(NC$_6$H$_3$-*i*-Pr$_2$)-AlH][B(C$_6$F$_5$)$_4$] (10). To a solution of **4** (0.183 g, 0.303 mmol) in 3 mL of toluene was slowly added $[Ph_3C][B(C_6F_5)_4]$ (0.279 g). Over time the orange solution turned colorless with the precipitation of a faint yellow oil. After the mixture was stirred overnight, 15 mL of *n*-pentane was added and the reaction vial was vigorously shaken. After several minutes a white powder separated and the mixture was stirred overnight. The solvent was then decanted, and the solids were washed 3 × 10 mL of *n*-pentane and dried to give **10** in 96% yield. ^1H NMR (C_6D_5Cl): 7.09−7.53 (m, 16H, *o*-, *m*-, *p*-PPh_2, *m*-, *p*-Dip), 4.74 (d, $|^2J_{P-H}| = 22$ Hz, 1H, C*H*P), ∼3.95 (vbr s, 1H, AlH), 3.13 (sept, $|J_{H-H}| = 7$ Hz, 2H, CH), 2.79 (sept, $|J_{H-H}| = 7$ Hz, 2H, CH), 1.79 (s, 3H, Me), 1.19 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 1.12 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 0.96 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr), 0.85 (d, $|J_{H-H}| = 7$ Hz, 6H, *i*-Pr). $^{31}P\{^1H\}$ NMR (C_6D_5Cl): 30.6. $^{13}C\{^1H\}$ NMR (C_6D_5Cl): 172.1, 150.4 (br), 147.2 (br), 146.5 (d, 4 Hz), 146.1, 140.2 (br), 138.4, 137.0 (br), 136.1, 135.1, 134.4, 132.6 (d, $|J_{P-C}| = 10$ Hz), 127.9−129.6 (m, obscured by C_6D_5Cl), 125.1−126.3 (m, obscured by C_6D_5Cl), 124.0, 122.1, 75.5 (d, $|^1J_{P-C}| = 109$ Hz, P−C−H), 34.3, 29.8, 28.4, 25.9, 25.1, 24.6 (d, $|^2J_{P-C}| = 16$ Hz), 24.5, 24.1, 22.6, 14.1. $^{11}B\{^1H\}$ NMR (C_6D_5Cl): −20.1. $^{19}F\{^1H\}$ NMR (C_6D_5Cl): −132.2 (s), −163.8 (d of d, $|^3J_{F-F}| = 21$ Hz), −166.8 (s). IR (KBr pellet): 1644 (AlH) cm^{-1}. Anal. Calcd for $C_{63}H_{49}AlN_2PBF_{20}$: C, 58.99; H, 3.85; N, 2.18. Found: C, 58.87; H, 4.35; N, 2.01.

X-ray Data Collection and Reduction. Crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O_2-free environment for each crystal. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer. The data were collected in a hemisphere of data in 1329 frames with 30 s exposure times. The observed extinctions were consistent with the space groups in each case. The data sets were collected ($4.5° < 2\theta < 45−50.0°$). A measure of decay was obtained by re-collecting the first 50 frames of each data set. The intensities of reflections within these frames showed no statistically significant change over the duration of the data collections. The data were processed using the SAINT and XPREP processing packages. An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using the SHELXTL solution package operating on a Pentium computer.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[13] The heavy-atom positions were determined using direct methods employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on *F*, minimizing the function $w(|F_o| - |F_c|)^2$, where the weight *w* is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors. C−H atom positions were calculated and allowed to ride on the carbon to which they are bonded, assuming a C−H bond length of 0.95 Å. H atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C atom to which they are bonded. The H atom contributions were not refined unless otherwise noted. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitudes of the residual electron densities in each case were of no chemical significance. Addition details are provided in the Supporting Information. Crystallographic data for **1**, **2**, **4**, and **7** are given in Table 1.

Table 1. Crystallographic Data[a]

	1	2	4	7
formula	$C_{39}H_{49}NP$	$C_{41}H_{54}AlN_2P$	$C_{39}H_{50}AlN_2P$	$C_{68}H_{61}AlBF_{20}N_2OP$
formula wt	576.77	632.81	604.76	2741.90
cryst syst	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	27.101(19)	17.971(9)	11.103(6)	18.464(10)
b (Å)	9.163(6)	13.291(7)	12.961(6)	19.653(11)
c (Å)	19.489(14)	17.687(8)	13.665(7)	20.277(11)
α (deg)			89.040(10)	85.584(11)
β (deg)	133.634(10)	115.228(9)	70.897(9)	68.372(11)
γ (deg)			86.943(9)	85.154(12)
V (Å^3)	3503(4)	3822(3)	1855.5(16)	6807(6)
Z	4	4	2	4
d(calcd), g cm^{-3}	1.094	1.100	1.082	1.338
abs coeff, *μ*, cm^{-1}	0.106	0.124	0.125	0.151
no. of data collected	14322	15904	7974	29324
no. of data, $F_o^2 > 3\sigma(F_o^2)$	5059	5404	5295	19333
no. of variables	379	406	396	1693
R^b	0.0533	0.0451	0.0410	0.0537
$R_w{}^c$	0.0839	0.1016	0.1045	0.1282
GOF	0.882	0.915	0.915	0.705

[a] All data collected at 24 °C with Mo Kα radiation ($\lambda = 0.710\ 69$ Å). [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$.

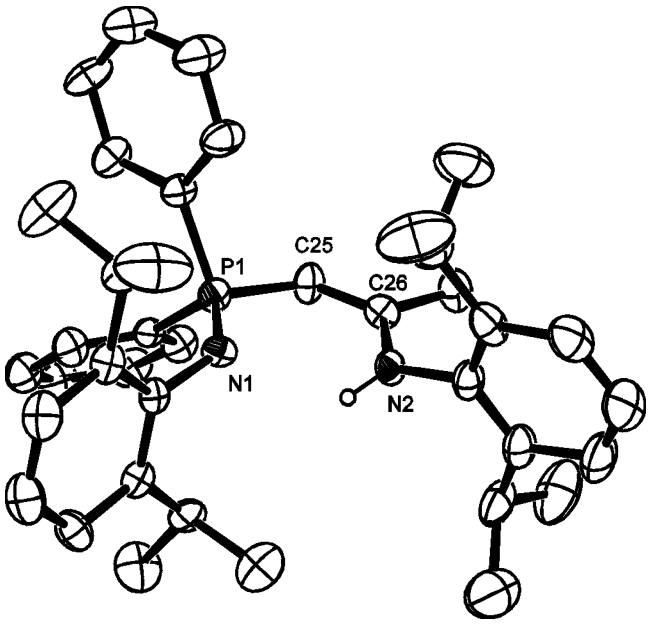
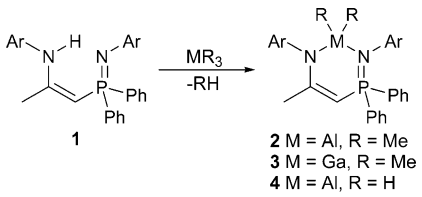


Figure 1. ORTEP drawings of **1** (30% thermal ellipsoids are shown). Hydrogen atoms are omitted for clarity. Selected distances (Å): P(1)−N(1) = 1.590(3), P(1)−C(25) = 1.738(3), N(2)−C(26) = 1.382(4), C(25)−C(26) = 1.363(4).

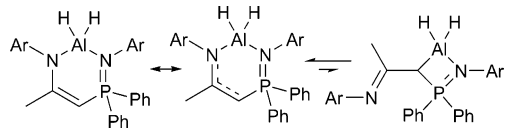
Results and Discussion

Neutral Complexes. The synthesis of the ligand **1** has been previously described.[10] Crystallographic characterization of **1** (Figure 1) confirmed the phosphinimine−amine nature. Ligand **1** reacts with MR_3 (M =

Scheme 1



Scheme 2



Al, Ga; R = Me, H) with loss of RH to form the complexes (i-$Pr_2C_6H_3N$)C(Me)CHPPh_2(NC_6H_3-i-Pr_2)-MMe_2 (M = Al (**2**), Ga (**3**)) and (i-$Pr_2C_6H_3N$)C(Me)-CHPPh_2(NC_6H_3-i-Pr_2)AlH_2 (**4**) in approximately 60% isolated yields (Scheme 1). ^{1}H, ^{13}C, and ^{31}P NMR data confirmed the formulations, and recrystallization from boiling n-heptane gave colorless crystalline blocks in the case of **2** and **4**. The NMR data of **2** and **3** showed metal-bound methyl resonances at −0.24 and 0.16 ppm, slightly upfield from the corresponding resonances for the β-diketimine complex (NacNac)MMe_2 (M = Al, −0.86 ppm;[3] M = Ga, −0.18 ppm[14]). In the case of **4**, the NMR data are consistent with the presence of two isomers in solution in a ratio of 3.5:1. This suggests the presence of six- and four-membered chelate rings with Al (Scheme 2). We have reported a similar observation for related Ni(II) and Pd(II) systems.[10] The ^{1}H NMR resonance derived from the methine proton of the ligand backbone in the minor isomer is a doublet of triplets arising from coupling to P ($^2J_{P-H}$ = 10 Hz) and the Al-bound hydrides ($^3J_{H-H}$ = 14 Hz), consistent with the four-membered chelate form. The corresponding resonance for the major isomer does not show the latter coupling. Infrared spectroscopy shows the Al−H absorptions at 1828 and 1770 cm^{-1}, similar to those reported for (NacNac)AlH_2 (1832 and 1795 cm^{-1}).[8] Synthesis of **4$_d$** confirmed these assignments and revealed Al−D absorptions at 1324 and 1286 cm^{-1} and showed a ^{2}D NMR resonance at 4.55 ppm. Efforts to acquire ^{27}Al NMR spectra for **2** and **4** were unsuccessful.[11]

Crystallographic studies of **2** (Figure 2) and the major isomer of **4** (Figure 3) confirmed pseudo-tetrahedral geometries about Al and a boat conformation of the six-membered chelate ring. The boat conformation of **2** results in an angle of 38.6° between the mean planes through AlN_2 and C_2P atoms of the chelate ring. This puckering results in an approach of the Al atom and C(39) at 3.087 Å. This chelated geometry stands in contrast to that seen in **4**, where the corresponding angle and distance are 10.3° and 3.304 Å, respectively. In an alternative description of **4**, the maximum deviation of the atoms of the chelate from the mean AlN_2-PC_2 plane is only 0.17 Å. For **2**, the Al−N bond distances were found to be 1.932(2) and 1.943(2) Å, similar to those seen in the analogous NacNac complex (1.920(2) and 1.942(2) Å).[2] The imine N−C bond is (1.353(3) Å) slightly longer than those seen in (NacNac)$AlMe_2$ (1.344(2) and 1.339(2) Å). Similarly, the adjacent C−C bond (C(38)−C(39) = 1.383(4) Å) is shorter than the corresponding distances (1.394(3), 1.407(3) Å) seen in (NacNac)$AlMe_2$, while the N−Al−N bite angle in **2** of

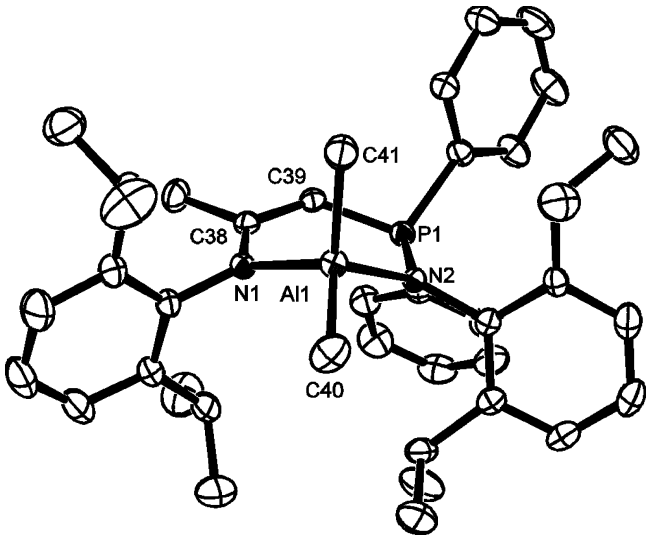


Figure 2. ORTEP drawings of **2** (30% thermal ellipsoids are shown). Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Al(1)−N(1) = 1.932(2), Al(1)−N(2) = 1.943(2), Al(1)−C(40) = 1.962(3), Al(1)−C(41) = 1.991(3), N(1)−C(38) = 1.353(3), N(2)−P(1) = 1.633(2), P(1)−C(39) = 1.741(3), C(38)−C(39) = 1.383-(4); N(1)−Al(1)−N(2) = 101.22(10), N(1)−Al(1)−C(40) = 110.36(13), N(2)−Al(1)−C(40) = 111.57(12), N(1)−Al(1)−C(41) = 107.23(12), N(2)−Al(1)−C(41) = 110.84(12), C(40)−Al(1)−C(41) = 114.69(15), C(38)−N(1)−Al(1) = 116.72(18), P(1)−N(2)−Al(1) = 115.91(11), N(2)−P(1)−C(39) = 109.19-(12), N(1)−C(38)−C(39) = 123.5(2), C(38)−C(39)−P(1) = 130.4(2).

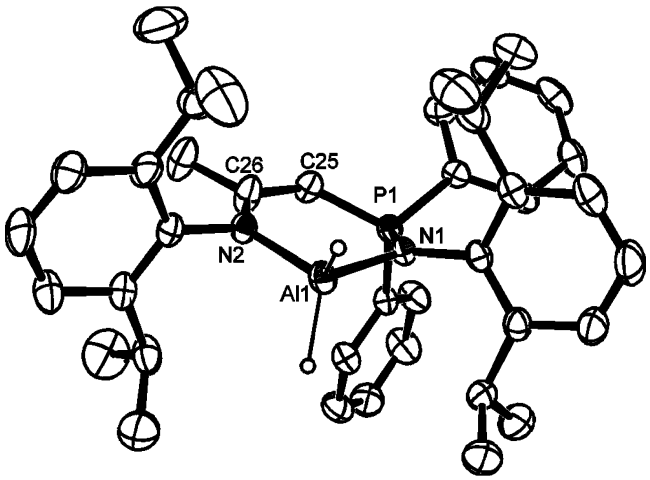


Figure 3. ORTEP drawings of **4** (30% thermal ellipsoids are shown). Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Al(1)−N(2) = 1.893(2), Al(1)−N(1) = 1.906(2), Al(1)−H(1) = 1.529(18), Al(1)−H(2) = 1.60(2), P(1)−N(1) = 1.6253(18), P(1)−C(25) = 1.746(2), N(2)−C(26) = 1.370(3); N(2)−Al(1)−N(1) = 102.10(8), N(2)−Al(1)−H(1) = 113.6(7), N(1)−Al(1)−H(1) = 108.7(7), N(2)−Al(1)−H(2) = 109.8(7), N(1)−Al(1)−H(2) = 110.0(7), H(1)−Al(1)−H(2) = 112.1(10), N(1)−P(1)−C(25) = 108.64(10), P(1)−N(1)−Al(1) = 121.65(10), C(26)−N(2)−Al(1) = 127.27(15), N(2)−C(26)−C(25) = 123.8(2).

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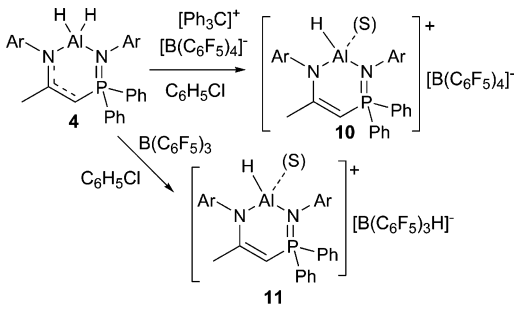
(14) Stender, M.; Eichler, B. E.; Hardman, N. J.; Power, P. P.; Prust, J.; Noltemeyer, M.; Roesky, H. W. *Inorg. Chem.* **2001**, *40*, 2794−2799.

Scheme 3



4 10 11

101.11(10)° is larger than that (96.17(7)°) in (NacNac)-$AlMe_2$. These data are consistent with a more localized charge distribution over the C−C−N fragment in the phosphinimine−amide ligand complex. In the case of **4**, location and refinement of the H atom positions revealed Al−H distances of 1.529(18) and 1.60(2) Å, which is in the range seen for other Al−hydride derivatives.[15] Although Al−N distances in **4** (1.906(2), 1.893(2) Å), are shorter than those in **2**, as expected, the N−Al−N bite angle of 102.10(8)° is similar to that seen for **2**.

Cationic Complexes. Reactions of **2** and **3** with $[Ph_3C][B(C_6F_5)_4]$ in toluene or benzene formed relatively insoluble clathrate oils,[16] but the resulting salts are soluble in C_6H_5Cl. These complexes, formulated as $[(i\text{-}Pr_2C_6H_3N)C(Me)CHPPh_2(NC_6H_3\text{-}i\text{-}Pr_2)MMe][B(C_6F_5)_4]$ (M = Al (**5**), Ga (**6**)), exhibited downfield shifts of the ^{31}P NMR resonances to 31.0 and 32.1 ppm, respectively. The ^1H NMR resonances for the ligand fragments were similar to those of the precursors. The remaining metal-bound methyl groups give rise to upfield-shifted resonances at −0.70 and −0.08 ppm in **5** and **6**, respectively. These shifts may result from the anisotropic shielding from coordinated C_6D_5Cl solvent molecules. These signals shift slightly (0.1 ppm) but do not broaden upon cooling to −40 °C. The corresponding ^{13}C NMR resonances for these methyl groups are broad at 25 °C and sharpen upon cooling to −40 °C. These observations are likely a result of the lower symmetry of the quadrupolar Al or Ga environment. ^{11}B and ^{19}F NMR signals were as expected for the presence of the free $[B(C_6F_5)_4]$ anion. In the case of **5**, efforts to acquire an ^{27}Al NMR spectrum were unsuccessful, as no discernible signals were observed. This too is attributed to the dissymmetry of the molecule. Similar difficulties have been reported in the literature.[17] Attempts to isolate these compounds as analytically pure materials were unsuccessful, as they are typically highly air-sensitive oils.

Similarly, reactions of **2** and **3** with $B(C_6F_5)_3$ result in methyl abstraction from Al or Ga, generating the species $[(i\text{-}Pr_2C_6H_3N)C(Me)CHPPh_2(NC_6H_3\text{-}i\text{-}Pr_2)MMe][B(C_6F_5)_3Me]$ (M = Al (**8**), Ga (**9**)). In a fashion similar to that for **6** and **7**, the ^1H NMR resonances for the metal-bound methyl groups are observed upfield of the precursors at −0.73 and −0.14 ppm for the Al and Ga species, respectively, while the borate-bound methyl groups are seen at 1.23 and 1.25 ppm. ^{11}B NMR and

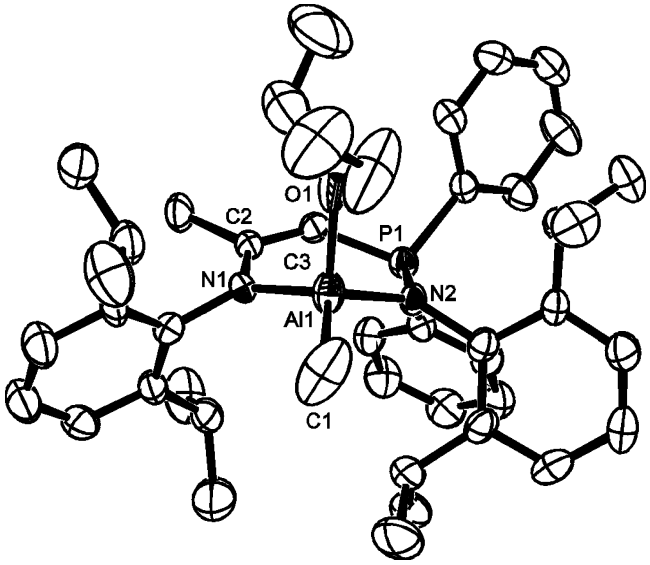


Figure 4. ORTEP drawing of the cation of **7** (one of the two in the asymmetric unit; 30% thermal ellipsoids are shown). Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Al(1)−N(1) = 1.853(4), Al(1)−N(2) = 1.875(4), Al(1)−C(1) = 1.946(6), Al(1)−O(1) = 1.998(5), P(1)−N(2) = 1.649(4), P(1)−C(3) = 1.751(4), N(1)−C(2) = 1.377(5); N(1)−Al(1)−N(2) = 105.61(17), N(1)−Al(1)−C(1) = 116.3(3), N(2)−Al(1)−C(1) = 117.0(2), N(1)−Al(1)−O(1) = 103.88(19), N(2)−Al(1)−O(1) = 105.08-(18), C(1)−Al(1)−O(1) = 107.3(3), N(2)−P(1)−C(3) = 107.7-(2), C(2)−N(1)−Al(1) = 118.5(3), P(1)−N(2)−Al(1) = 119.1-(2), C(3)−C(2)−N(1) = 123.2(4), C(2)−C(3)−P(1) = 130.6(4).

^{19}F NMR data are as expected for symmetric methyl−borate anions, showing no evidence of methyl or fluorine interactions with the cationic centers. Again, these compounds were not isolable as analytically pure materials, due their extreme air sensitivity and oily nature.

The analogous reactions of **4** with $[Ph_3C][B(C_6F_5)_4]$ resulted in the formation of the species formulated as $[(i\text{-}Pr_2C_6H_3N)C(Me)CHPPh_2(NC_6H_3\text{-}i\text{-}Pr_2)AlH][B(C_6F_5)_4]$-(**10**), which was obtained as an oil that upon addition of *n*-pentane and vigorous stirring afforded a white solid. In contrast to the precursor **4**, the NMR data for **10** showed only a single isomer. Coupling between the central methine proton of the ligand and the Al-bound hydride was not observed, in contrast to the minor isomer of **4**. Thus, **10** is proposed to be a six-membered chelate complex. Although X-ray-quality crystals could not be obtained, **10** was isolated as an analytically pure solid. It is presumably the extreme bulkiness of the ligand as well as the strong donor ability of the phosphinimine fragment that results in the stability of this cation.

In a similar fashion, reaction of **4** and $B(C_6F_5)_3$ results in the formation of $[(i\text{-}Pr_2C_6H_3N)C(Me)CHPPh_2(NC_6H_3\text{-}i\text{-}Pr_2)AlH][B(C_6F_5)_3H]$ (**11**) (Scheme 3). This species exhibits two broad hydride signals at 25 °C: a peak at 3.96 ppm attributed to the Al−H signal and a peak at 4.42 ppm attributed to a hydride bridging Al and B. At low temperature (−40 °C) the ^1H NMR spectra showed resonances at 3.89 and 4.75 ppm, attributed to the two distinct hydrides. In addition, resonances at 2.67 and 3.17 ppm were attributed to the inequivalent isopropyl protons. Each of these sets of resonances are observed to broaden with increasing temperature, suggesting the

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possibility of hydride exchange between the cation and anion. However, variable-temperature ^{1}H NMR experiments suggest coalescence well above 70 °C. Consequently, thermodynamic exchange parameters could not be determined.

Attempts to grow single crystals of any of the above base-free cations were uniformally unsuccessful; however, attempts to crystallize **5** from C_6H_5Cl/*n*-pentane/diethyl ether solution after several weeks afforded a few crystals of [(*i*-$Pr_2C_6H_3N$)C(Me)CHPPh_2(NC_6H_3-*i*-Pr_2)-AlMe(OEt_2)][$B(C_6F_5)_4$] (**7**). A crystallographic study of **7** (Figure 4) confirmed the formulation and, in particular, the monomeric nature of the cation. The geometry about the Al center of the cation of **7** is pseudo-tetrahedral, while the chelate ring is puckered, adopting a boat conformation. The angle between the AlN_2 and PC_2 planes of the chelate is 49.6°, which places Al and C(3) 3.094 Å apart. The Al−C (1.946(6) Å) and Al−N distances (1.853(4) and 1.875(4) Å) are shorter than those in **5**, as expected for a cation. The Al−O bond for the coordinated diethyl ether was found to be 1.998(5) Å. This is longer than that seen in [($CH(CPh(NSiMe_3))_2$-AlMe(OEt_2)][$B(C_6F_5)_4$][18] (1.987 Å), presumably a result of the increased donor ability and steric bulk of the phosphinimine-based ligand.

Conclusions

The phosphinimine−amine ligand described herein readily affords neutral group 13 alkyl and hydride complexes. Subsequent reaction with a Lewis acid results in conversion to a monomeric cation by abstraction of hydride or methyl groups. The steric bulk and strong donor ability of this ligand allowed the isolation of monometallic Al cations. Attempts to utilize this and related ligands for the stabilization of reduced low-coordinate main-group and transition-metal complexes are the subject of current efforts.

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Supporting Information Available: Crystallographic data in CIF format and figures giving ^{1}H NMR spectra for **5**, **6**, **8**, **9** and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0306776

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