

Neutral and Cationic Group 13 Phosphinimine and Phosphinimide Complexes

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Reactions of the silylphosphinines $R_3PNSiMe_3$ ($R = i\text{-Pr, Ph, Cy}$) with $AlCl_3$, $AlMe_2Cl$, and $AlMe_3$ afford the compounds ($i\text{-Pr}_3PNSiMe_3$) $AlCl_3$ (**1**), $(R_3PNSiMe_3)AlMe_2Cl$ ($R = i\text{-Pr, 2; Ph, 3; Cy, 4}$), $(R_3PNSiMe_3)AlMe_2Cl$ ($R = i\text{-Pr, 5; Ph, 6; Cy, 7}$), and $(R_3PNSiMe_3)AlMe_3$ ($R = i\text{-Pr, 8; Ph, 9; Cy, 10}$). Reaction of R_3PNH ($R = t\text{-Bu, Cy, Ph}$) with $AlMe_2Cl$ and $AlMe_3$ afforded $(R_3PNH)AlMe_2Cl$ ($R = Cy, 11; t\text{-Bu, 12}$) and $(Ph_3PNH)AlMe_3$ (**13**), respectively. The dimeric species $[Me_2Al(\mu\text{-NP}t\text{-Bu}_3)]_2$ (**14**) $[AlCl_2(\mu\text{-NP}t\text{-Bu}_3)]_2$ (**15**) were derived from reactions of ($t\text{-Bu}_3PNH$) and $AlMe_3$ and $t\text{-Bu}_3PNLi$ and $MeAlCl_2$, respectively. Reaction of the bisphosphinimine salt $LiCH(PPh_2(NSiMe_3))_2$ (**16**) with aluminum, gallium, and indium halides yielded $[CH(PPh_2(NSiMe_3))_2]MCl_2$ ($M = Al, 17; Ga, 18; In, 19$) while the analogous species $[CH(PPh_2(NSiMe_3))_2]AlMe_2$ (**20**) was prepared via reaction of **16** with Me_2AlCl . The compounds $[CH(PPh_2(NSiMe_3))_2]MR_2$ ($M = Al, Bz, 21; M = Ga, R = Me, 22; Bz, 23; M = In, R = Me, 24; Bz, 25$) were readily prepared by treatment of **17–19** with the appropriate alkylating reagents. The borane $B(C_6F_5)_3$ reacts stoichiometrically with the adducts **8–10** to give the products $[(R_3PNSiMe_3)AlMe_2][MeB(C_6F_5)_3]$ ($R = i\text{-Pr, 26; Ph, 27; Cy, 28}$) while treatment of **27** with PMe_3 affords clean conversion to the salt $[(Ph_3PNSiMe_3)_2AlMe(PMe_3)][MeB(C_6F_5)_3]$ (**29**). Similarly, species $[Me_2Al(\mu\text{-NP}t\text{-Bu}_3)_2AlMe][MeB(C_6F_5)_3]$ (**30**) and $[Me_2Al(\mu\text{-NP}t\text{-Bu}_3)_2AlMe(PMe_3)][MeB(C_6F_5)_3]$ (**31**) were obtained from **14**. Attempts to generate the related ionic derivatives from **20–25** yielded unstable mixtures of products. Under mild conditions these group 13 ionic species did not effect the polymerization of ethylene. Crystallographic data are reported for compounds **1, 3, 6, 8, 11, 13–15, 18, and 20**.

Introduction

In efforts to develop new catalysts for olefin polymerization, a number of groups have focused attention on complexes of non-cyclopentadienyl ligands. Of particular interest have been systems incorporating amide and imine based ligands. The research groups of McConville,^{1,2} Brookhart,^{3–8} and Gibson,^{9,10} among others, have led the way in developing catalysts derived from both early and late transition metal based complexes of these ligands. In our own efforts, we have focused attention on phosphinimide ligands. On the basis of the concept of the steric analogy to cyclopentadienyl ligands, we have recently investigated early transition metal

complexes of phosphinimides and shown that they can act as effective catalysts for ethylene polymerization.^{11,12} While transition metal based catalyst systems continue to be a fruitful area of study and development in general, several groups have begun to examine the potential of main-group Lewis acid species. The electrophilic nature of such species combined with the reactivity of the M–C bonds augurs well for insertion chemistry and thus applications in catalysis. In this vein, Jordan and co-workers^{13,14} have recently reported the characterization of aluminum cationic complexes incorporating aminotroponimate, β -diketiminato, and bisimidate ligands. In addition, Smith et al. have reported related diketiminato complexes.¹⁵ In this paper, we describe the syntheses and structures of phosphinimine complexes of group 13 metals. The synthesis of zwitterionic and cationic species derived from these compounds has been investigated and considered.

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Experimental Section

General Data. All preparations were done under an atmosphere of dry, O₂-free N₂ employing both Schlenk line techniques and an Innovative Technologies or Vacuum Atmospheres inert atmosphere glovebox. Solvents were purified employing Grubb's type column systems manufactured by Innovative Technology. All organic reagents were purified by conventional methods. ¹H and ¹³C{¹H} NMR spectra were recorded on Bruker Avance-300 and -500 spectrometers operating at 300 and 500 MHz, respectively. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to SiMe₄. ³¹P, ¹¹B, ²⁷Al, and ¹⁹F NMR spectra were recorded on a Bruker Avance-300. All NMR spectra were recorded at 25 °C unless otherwise indicated. Guelph Chemical Laboratories Inc., Guelph, Ontario, performed combustion analyses. The compounds R₃PNSiMe₃, R₃-PNH (R = *i*-Pr, Cy, Ph, *t*-Bu),^{16a} and CH₂(PPh₂(NSiMe₃))₂¹⁷ were prepared via literature methods. AlMe₂Cl, AlMe₂Cl, and AlMe₃ were purchased from the Aldrich Chemical Co.

Synthesis of (*i*-Pr)₃PNSiMe₃AlCl₃ (1). To a solution of *i*-Pr₃PNSiMe₃ (0.073 g, 0.295 mmol) in benzene was added AlCl₃ (0.040 g, 0.295 mmol). The reaction mixture was stirred for 10 h and then filtered. The remaining solvent was removed under vacuum to yield a white powder. Yield: 74%. ¹H NMR (C₆D₆): δ 3.0 (3H, m), 0.9 (18H, q, |J_{H-H}| = 8.5 Hz), 0.5 (9H, s). ¹³C{¹H} NMR (C₆D₆): δ 27.6 (d, |J_{C-P}| = 52.2 Hz), 17.5, 7.3. ³¹P NMR (C₆D₆): δ 66.2.

Synthesis of (R₃PNSiMe₃)AlMeCl₂ (R = *i*-Pr, 2; Ph, 3; Cy, 4), (R₃PNSiMe₃)AlMe₂Cl (R = *i*-Pr, 5; Ph, 6; Cy, 7), and (R₃PNSiMe₃)AlMe₃ (R = *i*-Pr, 8; Ph, 9; Cy, 10). These compounds were prepared in a similar fashion with the appropriate substitution of phosphinimine and aluminum reagent; thus, a single representative synthesis is detailed. To a solution of *i*-Pr₃PNSiMe₃ (0.03 g, 0.121 mmol) in hexane was added MeAlCl₂ (1.0 M, 0.121 mL, 0.121 mmol). The reaction mixture was stirred for 10 h and then filtered and the solvent removed to afford a white powder. Yield: 71%. (2) ¹H NMR (C₆D₆): δ 2.8 (3H, m), 0.9 (18H, m), 0.5 (9H, s), 0.1 (3H, s). ¹³C{¹H} NMR (C₆D₆): δ 27.4 (d, |J_{C-P}| = 45.7 Hz), 17.4, 7.0. ³¹P NMR (C₆D₆): δ 64.6. Anal. Calcd for C₁₃H₃₃PNSiAlCl₂: C, 43.33; H, 9.23. Found: C, 43.08; H, 9.51. (3) Yield: 99%. ¹H NMR (C₆D₆): δ 7.7 (6H, m), 7.0 (12H, m), 0.3 (9H, s), -0.5 (3H, s). ¹³C{¹H} NMR (C₆D₆): δ 134.4, 133.3, 128.9, 128.5, 14.3, 4.9, -1.0. ³¹P NMR (C₆D₆): δ 34.5. (4) Yield: 83%. ¹H NMR (C₆D₆): δ 2.8 (3H, m), 1.9 (6H, m), 1.5 (12H, m), 1.1 (12H, m), 0.5 (9H, s), 0.2 (3H, s). ¹³C{¹H} NMR (C₆D₆): δ 37.7 (d, |J_{C-P}| = 52.2 Hz), 27.7, 27.1 (d, |J_{C-P}| = 12.2 Hz), 7.2, -1.2. ³¹P NMR (C₆D₆): δ 55.3. (5) Yield: 71%. ¹H NMR (C₆D₆): δ 2.7 (3H, sept, |J_{H-H}| = 7.5 Hz), 0.9 (18H, q, |J_{H-H}| = 7.3 Hz), 0.4 (9H, s), 0.0 (6H, s). ¹³C{¹H} NMR (C₆D₆): δ 27.2 (3H, d, |J_{C-P}| = 54.4 Hz), 17.5, 6.9, -1.1. ³¹P NMR (C₆D₆): δ 61.5. (6) Yield: 99%. ¹H NMR (C₆D₆): δ 7.7 (6H, m), 7.0 (12H, m), 0.3 (9H, s), -0.4 (6H, s). ¹³C{¹H} NMR (C₆D₆): δ 134.3, 133.3, 133.0, 128.7, 4.8, -1.4. ³¹P NMR (C₆D₆): δ 32.5. (7) Yield: 73%. ¹H NMR (C₆D₆): δ 2.8 (3H, m), 1.9 (6H, m), 1.6 (12H, m), 1.2 (12H, m), 0.5 (9H, s), 0.1 (6H, s). ¹³C{¹H} NMR (C₆D₆): δ 37.7 (d, |J_{C-P}| = 52.9 Hz), 27.7, 27.1 (d, |J_{C-P}| = 12.4 Hz), 26.3, 6.9, -1.4. ³¹P NMR (C₆D₆): δ 53.2. (8) Yield: 72%. ¹H NMR (C₆D₆): δ 2.4 (3H, m), 0.9 (18H, q, |J_{H-H}| = 7.3 Hz), 0.4 (9H, s), -0.2 (9H, s). ¹³C{¹H} NMR (C₆D₆): δ 26.8 (d, |J_{C-P}| = 55.5 Hz), 17.4, 6.8, 1.6. ³¹P NMR (C₆D₆): δ 57.9. Anal. Calcd for C₁₅H₃₉PNSiAl: C, 56.39; H, 12.30. Found: C, 56.58; H, 11.94. (9) Yield: 83%. ¹H NMR (C₆D₆): δ 7.7 (6H, m), 7.0 (9H, m), 0.2 (9H, s), -0.4 (9H, s). ¹³C{¹H} NMR (C₆D₆): δ 134.3, 132.7, 130.9, 128.7, 4.9, -1.3. ³¹P NMR (C₆D₆): δ 29.2. (10) Yield: 67%. ¹H NMR (C₆D₆): δ 2.5 (3H, m), 1.9 (6H, m), 1.5 (12H,

m), 1.2 (12H, m), 0.5 (9H, s), -0.1 (9H, s), -0.4 (9H, s). ¹³C{¹H} NMR (C₆D₆): δ 37.6 (d, = 54.6 Hz), 27.6, 27.3 (d, |J_{C-P}| = 10.9 Hz), 26.4, 6.8, 2.4. ³¹P NMR (C₆D₆): δ 49.6.

Synthesis of (R₃PNH)AlMe₂Cl (R = Cy, 11; *t*-Bu, 12) and (Ph₃PNH)AlMe₃ (13). These compounds were prepared in a similar fashion with the appropriate substitution of phosphinimine and aluminum reagent; thus, a single representative synthesis is detailed. To a solution of Cy₃PNH (0.03 g, 0.102 mmol) in benzene was added Me₂AlCl (1.0 M, 0.102 mL, 0.102 mmol). The reaction mixture was stirred for 10 h and then filtered. The remaining solvent was removed under vacuum. Recrystallization of the product from benzene afforded crystals. Yield: 83%. (11) ¹H NMR (C₆D₆): δ 3.3 (3H, m), 1.8 (12H, m), 1.4 (6H, m), 1.2 (12H, m), 0.5 (1H, s), -0.4 (6H, s). ¹³C{¹H} NMR (C₆D₆, 25 °C): δ 37.6 (d, |J_{H-H}| = 53.5 Hz), 27.8, 27.3 (d, |J_{H-H}| = 11.7 Hz), 26.3, -0.9. ³¹P NMR (C₆D₆): δ 52.5. Anal. Calcd for C₂₀H₄₀PNAI: C, 61.92; H, 10.39. Found: C, 61.41; H, 10.62. (12) Yield: 64%. ¹H NMR (C₆D₆): δ 1.0 (27H, d, |J_{H-H}| = 13.5 Hz), -0.1 (6H, s), -0.3 (1H, s). ¹³C{¹H} NMR (C₆D₆): δ 39.2 (d, |J_{C-P}| = 44.2 Hz), 29.1, 9.3. ³¹P NMR (C₆D₆): δ 69.4. (13) Yield: 75%. ¹H NMR (C₆D₆): δ 7.7 (6H, m), 7.1 (9H, m), 0.3 (1H, s), -0.4 (9H, s). ¹³C{¹H} NMR (C₆D₆): δ 136.1, 132.9, 131.6, 129.0, 5.1. ³¹P NMR (C₆D₆): δ -0.4. Anal. Calcd for C₂₁H₂₅PNAI: C, 72.19; H, 7.21. Found: C, 72.63; H, 7.14.

Synthesis of [AlMe₂(μ-NP*t*-Bu₃)]₂ (14). To a solution of *t*-Bu₃PNH (0.03 g, 0.138 mmol) in benzene was added Me₃Al (2.0 M, 0.069 mL, 0.138 mmol). The reaction mixture was refluxed for 10 h and then filtered. The remaining solvent was removed under vacuum. Recrystallization of the product from benzene afforded colorless crystals. Yield: 62%. ¹H NMR (C₆D₆): δ 1.4 (27H, d, |J_{H-H}| = 12.5 Hz), 0.0 (6H, s). ¹³C{¹H} NMR (C₆D₆): δ 41.0 (d, |J_{C-P}| = 49.0 Hz), 31.0, 15.5, 0.5. ³¹P NMR (C₆D₆): δ 56.7. Anal. Calcd for C₂₈H₆₄P₂N₂Al₂: C, 61.74; H, 11.84; N, 5.14. Found: C, 61.20; H, 12.33; N, 5.04.

Synthesis of [AlCl₂(μ-NP*t*-Bu₃)]₂ (15). To a solution of *t*-Bu₃PNLi (0.062 g, 0.278 mmol) in benzene was added MeAlCl₂ (1.0 M, 0.28 mL, 0.278 mmol). The reaction mixture was refluxed for 10 h and then filtered. The remaining solvent was removed under vacuum. Recrystallization of the product from benzene afforded colorless crystals. Yield: 67%. ¹H NMR (C₆D₆): δ 1.5 (54H, d, |J_{H-H}| = 13.0 Hz). ¹³C{¹H} NMR (C₆D₆): δ 39.2 (d, |J_{C-P}| = 45.5 Hz), 29.2. ³¹P NMR (C₆D₆): δ 66.5. Anal. Calcd for C₂₄H₅₄P₂N₂Al₂Cl₂: C, 51.70; H, 9.76. Found: C, 51.47; H, 9.66.

Generation of LiCH(PPh₂(NSiMe₃))₂ (16). To a solution of CH₂(PPh₂(NSiMe₃))₂ (0.071 g, 0.127 mmol) in THF was added *n*-butyllithium (2.5 M, 0.5 mL, 0.127 g). The reaction was stirred for 12 h and filtered. The remaining solvent was removed under vacuum to yield a lime yellow compound. Yield: 78%. ¹H NMR (C₆D₆): δ 7.7 (8H, m), 7.1 (12H, m), 3.6 (1H, m), 0.1 (18H, s). ¹³C{¹H} NMR (C₆D₆): δ 142.2 (d, |J_{C-P}| = 95.8 Hz), 131.6 (t, |J_{C-P}| = 3.8 Hz), 129.4, 127.8, 23.8 (t, |J_{C-P}| = 129 Hz), 4.5. ³¹P NMR (C₆D₆): δ 17.5.

Synthesis of [CH(PPh₂(NSiMe₃))₂][MCl₂] (M = Al, 17; Ga, 18; In, 19). These complexes were prepared in a similar manner, and thus only a single representative preparation is described. To a solution of 16 (0.082 g, 0.145 mmol) in benzene was added a solution of AlCl₃ (0.020 g, 0.145 mmol). The mixture was stirred for 12 h and filtered. The remaining solvent was removed under vacuum to yield a white powder. (17) Yield: 91%. ¹H NMR (C₆D₆): δ 7.8 (8H, m), 6.9 (12H, m), 4.0 (1H, t, |J_{P-H}| = 3.75), 0.4 (18H, s). ¹³C{¹H} NMR (C₆D₆): δ 133.1 (d, |J_{C-P}| = 51.6 Hz), 132.4 (t, |J_{C-P}| = 3.08 Hz), 131.1, 128.3, 27.4 (t, |J_{C-P}| = Hz), 4.2. ³¹P NMR (C₆D₆): δ 24.3. (18) Yield: 71%. ¹H NMR (C₆D₆): δ 7.8 (8H, m), 7.0 (12H, m), 4.0 (1H, t, |J_{P-H}| = 12.82), 0.4 (18H, s). ¹³C{¹H} NMR (C₆D₆): δ 134.7 (d, |J_{C-P}| = 86 Hz), 132.6 (t, |J_{C-P}| = 4.4 Hz), 131.3, 128.4, 29.5 (t, |J_{C-P}| = 117.4 Hz), 4.3. ³¹P NMR (C₆D₆): δ 32.3. Anal. Calcd for C₃₁H₃₉P₂N₂Si₂GaCl₂: C, 53.31; H, 5.63. Found: C, 53.54; H, 5.91. (19) Yield: 87%. ¹H NMR (C₆D₆): δ 7.7 (8H,

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m), 7.0 (12H, m), 2.7 (1H, br t), 0.3 (18H, s). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 133.0, 132.3 (t, $|J_{\text{C-P}}| = 3.2$ Hz), 131.2, 128.3 (t, $|J_{\text{C-P}}| = 3.75$ Hz), 41.8 (t, $|J_{\text{C-P}}| = 69.8$ Hz), 3.6. ^{31}P NMR (C_6D_6): δ 32.4.

Synthesis of $[\text{CH}(\text{PPh}_2(\text{NSiMe}_3))_2]\text{AlMe}_2$ (20**).** To a solution of **17** (0.116 g, 0.206 mmol) in benzene was added $\text{Me}_2\text{-AlCl}$ (1.0 M, 0.21 mL, 0.206 mmol). The mixture was stirred for 12 h and filtered. The remaining solvent was removed under vacuum to yield a white powder. Yield: 79%. ^1H NMR (C_6D_6): δ 7.6 (8H, m), 6.9 (12H, m), 3.5 (1H, t, $|J_{\text{P-H}}| = 6.6$ Hz), 0.2 (18H, s), 0.2 (6H, s). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 136.5 (d, $|J_{\text{C-P}}| = 100.8$ Hz), 132.3 (t, $|J_{\text{C-P}}| = 4.1$ Hz), 130.6, 128.3, 25.2 (t, $|J_{\text{C-P}}| = 122.1$ Hz), 4.8. ^{31}P NMR (C_6D_6): δ 28.7. Anal. Calcd for $\text{C}_{33}\text{H}_{45}\text{P}_2\text{N}_2\text{Si}_2\text{Al}$: C, 64.47; H, 7.38; N, 4.56. Found: C, 64.32; H, 7.27; N, 4.11.

Synthesis of $[\text{CH}(\text{PPh}_2(\text{NSiMe}_3))_2]\text{MR}_2$ ($\text{M} = \text{Al}$, **Bz, **21**; $\text{M} = \text{Ga}$, $\text{R} = \text{Me}$, **22**; Bz , **23**; $\text{R} = \text{In}$, $\text{R} = \text{Me}$, **24**; Bz , **25**).** These complexes were prepared in a similar manner employing either benzylmagnesium bromide or methylmagnesium chloride, and thus only a single representative preparation is described. To a solution of **17** (0.090 g, 0.137 mmol) in benzene was added BzMgCl (1.0 M, 0.27 mL, 0.270 mmol). The mixture was stirred for 12 h and filtered. The remaining solvent was removed under vacuum to a yield white powder. (**21**) Yield: 81%. ^1H NMR (C_6D_6): δ 7.5 (8H, m), 7.4 (4H, d, $|J_{\text{P-H}}| = 7.7$ Hz), 7.3 (4H, t, $|J_{\text{P-H}}| = 7.5$ Hz), 7.2 (2H, m), 7.0 (8H, m), 6.9 (4H, m), 3.0 (1H, t, $|J_{\text{P-H}}| = 6.8$), 2.5 (4H, s), 0.0 (18H, s). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 148.5, 135.5 (d, $|J_{\text{C-P}}| = 60.7$ Hz), 132.3 (d, $|J_{\text{C-P}}| = 6.2$ Hz), 130.6, 129.6, 128.6, 128.1, 127.5, 121.9, 25.4 (t, $|J_{\text{C-P}}| = 69.2$ Hz), 5.1. ^{31}P NMR (C_6D_6): δ 29.8. (**22**) Yield: 86%. ^1H NMR (C_6D_6): δ 7.6 (8H, m), 6.9 (12H, m), 3.4 (1H, br t), 0.4 (18H, s), -0.1 (6H, s). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 135.5 (m), 132.1, 130.4, 128.1, 29.5 (t, $|J_{\text{C-P}}| = 107.4$ Hz), 4.8. ^{31}P NMR (C_6D_6): δ 25.6. Anal. Calcd for $\text{C}_{33}\text{H}_{45}\text{P}_2\text{N}_2\text{Si}_2\text{Ga}$: C, 60.28; H, 6.90; N, 4.26. Found: C, 60.02; H, 6.67; N, 4.08. (**23**) Yield: 83%. ^1H NMR (C_6D_6): δ 7.7 (8H, m), 7.5 (4H, m), 6.9 (12H, m), 6.8 (6H, m), 3.2 (1H, m), 2.1 (4H, s), 0.4 (18H, s). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 146.3, 135.2 (d, $|J_{\text{C-P}}| = 99.3$ Hz), 132.2, 131.3, 128.7, 128.3, 128.0, 122.5, 70.6, 32.1 (t, $|J_{\text{C-P}}| = 102.7$ Hz), 3.9. ^{31}P NMR (C_6D_6): δ 25.4. (**24**) Yield: 78%. ^1H NMR (C_6D_6): δ 7.6 (8H, m), 7.0 (12H, m), 3.4 (1H, br t), 0.4 (18H, s), -0.2 (6H, s). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 136.0, 132.2, 130.3, 128.0, 29.4 (t, $|J_{\text{C-P}}| = 106.6$ Hz), 5.1. ^{31}P NMR (C_6D_6): δ 25.6. Anal. Calcd for $\text{C}_{33}\text{H}_{45}\text{P}_2\text{N}_2\text{Si}_2\text{In}$: C, 56.41; H, 6.46; N, 3.99. Found: C, 56.26; H, 6.23; N, 3.71. (**25**) Yield: 73%. ^1H NMR (C_6D_6): δ 7.3 (8H, m), 7.2 (8H, m), 7.1 (2H, m), 7.0 (12H, m), 2.1 (4H, s), 3.2 (1H, m), 0.5 (18H, s). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 146.2, 136.4, 135.6, 132.2, 130.2, 128.7, 128.2, 127.3, 122.4, 28.6 (t, $|J_{\text{C-P}}| = 108.1$ Hz), 5.1. ^{31}P NMR (C_6D_6): δ 25.4.

Synthesis of $[\text{R}_3\text{PNSiMe}_3]\text{AlMe}_2[\text{MeB}(\text{C}_6\text{F}_5)_3]$ ($\text{R} = i\text{-Pr}$, **26; Ph , **27**; Cy , **28**).** These compounds were prepared in a similar fashion with the appropriate substitution of phosphinimine and aluminum reagent; thus, a single representative synthesis is detailed. To a solution of $\text{B}(\text{C}_6\text{F}_5)_3$ (0.069 g, 0.134 mmol) in a 50/50 benzene/hexane solution was added **8** (0.043 g, 0.134 mmol) in a similar solution mixture. The reaction mixture was stirred for 0.5 h and followed by decanting of the solvent. The remaining solvent was removed under vacuum to yield a light-yellow oil. (**26**) ^1H NMR ($\text{CD}_2\text{-Cl}_2$): δ 2.5 (3H, m), 1.3 (9H, d, $|J_{\text{H-H}}| = 7.2$ Hz), 1.4 (9H, d, $|J_{\text{H-H}}| = 7.2$ Hz), 0.6 (9H, s), 0.5 (3H, s), -0.2 (6H, s). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{CD}_2\text{-Cl}_2$): δ 150.2, 147.0, 138.8, 135.6, 25.6 (d, $|J_{\text{C-P}}| = 53.9$ Hz), 17.3, 3.6, 10.1, 1.2. ^{31}P NMR ($\text{CD}_2\text{-Cl}_2$): δ 66.6. ^{11}B NMR ($\text{CD}_2\text{-Cl}_2$): δ -15.3. ^{27}Al NMR ($\text{CD}_2\text{-Cl}_2$): δ 62.1. ^{19}F NMR ($\text{CD}_2\text{-Cl}_2$): δ -55.8 (d, $|J_{\text{B-F}}| = 23.1$ Hz), -87.9 (t, $|J_{\text{B-F}}| = 20.3$ Hz), -90.6 (t, $|J_{\text{B-F}}| = 21.2$ Hz). (**27**) ^1H NMR ($\text{CD}_2\text{-Cl}_2$): δ 7.8 (6H, m), 7.7 (9H, m), 0.5 (3H, s), 0.2 (9H, s), -0.6 (6H, s). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{CD}_2\text{-Cl}_2$): δ 150.4, 147.2, 138.9, 133.9, 136.2, 132.4, 131.8, 125.1, 10.0, 2.5, 1.2. ^{31}P NMR ($\text{CD}_2\text{-Cl}_2$): δ 33.3. ^{11}B NMR ($\text{CD}_2\text{-Cl}_2$): δ -15.3. ^{27}Al NMR ($\text{CD}_2\text{-Cl}_2$): δ 62.3. ^{19}F NMR ($\text{CD}_2\text{-Cl}_2$): δ -55.9 (d, $|J_{\text{B-F}}| = 22.9$ Hz), -88.0 (t, $|J_{\text{B-F}}| = 20.8$ Hz),

-90.6 (t, $|J_{\text{B-F}}| = 20.3$ Hz). (**28**) ^1H NMR ($\text{CD}_2\text{-Cl}_2$): δ 1.9 (12H, m), 1.8 (3H, m), 1.5 (6H, m), 1.3 (12H, m), 0.6 (9H, s), 0.5 (3H, s), -0.2 (6H, s). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{CD}_2\text{-Cl}_2$): δ 152.0, 148.9, 140.8, 137.6, 38.3 (d, $|J_{\text{C-P}}| = 52.0$ Hz), 29.7, 28.6 (d, $|J_{\text{C-P}}| = 15.9$ Hz), 27.5, 15.4, 5.7, 3.8. ^{31}P NMR ($\text{CD}_2\text{-Cl}_2$): δ 57.1. ^{11}B NMR ($\text{CD}_2\text{-Cl}_2$): δ -15.3. ^{27}Al NMR ($\text{CD}_2\text{-Cl}_2$): δ 59.2. ^{19}F NMR ($\text{CD}_2\text{-Cl}_2$): δ -55.9 (d, $|J_{\text{B-F}}| = 23.1$ Hz), -88.1 (t, $|J_{\text{B-F}}| = 19.7$ Hz), -90.7 (t, $|J_{\text{B-F}}| = 16.9$ Hz).

Synthesis of $[(\text{Ph}_3\text{PNSiMe}_3)\text{AlMe}_2(\text{PMe}_3)][\text{MeB}(\text{C}_6\text{F}_5)_3]$ (29**).** To a solution of **27** (0.053 g, 0.06 mmol) in a 50/50 benzene/hexane solution was added PMe_3 (0.006 mL, 0.06 mmol) in a similar solution. The reaction mixture was stirred for 0.5 h and followed by decanting of the solvent. The remaining solvent was removed under vacuum to yield a light yellow oil. ^1H NMR ($\text{CD}_2\text{-Cl}_2$): δ 7.7 (6H, m), 7.7 (9H, m), 0.9 (9H, d, $|J_{\text{P-H}}| = 6.9$ Hz), 0.5 (3H, s), 0.1 (9H, s), -0.7 (6H, s). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{CD}_2\text{-Cl}_2$): δ 150.2, 147.1, 139.5, 138.4, 136.2, 135.0 (d, $|J_{\text{C-P}}| = 12.5$ Hz), 133.9 (d, $|J_{\text{C-P}}| = 10.2$ Hz), 130.0, 126.9 (d, $|J_{\text{C-P}}| = 99.9$ Hz), 11.5 (d, $|J_{\text{C-P}}| = 18.6$ Hz), 4.2, 1.6, 1.6. ^{31}P NMR ($\text{CD}_2\text{-Cl}_2$): δ 33.9, -47.6. ^{11}B NMR ($\text{CD}_2\text{-Cl}_2$): δ -15.3. ^{27}Al NMR ($\text{CD}_2\text{-Cl}_2$): δ 62.3. ^{19}F NMR ($\text{CD}_2\text{-Cl}_2$): δ -55.8 (d, $|J_{\text{B-F}}| = 22.56$), -88.0 (t, $|J_{\text{B-F}}| = 20.59$), -90.6 (t, $|J_{\text{B-F}}| = 21.7$ Hz).

Synthesis of $[\text{Me}_2\text{Al}(\mu\text{-NPt-Bu}_3)_2\text{AlMe}][\text{MeB}(\text{C}_6\text{F}_5)_3]$ (30**).** To a solution of $\text{B}(\text{C}_6\text{F}_5)_3$ (0.066 g, 0.129 mmol) in a 50/50 benzene/hexane solution was added a solution of compound **14** (0.070 g, 0.129 mmol). The reaction mixture was stirred for 0.5 h and followed by decanting of the solvent. The remaining solvent was removed under vacuum to yield a light yellow oil. ^1H NMR ($\text{CD}_2\text{-Cl}_2$): δ 1.6 (3H, s), 1.5 (54H, d, $|J_{\text{H-H}}| = 13.5$ Hz), 0.5 (3H, s), -0.2 (6H, s). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{CD}_2\text{-Cl}_2$): δ 150.4, 147.2, 138.9, 135.6, 40.7 (d, $|J_{\text{C-P}}| = 45.9$ Hz), 31.7, 29.6, 10.0, 0.4. ^{31}P NMR ($\text{CD}_2\text{-Cl}_2$): δ 67.1. ^{11}B NMR ($\text{CD}_2\text{-Cl}_2$): δ -15.3. ^{27}Al NMR ($\text{CD}_2\text{-Cl}_2$): δ 56.8. ^{19}F NMR ($\text{CD}_2\text{-Cl}_2$): δ -55.8 (d, $|J_{\text{B-F}}| = 22.6$ Hz), -88.0 (t, $|J_{\text{B-F}}| = 19.7$ Hz), -90.6 (t, $|J_{\text{B-F}}| = 19.7$ Hz).

Synthesis of $[\text{AlMe}_2(\mu\text{-NPt-Bu}_3)_2\text{AlMe}(\text{PMe}_3)][\text{MeB}(\text{C}_6\text{F}_5)_3]$ (31**).** To a solution of **19** (0.070 g, 0.137 mmol) in $\text{CH}_2\text{-Cl}_2$ was added PMe_3 (0.005 mL, 0.137 mmol). The reaction mixture was stirred for 0.5 h and followed by decanting of the solvent. The remaining solvent was removed under vacuum to yield a light-yellow oil. ^1H NMR ($\text{CD}_2\text{-Cl}_2$): δ 1.5 (57H, d, $|J_{\text{P-H}}| = 13.2$ Hz), 1.3 (9H, d, $|J_{\text{P-H}}| = 5.6$ Hz), 0.5 (3H, s), -0.3 (6H, s). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{CD}_2\text{-Cl}_2$): δ 150.3, 147.2, 139.5, 138.5, 136.3, 135.3, 40.2 (d, $|J_{\text{C-P}}| = 42$ Hz), 30.7, 29.5, 14.9, 2.6. ^{31}P NMR ($\text{CD}_2\text{-Cl}_2$): δ 65.4, -49.8. ^{11}B NMR ($\text{CD}_2\text{-Cl}_2$): δ -15.3. ^{27}Al NMR ($\text{CD}_2\text{-Cl}_2$): δ 60.5. ^{19}F NMR ($\text{CD}_2\text{-Cl}_2$): δ -55.7 (d, $|J_{\text{B-F}}| = 23.1$ Hz), -87.9 (t, $|J_{\text{B-F}}| = 20.3$ Hz), -90.5 (t, $|J_{\text{B-F}}| = 21.4$ Hz).

X-ray Data Collection and Reduction. X-ray-quality crystals of **1**, **3**, **6**, **8**, **13**–**15**, **18**, and **20** were obtained directly from the preparation as described above. The 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 collecting a hemisphere of data in 1329 frames with 10 s exposure times. Crystal data are summarized in Table 1. The observed extinctions were consistent with the space groups in each case. The data sets were collected ($4.5^\circ < 2\theta < 45$ – 50.0°). A measure of decay was obtained by recollecting 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 SGI Challenge mainframe computer with remote X-terminals or PC employing X-emulation. The reflections with $F_o^2 > 3\sigma F_o^2$ were used in the refinements.

Table 1. Crystallographic Parameters^a

	1	3	6	8	11	13	14	15	18	20
formula	C ₁₂ H ₃₀ AlCl ₃ -NPSi	C ₂₅ H ₃₀ AlCl ₂ -NPSi	C ₂₃ H ₃₀ AlCl-PSi	C ₁₅ H ₃₉ AlN-PSi	C ₂₀ H ₄₀ AlCl-NP	C ₂₁ H ₂₅ AlNP	C ₂₈ H ₆₆ Al ₂ N ₂	C ₂₄ H ₅₄ Al ₂ -Cl ₄ N ₂ P ₂	C ₃₁ H ₃₉ Cl ₂ Ga-N ₂ P ₂ Si ₂	C ₃₃ H ₄₅ Cl ₂ Al-N ₂ P ₂ Si ₂
formula wt	380.76	501.44	441.97	319.51	387.93	349.37	546.73	628.39	698.38	614.81
a, Å	9.057(3)	11.486(3)	10.0480(1)	9.2831(19)	12.18710(10)	20.302(2)	16.4295(3)	13.316(4)	12.164(6)	12.240
b, Å	14.296(3)	15.496(4)	23.0088(3)	14.594(2)	15.2395(2)	8.6588(11)	13.48230(10)	16.339(4)	20.921(7)	21.09900(10)
c, Å	15.618(3)	30.737(12)	11.1174(2)	31.366(5)	12.6737(2)	23.725(5)	15.30300(10)	15.225(6)	15.076(10)	15.0698(2)
β, deg	92.73(3)	95.019(14)	103.7790(10)	91.20(2)	91.2510(10)				113.11(3)	112.2760(10)
V, Å ³	2020.1(8)	5449.7(29)	2496.22(6)	4248.4(13)	2353.27(5)	4170.7(11)	3389.73(7)	3312.5(18)	3529(3)	3601.41(5)
space group	P2 ₁ /n	Cc	P2 ₁ /n	P2 ₁ /c	P2 ₁ /n	Pca2 ₁	Pca2 ₁	Pbcm	P2 ₁ /c	P2 ₁ /c
d(calcd), g cm ⁻³	1.252	1.222	1.176	0.999	1.095	1.113	1.071	1.260	1.315	1.134
Z	4	8	4	8	4	8	4	4	4	4
μ, cm ⁻¹	0.626	0.386	0.309	0.219	0.271	0.176	0.198	0.524	1.113	0.235
no. of data collected	10086	9429	12471	4066	11595	12158	9811	15770	17734	18396
no. of data used	3521	4976	4330	3319	4065	4874	4296	3022	6144	6304
no. of variables	172	309	253	343	217	451	307	166	361	361
R, %	0.0423	0.0730	0.0436	0.0636	0.0583	0.0558	0.0652	0.0869	0.0326	0.0370
R _w , %	0.1348	0.1664	0.1297	0.1786	0.1916	0.1490	0.1881	0.1300	0.0987	0.1258
GOF	1.079	1.160	1.055	1.375	1.648	1.214	1.558	1.451	0.829	1.080

^a All data collected at 24 °C with Mo Kα radiation (λ = 0.710 69 Å). R = Σ||F_o - |F_c||/Σ|F_o|. R_w = [Σ(|F_o - |F_c||)²/Σ|F_o|²]^{0.5}.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.^{18,19} The heavy atom positions were determined using direct methods employing either of the SHELXTL direct method routines. 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 ω(|F_o - |F_c||)², where the weight ω is defined as 4F_o²/2σ(F_o²) 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. Carbon-bound hydrogen 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. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. The hydrogen atom contributions were calculated, but not refined. The final values of refinement parameters are given in Table 1. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, and bond distances and angles have been deposited as Supporting Information.

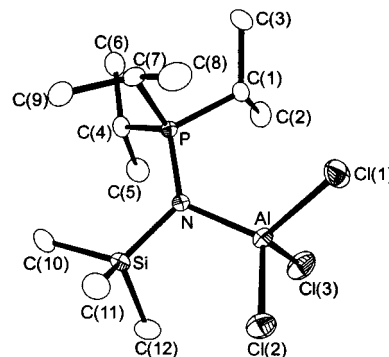
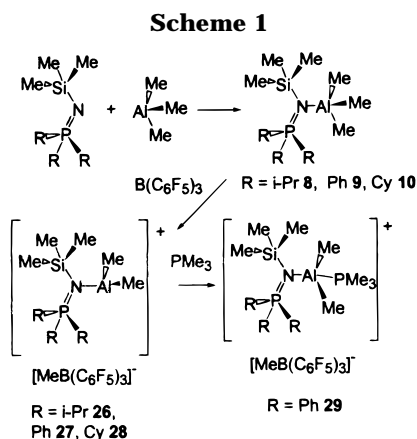


Figure 1. ORTEP drawings of **1**; 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Al(1)–N(1), 1.902(2) Å; Al(1)–Cl(2), 2.1313(12) Å; Al(1)–Cl(3), 2.1372(13) Å; Al(1)–Cl(1), 2.1481(13) Å; P(1)–N(1), 1.646(2) Å; N(1)–Si(1), 1.804(2) Å; N(1)–Al(1)–Cl(2), 112.51(8)°; N(1)–Al(1)–Cl(3), 109.36(8)°; Cl(2)–Al(1)–Cl(3), 108.02(6)°; N(1)–Al(1)–Cl(1), 116.62(8)°; Cl(2)–Al(1)–Cl(1), 102.47(5)°; Cl(3)–Al(1)–Cl(1), 107.35(6)°; P(1)–N(1)–Si(1), 124.00(12)°; P(1)–N(1)–Al(1), 123.92(12)°; Si(1)–N(1)–Al(1), 112.07(11)°.

Results and Discussion

Synthesis. Reactions of the silylphosphinimines R₃-PNSiMe₃ (R = *i*-Pr, Ph, Cy) with the aluminum Lewis acids AlCl₃, AlMeCl₂, AlMe₂Cl, and AlMe₃ are in general straightforward acid–base reactions, resulting in the formation of the corresponding donor–acceptor adducts. In this manner the compounds (*i*-Pr)₃PNSiMe₃AlCl₃ (**1**), (R₃PNSiMe₃)AlMeCl₂ (R = *i*-Pr, **2**; Ph, **3**; Cy, **4**), (R₃-PNSiMe₃)AlMe₂Cl (R = *i*-Pr, **5**; Ph, **6**; Cy, **7**), and (R₃-PNSiMe₃)AlMe₃ (R = *i*-Pr, **8**; Ph, **9**; Cy, **10**) were readily prepared and isolated (Scheme 1). NMR spectroscopic data are consistent with these formulations. As is typical, a downfield shift of the ³¹P resonance upon ligand coordination of the phosphinimine nitrogen to



aluminum is observed. Crystallographic data were obtained for compounds **1**, **3**, **6**, and **8** (Figures 1–4). The structural features of these molecules are as expected with a pseudotetrahedral geometry about the aluminum centers. The Al–N distances range from 1.902(2) to 1.968(2) Å. These distances are significantly

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(19) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 390.

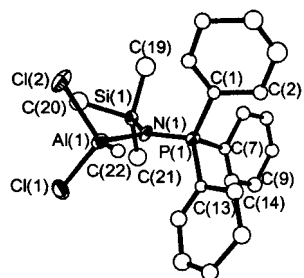


Figure 2. ORTEP drawing of one of the two independent molecules of **3** in the asymmetric unit; 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Al(1)–N(1), 1.93(2) Å; Al(1)–C(22), 1.96(2) Å; Al(1)–Cl(1), 2.138(9) Å; Al(1)–Cl(2), 2.214(8) Å; P(1)–N(1), 1.58(2) Å; N(1)–Al(1)–C(22), 115.2(7)°; N(1)–Al(1)–Cl(1), 107.5(6)°; C(22)–Al(1)–Cl(1), 113.4(6)°; N(1)–Al(1)–Cl(2), 108.2(5)°; C(22)–Al(1)–Cl(2), 102.7(6)°; Cl(1)–Al(1)–Cl(2), 109.5(4)°; P(1)–N(1)–Si(1), 121.8(9)°; P(1)–N(1)–Al(1), 120.8(9)°; Si(1)–N(1)–Al(1), 117.3(8)°.

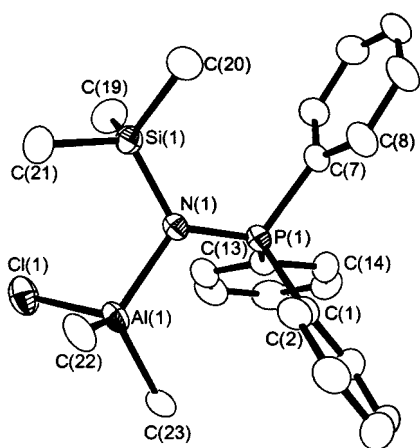


Figure 3. ORTEP drawings of **6**; 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Al(1)–N(1), 1.968(2) Å; Al(1)–C(23), 1.982(3) Å; Al(1)–C(22), 1.993(2) Å; Al(1)–Cl(1), 2.2150(12) Å; Si(1)–N(1), 1.781(2) Å; P(1)–N(1), 1.612(2) Å; N(1)–Al(1)–C(23), 113.93(10)°; N(1)–Al(1)–C(22), 109.93(10)°; C(23)–Al(1)–C(22), 114.34(14)°; N(1)–Al(1)–Cl(1), 103.86(7)°; C(23)–Al(1)–Cl(1), 103.21(10)°; C(22)–Al(1)–Cl(1), 110.84(10)°; P(1)–N(1)–Si(1), 125.52(12)°; P(1)–N(1)–Al(1), 117.00(11)°; Si(1)–N(1)–Al(1), 117.11(10)°.

longer than those found in iminoaluminum dimer [CpAl(μ -Naryl)]₂ (1.796(2) Å, 1.811(3) Å)²⁰ but in the range of those found in the diketiminato derivatives described by Smith et al.¹⁵ Comparing the *i*-Pr₃PNSiMe₃ adducts **1** and **8**, the Al–N bond distances in **1** (1.646(2) Å) are significantly shorter than those found in **8** (1.763(6) Å) consistent with the greater electron-withdrawing nature of chloride versus methyl. Among **1**, **3**, **6**, and **8**, the Al–Cl and Al–C distances average 2.155(9) and 1.98(3) Å, respectively. These distances are typical of the Al–Cl distances in [Cp*AlCl(μ -Cl)]₂²¹ and [Cp*AlMe(μ -Cl)]₂,²² and the Al–C distances are similar to those in the complexes (CH(C(CH₃)NR)₂)Al(CH₃)₂ (R = tolyl, 2,6-*i*-Pr₂C₆H₄)¹⁵ and the terminal Al–Me bond in Cp₂AlMe (1.943(5) Å).²³ P–N multiple bonding is reflected by the P–N bond distance range of 1.58(2)–1.651(14) Å. Si–N

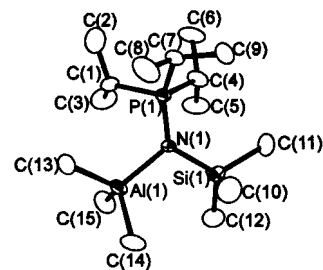


Figure 4. ORTEP drawing of one of the two independent molecules of **8** in the asymmetric unit; 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Al(1)–C(15), 1.982(9) Å; Al(1)–C(14), 1.990(10) Å; Al(1)–C(13), 1.991(11) Å; Al(1)–N(1), 2.022(4) Å; Si(1)–N(1), 1.762(6) Å; P(1)–N(1), 1.606(6) Å; C(15)–Al(1)–C(14), 110.3(5)°; C(15)–Al(1)–C(13), 112.7(4)°; C(14)–Al(1)–C(13), 100.1(4)°; C(15)–Al(1)–N(1), 107.9(3)°; C(14)–Al(1)–N(1), 111.8(3)°; C(13)–Al(1)–N(1), 113.9(3)°; P(1)–N(1)–Si(1), 125.8(2)°; P(1)–N(1)–Al(1), 124.0(3)°; Si(1)–N(1)–Al(1), 110.1(3)°.

bond distances are typical, averaging 1.781(4) Å. The geometry about the nitrogen atoms is approximately trigonal planar with P–N–Si angles ranging from 121.8(9)° to 126.6(2)°.

In contrast to the above Lewis acid–base chemistry, attempts to form analogous complexes with *t*-Bu₃PNSiMe₃ with all of the aluminum species Al(Me)_{3–*n*}Cl_{*n*} resulted in no reaction under a variety of conditions. The failures of adduct formation in these cases are attributed to the steric crowding as the cone angle of the (*t*-Bu₃P) fragment is significantly larger than those of the other phosphines.

This view is also supported by the observation that for the parent phosphinimines R₃PNH, where the steric crowding is alleviated by the removal of the trimethylsilyl substituent, adduct formation occurs readily. In this vein, reaction of R₃PNH (R = *t*-Bu, Cy, Ph) with AlMe₂Cl and AlMe₃ afforded the synthesis of (R₃PNH)AlMe₂Cl (R = Cy, **11**; *t*-Bu, **12**) and (Ph₃PNH)AlMe₃ (**13**), respectively. Spectroscopic data as well as crystallographic data for **11** and **13** confirmed the above formulations (Figures 5 and 6). In general the geometries of these adducts are similar to those observed for **1**, **3**, **6**, and **8**. Reduced steric congestion about nitrogen is reflected in the shorter Al–N bond distances, in **11** (1.892(2) Å) and **13** (1.665(5) Å) as well as the P–N–Al angles in **11** (142.0(2)°) and **13** (152.2(4)°) which are significantly greater than those observed for the trimethylsilylphosphinimine adducts described above. While the P–N distance in **11** (1.623(2) Å) falls in the range observed for **1**, **3**, **6**, and **8**, the P–N distance in **13** averages 1.520(5) Å, suggesting stronger P–N multiple bonding.

In early studies, Schmidbaur et al.^{24–27} showed that aluminum–phosphinimine adducts were not thermally stable. For the complexes (Me₃PNSiMe₃)AlMe₃ thermalolysis resulted in ligand liberation. In contrast, alu-

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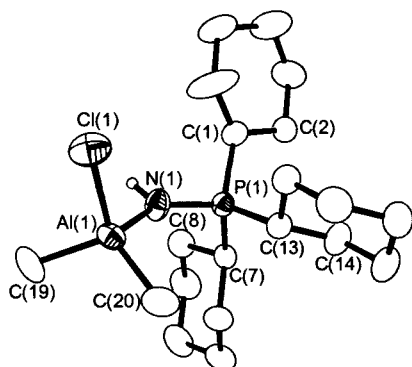


Figure 5. ORTEP drawings of **11**; 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Al(1)–N(1), 1.892(2) Å; Al(1)–C(20), 1.990(3) Å; Al(1)–C(19), 1.995(3) Å; Al(1)–Cl(1), 2.2166(12) Å; P(1)–N(1), 1.623(2) Å; N(1)–Al(1)–C(20), 113.90(14)°; N(1)–Al(1)–C(19), 106.1(2)°; C(20)–Al(1)–C(19), 115.8(2)°; N(1)–Al(1)–Cl(1), 104.30(9)°; C(20)–Al(1)–Cl(1), 108.18(13)°; C(19)–Al(1)–Cl(1), 107.89(14)°; P(1)–N(1)–Al(1), 142.0(2)°.

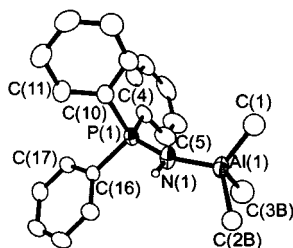


Figure 6. ORTEP drawing of one of the two independent molecules of **13** in the asymmetric unit; 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. One set of the disordered Al-bound carbon positions are depicted: Al(1)–N(1), 1.672(4) Å; P(1)–N(1), 1.513(4) Å; P(1)–N(1)–Al(1), 152.8(3)°.

minum–phosphinimide derivatives of formulation $[X_2\text{-Al}(\mu\text{-NPR}_3)_2]$ (X = Br, Me) were derived via reaction of the tin–phosphinimine reagents $\text{R}_3\text{PNSnMe}_3$ with AlMe_3 or upon heating the adduct $(\text{Me}_3\text{PNSiMe}_3)\text{AlBr}_3$ to 215 °C. In a similar manner, the adducts **1–10** are not thermally stable. However, upon heating to 80–90 °C loss of Me_3SiCl is not observed; rather the phosphinimine ligand is simply liberated. Similarly, heating of adducts **11–13** also resulted in ligand liberation. However, heating the reaction mixture of $(t\text{-Bu}_3\text{PNH})$ and AlMe_3 to 80 °C for 10 h resulted in the formation of the species $[\text{Me}_2\text{Al}(\mu\text{-NP}t\text{-Bu}_3)]_2$ (**14**) in 62% isolated yield (Scheme 2). Monitoring the reaction mixture by ^{31}P NMR spectroscopy revealed the initial formation of the adduct $(t\text{-Bu}_3\text{PNH})\text{AlMe}_3$ as evidenced by the observation of the resonance at 68.25 ppm. Upon heating, this signal is replaced with the resonance at 56.72 ppm attributed to **14**. The dimeric formulation of **14** in which two phosphinimide ligands bridge two aluminum centers has been confirmed by X-ray crystallography (Figure 7). The coordination sphere of each aluminum center is a significantly distorted pseudotetrahedral geometry with Al–N and Al–C bond distances averaging 1.929(7) and 1.994(10) Å, respectively, with C–Al–C and N–Al–C angles of 110.6(5)° and 113.6(5)°. This bridged

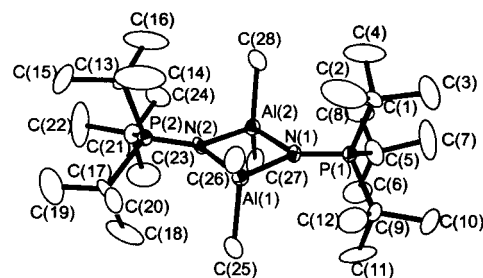
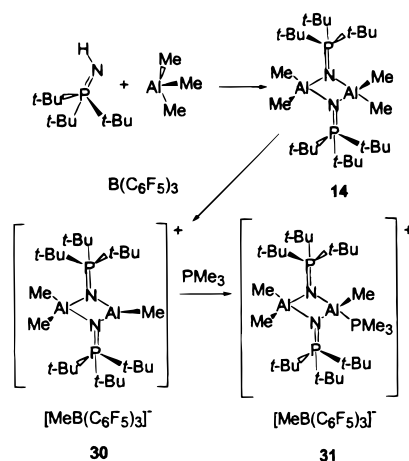


Figure 7. ORTEP drawings of **14**; 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Al(1)–N(2), 1.925(7) Å; Al(1)–N(1), 1.940(7) Å; Al(1)–C(25), 1.944(10) Å; Al(1)–C(26), 1.989(9) Å; Al(1)–Al(2), 2.704(2) Å; Al(2)–N(1), 1.914(7) Å; Al(2)–N(2), 1.936(7) Å; Al(2)–C(27), 2.020(9) Å; Al(2)–C(28), 2.026(11) Å; P(1)–N(1), 1.604(3) Å; P(2)–N(2), 1.604(3) Å; N(2)–Al(1)–N(1), 90.6(3)°; N(2)–Al(1)–C(25), 112.3(4)°; N(1)–Al(1)–C(25), 111.8(4)°; N(2)–Al(1)–C(26), 115.7(3)°; N(1)–Al(1)–C(26), 116.2(3)°; C(25)–Al(1)–C(26), 109.3(5)°; N(1)–Al(2)–N(2), 91.1(3)°; N(1)–Al(2)–C(27), 111.6(2)°; N(2)–Al(2)–C(27), 110.4(3)°; N(1)–Al(2)–C(28), 115.7(4)°; N(2)–Al(2)–C(28), 114.7(4)°; C(27)–Al(2)–C(28), 111.8(5)°; P(1)–N(1)–Al(2), 135.7(5)°; P(1)–N(1)–Al(1), 135.1(5)°; Al(2)–N(1)–Al(1), 89.14(12)°; P(2)–N(2)–Al(1), 135.4(5)°; P(2)–N(2)–Al(2), 135.7(5)°; Al(1)–N(2)–Al(2), 88.92(12)°.

Scheme 2



geometry results in an Al–Al separation of 2.704(2) Å. The four-membered Al_2N_2 core gives rise to N–Al–N and Al–N–Al angles averaging 90.9(3)° and 89.03(12)°, respectively. Correspondingly, the planarity at the nitrogen atoms results in average P–N–Al angles of 135.5(5)°.

Attempts to prepare the chloromethyl analogue of **14** were undertaken via the reaction of $t\text{-Bu}_3\text{PNLi}$ and MeAlCl_2 . NMR data of the isolated colorless, crystalline product **15** revealed no evidence of aluminum-bound methyl groups. X-ray crystallographic studies of **15** confirmed the dimeric formulation as $[\text{AlCl}_2(\mu\text{-NP}t\text{-Bu}_3)]_2$ (Figure 8). Although not anticipated it appears that methyl for halide redistribution is favored during this reaction as **15** is isolated in 67% yield based on Al and ligand. The general structural features of **15** are very similar to those described above for **14** and to those reported for $[\text{AlCl}_2(\mu\text{-NPPH}_3)]_2$ by Dehnicke et al.¹⁶ The bridging phosphinimide groups give rise to Al–N distances that are shorter in **15** than in **14**, averaging 1.888(4) Å. This is consistent with the presence of the electron-withdrawing chlorides on aluminum. The Al–

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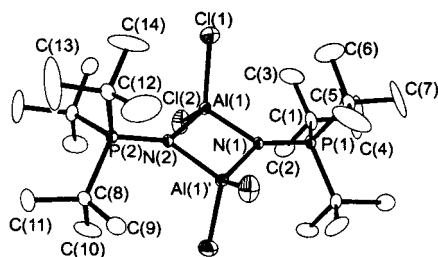


Figure 8. ORTEP drawings of **15**; 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Al(1)–N(2), 1.888(4) Å; Al(1)–N(1), 1.887(4) Å; Al(1)–Cl(1), 2.126(2) Å; Al(1)–Cl(2), 2.148(2) Å; Al(1)–Al(1), 2.633(3) Å; P(1)–N(1), 1.623(5) Å; P(2)–N(2), 1.627(5) Å; N(1)–Al(1), 1.887(4) Å; N(2)–Al(1), 1.888(4) Å; N(2)–Al(1)–N(1), 91.42(17)°; N(2)–Al(1)–Cl(1), 115.76(17)°; N(1)–Al(1)–Cl(1), 116.71(17)°; N(2)–Al(1)–Cl(2), 109.93(17)°; N(1)–Al(1)–Cl(2), 112.44(18)°; Cl(1)–Al(1)–Cl(2), 109.53(11)°; P(1)–N(1)–Al(1), 135.76(12)°; P(1)–N(1)–Al(1), 135.76(12)°; Al(1)′–N(1)–Al(1), 88.4(2)°; P(2)–N(2)–Al(1), 135.77(11)°; P(2)–N(2)–Al(1), 135.77(11)°; Al(1)′–N(2)–Al(1), 88.4(2)°.

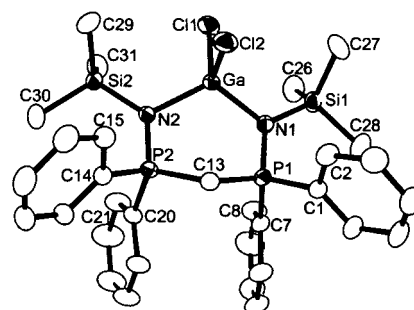
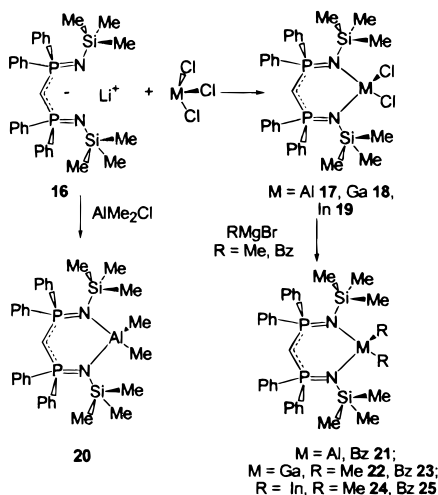


Figure 9. ORTEP drawings of **18**; 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Ga(1)–N(1), 1.926(2) Å; Ga(1)–N(2), 1.930(2) Å; Ga(1)–Cl(2), 2.200(2) Å; Ga(1)–Cl(1), 2.2006(10) Å; Si(1)–N(1), 1.771(2) Å; P(1)–N(1), 1.637(2) Å; P(2)–N(2), 1.639(2) Å; N(1)–Ga(1)–N(2), 113.53(9)°; N(1)–Ga(1)–Cl(2), 107.34(8)°; N(2)–Ga(1)–Cl(2), 106.46(7)°; N(1)–Ga(1)–Cl(1), 111.60(7)°; N(2)–Ga(1)–Cl(1), 112.37(7)°; Cl(2)–Ga(1)–Cl(1), 104.89(4)°; P(1)–N(1)–Si(1), 126.99(13)°; P(1)–N(1)–Ga(1), 109.71(12)°; Si(1)–N(1)–Ga(1), 121.85(12)°; P(2)–N(2)–Si(2), 127.51(13)°; P(2)–N(2)–Ga(1), 109.36(11)°; Si(2)–N(2)–Ga(1), 120.53(11)°.

Scheme 3



Cl distances in **15** average 2.137(2) Å, and the corresponding Al–Al separation is 2.633(3) Å.

An alternative approach to group 13 phosphinimine derivatives involves the use of the bidentate anion of $\text{LiCH}(\text{PPh}_2(\text{NSiMe}_3))_2$ (**16**). Reaction of **16** with aluminum, gallium, and indium halides readily gives the four-coordinate complexes of the form $[\text{CH}(\text{PPh}_2(\text{NSiMe}_3))_2]\text{MCl}_2$ (M = Al, **17**; Ga, **18**; In, **19**) (Scheme 3). In the case of **18**, this formulation was confirmed by X-ray crystallography (Figure 9). The pseudotetrahedral coordination sphere about Ga is defined by the two phosphinimine nitrogen atoms ($\text{Ga}-\text{N}_{\text{av}} = 1.928(2)$ Å) and the two chlorides ($\text{Ga}-\text{Cl}_{\text{av}} = 2.203(2)$ Å). The “bite angle” of the bisphosphinimine anion is 113.53(9)°, while the Cl–Ga–Cl angle is 104.89(4)°. The ligand geometry is as expected, although it is noteworthy that the central carbon and Ga atoms are displaced from the N_2P_2 plane by 0.60 and 0.75 Å, respectively.

The analogous species $[\text{CH}(\text{PPh}_2(\text{NSiMe}_3))_2]\text{AlMe}_2$ (**20**) was prepared via reaction of **16** with Me_2AlCl . This formulation was confirmed by X-ray crystallography (Figure 10). The pseudotetrahedral coordination sphere about Al is similar to that of the Ga atom in **18**. The Al– N_{av} and Al– C_{av} distances in **20** average 1.955(2) and 1.991(2) Å, respectively. The pseudochair conformation

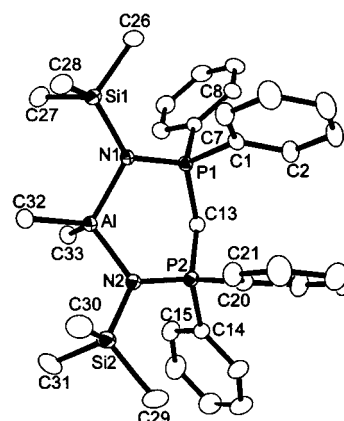


Figure 10. ORTEP drawings of **20**; 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Al(1)–N(2), 1.952(2) Å; Al(1)–N(1), 1.959(2) Å; Al(1)–C(33), 1.986(2) Å; Al(1)–C(32), 1.996(2) Å; Si(1)–N(1), 1.765(2) Å; Si(1)–C(26), 1.870(2) Å; Si(1)–C(27), 1.874(2) Å; Si(1)–C(28), 1.883(2) Å; Si(2)–N(2), 1.767(2) Å; P(1)–N(1), 1.640(2) Å; P(2)–N(2), 1.637(2) Å; N(2)–Al(1)–N(1), 108.96(7)°; N(2)–Al(1)–C(33)°, 111.76(9)°; N(1)–Al(1)–C(33), 111.58(8)°; N(2)–Al(1)–C(32), 106.78(8)°; N(1)–Al(1)–C(32), 106.01(8)°; C(33)–Al(1)–C(32), 111.46(9)°; P(1)–N(1)–Si(1), 125.94(9)°; P(1)–N(1)–Al(1), 111.94(8)°; Si(1)–N(1)–Al(1), 119.52(8)°; P(2)–N(2)–Si(2), 125.18(9)°; P(2)–N(2)–Al(1), 112.77(8)°; Si(2)–N(2)–Al(1), 120.59(8)°.

of the chelate ring in **20** is similar to that seen in **18**, with the central carbon and Al atoms displaced from the N_2P_2 plane by 0.63 and 0.77 Å, respectively. A variety of other alkyl and aryl derivatives, including $[\text{CH}(\text{PPh}_2(\text{NSiMe}_3))_2]\text{MR}_2$ (M = Al, Bz, **21**; M = Ga, R = Me, **22**; Bz, **23**; R = In, R = Me, **24**; Bz, **25**), were readily prepared by treatment of the halide compounds **17**–**19** with the appropriate lithium or Grignard reagents. ^1H , ^{13}C , and ^{31}P NMR data as well as elemental analyses of a representative sampling of these species were consistent with these formulations.

Ionic Salts. Attempts to generate related zwitterionic and/or cationic derivatives from **20**–**25** proved to yield highly sensitive species. In general, the aluminum and gallium species gave unstable mixtures of products upon

reactions with the borane $B(C_6F_5)_3$. Similarly reaction of **24** with the trityl borate $Ph_3C[B(C_6F_5)_4]$ gave a mixture of unidentified, unstable products as evidenced by ^{31}P NMR.

In contrast, the Lewis acidic borane $B(C_6F_5)_3$ reacts stoichiometrically with the phosphinimine adducts **8–10** in a facile manner to form the ionic species. These species proved to have extreme sensitivity. While this precluded the acquisition of elemental analytical data, 1H , ^{13}C , ^{31}P , ^{11}B , ^{27}Al , and ^{19}F NMR spectral data were consistent with the formulation of these products as $[(R_3PNSiMe_3)AlMe_2][MeB(C_6F_5)_3]$ ($R = i\text{-Pr}$, **26**; Ph , **27**; Cy , **28**) (Scheme 1). Particularly characteristic of these species were the broadened 1H NMR resonance attributed to the borane-bound methyl group at approximately 0.48 ppm and the single resonance attributable to the Al-bound methyl groups between -0.2 and -0.6 ppm. These observations, together with the fact that these resonances are temperature invariant to -80 °C, infer that migration of the borane among the methyl groups does not occur. Treatment of **27** with PMe_3 affords clean conversion to the salt $[(Ph_3PNSiMe_3)_2AlMe(PMe_3)][MeB(C_6F_5)_3]$ (**29**) as confirmed by the NMR data. For example, the ^{31}P NMR spectrum of **29** shows resonances at 33.9 and -47.6 ppm attributable to the phosphinimine and coordinated phosphine ligands, respectively. The similarity of these data to those observed for **27** suggests that these compounds are discrete ions in solutions, although this has not been confirmed via conductivity measurements.

In a similar vein, stoichiometric treatment of the dimeric species **14** with the borane $B(C_6F_5)_3$ results in the formation of the ionic product $[Me_2Al(\mu\text{-NP-}t\text{-Bu}_3)_2AlMe][MeB(C_6F_5)_3]$ **30** (Scheme 2) as evidenced by the NMR data. It is noteworthy that the resonances attributable to the terminal methyl groups on the unaltered aluminum center are observed at 1.57 ppm while the resonances for the bridging and terminal methyl groups at the zwitterionic aluminum center occur at 0.46 and -0.21 ppm, respectively. As with **28**, the 1H

NMR spectrum of **30** is temperature invariant to -80 °C. Moreover, it is noteworthy that, even in the presence of a large excess of borane, compound **30** does not undergo further reaction. This lack of reactivity is in contrast to that of the related titanium complex $(t\text{-Bu}_3\text{PN})_2TiMe(\mu\text{-MeB(C}_6\text{F}_5)_3)$ ¹¹ which readily converts to $(t\text{-Bu}_3\text{PN})_2Ti(\mu\text{-MeB(C}_6\text{F}_5)_3)_2$.²⁸ As with compound **27**, the zwitterionic species **30** reacts with PMe_3 to give the complex salt $[Me_2Al(\mu\text{-NP-}t\text{-Bu}_3)_2AlMe(PMe_3)][MeB(C_6F_5)_3]$ (**31**) as confirmed by the spectroscopic data.

Preliminary screening of these group 13 zwitterionic systems for their ability to catalyze ethylene polymerization was undertaken. The species **28**, **29**, and **31** failed to effect polymerization under mild conditions of 25 °C and 1 atm of the ethylene. This may result from the inherent strength of the Al–C bond and thus its resistance to facile insertion.

Summary

The preparation and structural and spectroscopic features of a variety of group 13 complexes of phosphinimine ligands have been described. The ionic derivatives demonstrate the expected electrophilic nature, which augurs well for the olefin polymerization catalysts. Nonetheless, the present phosphinimine and phosphinimide group 13 systems are not operative as ethylene polymerization catalysts under ambient conditions. Under more forcing conditions, Jordan et al. have effected ethylene polymerization by aluminum catalysts at 80 °C.^{13,14}

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Supporting Information Available: Crystallographic data and NMR spectra for **26–31**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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