(cis CO), 206.5 (trans CO), 290.9 (Cr=C). IR (cm^{-1}): 2015 (w), 1945 (s), 1905 (s) (ν_{CO}). Anal. Calcd for $C_8H_6CrO_7$ (M_r 266.125): C, 36.11; H, 2.27; Cr, 19.54. Found: C, 37.01; H, 2.27; Cr, 19.41.

A mixture of Me_2SiCl_2 and $Na_2Cr(CO)_5$ in THF at −60 °C gave **32**. ^1H NMR (toluene-d_8): δ 0.5 (s, H_3CSi), 1.4, 3.6 (m, *THF*). ^{29}Si NMR (toluene-d_8): δ 97.4. The complex dimerized at room temperature to give **21**. The reaction could also be monitored by ^{29}Si NMR spectroscopy.

21: ^1H NMR (C_6D_6) δ 0.99 (s, H_3C); ^{29}Si NMR (C_6D_6) δ 159.0; MS (EI, 70 eV; *m/e*) 444 (0.5%, M^+), 416 (3%, $M^+ - CO$), further fragments for loss of CO. Anal. Calcd for $C_{12}H_{12}CrO_8Si_2$ (M_r 444.384): C, 32.43; H, 2.72; Cr, 23.40. Found: C, 32.01; H, 2.69; Cr, 22.91.

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Supplementary Material Available: Tables of hydrogen atom coordinates and anisotropic displacement parameters for 4, 5, 7, and 8 (16 pages); listings of structure factors (89 pages). Ordering information is given on any current masthead page.

Syntheses, Structures, and Isomerization Processes of Dialkylaluminum Silylamido Complexes

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Reactions of R_3SiNH_2 with R'_3Al in refluxing hexane afford a family of dimeric aluminum silylamides, $[R'_2AlN(H)SiR_3]_2$ (R′ = Me, R_3 = Ph_3, Et_3; R′ = *i*-Bu, R_3 = Ph_3, R_3 = *t*-Bu_2H). $[Me_2AlN(H)SiMe_3]_2$ is prepared from $[Cl_2AlN(H)SiMe_3]_2$ and dimethylmagnesium. X-ray crystallography of $[Me_2AlN(H)SiEt_3]_2$ and $[Me_2AlN(H)SiPh_3]_2$ indicates planar Al_2N_2 ring frameworks with the silyl groups oriented trans about the ring. A distorted-tetrahedral geometry at nitrogen places the silyl groups nearly in the plane of the Al_2N_2 ring, while the N–H bond vector is nearly orthogonal to the Al_2N_2 plane. The degree of distortion depends on the steric bulk of SiR_3. All dimers undergo a cis–trans isomerization process in benzene. This process is fast for methylaluminum compounds but slow for isobutylaluminum ones: the methylaluminum amides attain equilibrium solution isomer distributions of ca. 50/50, while the isobutyl compounds are strongly biased toward the cis or trans isomer and do not attain equilibrium. Isomerization of the methylaluminum compounds is catalyzed by less than one equiv of 4-methylpyridine, while hindered pyridines have no effect. Greater amounts of 4-methylpyridine lead to adduct formation; the adduct $(i\text{-}Bu)_2(4\text{-}Me\text{-}py)AlN(H)SiPh_3$ is isolated. A mechanism with rate-determining attack of base at aluminum is discussed. Crystal data for $[Me_2AlN(H)SiPh_3]_2$: M_r = 662.96, triclinic, $P\bar{1}$, a = 8.821 (2) Å, b = 9.435 (3) Å, c = 13.342 (4) Å, α = 70.97 (3)°, β = 74.23 (2)°, γ = 66.02 (2)°, Z = 1, R = 0.041, R_w = 0.042. Crystal data for $[Me_2AlN(H)SiEt_3]_2$: M_r = 374.6, monoclinic, $P2_1/n$, a = 7.095 (3) Å, b = 11.452 (5) Å, c = 15.467 (5) Å, β = 96.83 (3)°, Z = 2, R = 0.055, R_w = 0.052.

Introduction

The well-known reaction of alkylamines with alkylaluminum compounds affords oligomeric or polymeric ring and cage structure aluminum amides and imides.[1] Very few alkylaluminum silylamides have been prepared, however.[2] The possible influence of silyl groups on the geometry and coordinating ability of nitrogen, and therefore the ability of silylamides to function as bridging ligands, is of fundamental interest.[3] Thus, while no monomer of the type $R_2Al\text{–}N(R')(R'')$ (R, R′, R″ = alkyl) is presently known, we are interested in preparation of such a monomer (where R′ or R′ = alkylsilyl group), which may exist because of a reduced tendency of nitrogen to form a dimer by bridging aluminum centers. There may be a π interaction between nitrogen and aluminum in such compounds.[4] Known amido monomers, such as $Al[N(SiMe_3)_2]_3$,[5] $Al(N\text{-}i\text{-}Pr_2)_3$,[6] and $(Me_2N)_2AlCl$,[6] have more than one π-donating ligand. Another goal is preparation

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of alkoxoaluminum silylamides, also unknown, which may serve as ceramic precursors for AlN or SiAlON species.[7] Herein we desicrbe the preparation of aluminum silylamides, the effects of the steric bulk of silyl substituents on structure, and solution isomerization processes.

Experimental Section

Reagents, Solvents, and General Procedures. Unless otherwise stated, all operations were conducted under an atmosphere of high-purity nitrogen using standard Schlenk techniques. The following were obtained from commercial sources and used without further purification: Et_3SiCl (Silar); t-Bu_2HSiCl (Petrarch); NH_3 (Linde Specialty Gases, anhydrous grade); Me_3Al (Ethyl Corp.). Pyridines (Aldrich) were dried over molecular sieves. Benzene (Fisher) was distilled from potassium, and toluene (Fisher) was distilled from sodium. Pentane (American Scientific), hexane (American Scientific), tetrahydrofuran (Aldrich), and diethyl ether (Fisher) were distilled from sodium/potassium alloy.

Analytical Procedures. Elemental analyses were performed by the University Instrumentation Center at the University of New Hampshire and by Galbraith Laboratories. Problems with obtaining complete combustion affected the accuracy of elemental analyses of aluminum amides.[7d] Irreproducibility of the combustion process necessitated making several determinations in some cases. In these cases, the number of determinations and largest deviations from the average are given. Infrared spectra were measured from mineral oil (Nujol) mulls between KBr plates on a Perkin-Elmer 283B spectrometer and were referenced to the 1028-cm^{-1} band of a 0.05-mm polystyrene film. Absorptions are described below as follows: strong (s), medium (m), weak (w), shoulder (sh), and broad (br). Proton and carbon NMR spectra were recorded on a Bruker AM-360 spectrometer (360 and 90 MHz, respectively) and were referenced internally to tetramethylsilane. Mass spectra were obtained at the Mass Spectrometry Facility at Pennsylvania State University and the University Instrumentation Center at the University of New Hampshire.

Preparation of (Triethylsilyl)amine.[8] Ammonia was bubbled (ca. 3 bubbles/s) into Et_3SiCl (43 mL, 0.255 mol) in benzene (165 mL), at 15–20 °C, with stirring. The reaction was stopped when formation of the white precipitate (NH_4Cl) had stopped (ca. 1 h). The solution was filtered, the solid was washed with benzene (50 mL), and the filtrate and washings were combined. Ammonia was then bubbled into the filtrate and wash solution (35 min), producing a small amount of white solid. The solution was filtered and tested for Cl^- with silver nitrate to ensure that ammonolysis was complete. The filtrate was distilled, and the fraction boiling at 120–140 °C (25 mL) was collected and used in the subsequent reaction. The fraction boiling at 100–120 °C (20 mL) may be collected and redistilled (bp 135 °C) to give a total yield of 34 mL (82%, 0.208 mol) of Et_3SiNH_2. The product was stored at −78 °C. IR (neat, 400–4000 cm^{-1}): 671 (m), 712 (br), 828 (s), 967 (m), 1011 (s) (ν(Si–N)[9]), 1238 (s), 1378 (w), 1417 (m), 1464 (m), 1556 (m), 2724 (w), 2801 (w), 2878 (s), 2914 (s), 2953 (s), 3386 (w, br), 3454 (w). ^1H NMR (C_6D_6, 25 °C): δ 0.95 (t, J = 7.9 Hz, 9 H, $-CH_2CH_3$); 0.47 (q, J = 7.9 Hz, 6 H, $-CH_2CH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 7.29 (s, $-CH_2CH_3$); 6.31 (s, $-CH_2CH_3$).

Preparation of (Triphenylsilyl)amine.[10] Ammonia was bubbled into Ph_3SiCl (11.13 g, 0.038 mol) in diethyl ether (250 mL) at 20–25 °C with stirring. The reaction was stopped when the white precipitate (NH_4Cl) was no longer formed (3.75 h). The solution was filtered, and $AgNO_3$ was used to indicate the absence of Cl^- and thus the completion of the reaction. Diethyl ether was removed under vacuum to yield 9.4 g of the pure Ph_3SiNH_2 as a white crystalline solid (91%, 0.034 mol, mp 55–56 °C). Anal. Calcd for $C_{18}H_{17}NSi$: C, 78.52; H, 6.18; N, 5.09. Found: C, 78.87; H, 6.26; N, 5.05. IR (Nujol, 400–4000 cm^{-1}): 495 (s), 695 (s), 735 (s), 840 (s), 1110 (s), 1255 (m), 1375 (m), 1425 (s), 1465 (m), 1480 (sh), 1540 (m), 1585 (w), 1770 (w), 1820 (w), 1885 (w), 1960 (w), 2940 (s), 3080 (w), 3380 (m), 3440 (m).

Preparation of (Di-*tert*-butylsilyl)amine. Ammonia was bubbled into t-Bu_2HSiCl (15 mL, 0.0739 mol) in diethyl ether (250 mL) at 20–25 °C with stirring. The reaction was stopped when the white precipitate (NH_4Cl) was no longer formed (6 h). The solution was filtered, and $AgNO_3$ (aqueous) was used to indicate the absence of Cl^- to ensure the completion of the reaction. The diethyl ether was removed under vacuum to yield a clear colorless liquid. This viscous liquid was distilled under vacuum (0.2 Torr), and the distillate boiling at 33–37 °C (8 mL) was collected as product (d 1.05 g mL^{-1}, 71%, 8.4 g, 0.053 mol). Anal. Calcd for $C_8H_{21}NSi$: C, 60.30; H, 13.28; N, 8.79. Found: C, 60.30; H, 13.12; N, 8.40. IR (neat, 400–4000 cm^{-1}): 610 (m), 850 (s, br), 930 (m), 1000 (m), 1010 (m), 1365 (s), 1390 (m), 1470 (s), 1550 (m), 2090 (s), 2710 (w), 2870 (s), 2900 (s), 2940 (s), 3410 (m), 3480 (w) cm^{-1}. ^1H NMR (C_6D_6, 25 °C): δ 0.48 (d, 2 H, NH_2); 0.99 (s, 18 H, $-C(CH_3)_3$); 4.07 (s, br, 1 H, Si-H).

Preparation of $[Me_2AlN(H)SiPh_3]_2$ (1). Trimethylaluminum (2.25 mL of a 1.41 M solution in hexane, 0.0032 mol) was layered over (triphenylsilyl)amine (0.87 g, 0.0032 mol) in hexane (15 mL). White crystals grew as the layers were mixed by gentle swirling. The slurry was refluxed for 3 h. The white solid was recrystallized from toluene to yield colorless needles (0.71 g, 67%), mp 211–212 °C. Anal. Calcd for $C_{40}H_{44}Al_2N_2Si_2$: C, 72.47; H, 6.69; N, 4.22. Found: C, 71.88; H, 6.80; N, 4.10. Four determinations were made, and the greatest deviations from the average were as follows: C, 0.52; H, 0.13; N, 0.06. IR (Nujol, 400–4000 cm^{-1}): 500 (m), 528 (m), 580 (m), 690 (s), 710 (s), 735 (s), 775 (s), 790 (s), 992 (m), 1108 (s), 1125 (s), 1200 (m), 1430 (s), 1585 (w), 1770 (w, br), 1820 (w, br), 1890 (w, br), 1960 (w, br), 3070 (w), 3220 (w). ^1H NMR (C_6D_6, 25 °C): δ 7.58–7.66 (m, Ph H); 7.09–7.18 (m, Ph H); 1.66 (s, 1 H, N–H); 1.59 (s, 1 H, N–H); −0.26, −0.92 (s, 6 H, Al–CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 136.28, 136.22, 135.66, 135.06, 135.03, 130.56, 130.46, 129.77 (s, C_6H_5); −6.45, −5.17, −4.21 (s, Al–CH_3). MS (CI, CH_5^+): 662 amu (M − 1).

Preparation of $[Me_2AlN(H)SiEt_3]_2$ (2). Trimethylaluminum in hexane (66.2 mL of a 0.74 M solution, 0.049 mol) was added to (triethylsilyl)amine (8.0 mL, 0.049 mol) in pentane (35 mL) over a 1.5-h period, with stirring. The colorless solution was refluxed for 1.5 h. Pentane and hexane were removed under reduced pressure, and the remaining sticky, white crystalline solid was sublimed twice under high vacuum (40 °C and 10^{-3} Torr for 72 h) to the cooler upper walls of a large Schlenk tube. A 5.0-g (60%, 0.013 mol, mp 61–62 °C) yield of colorless prisms was obtained. Anal. Calcd for $C_{16}H_{44}Al_2N_2Si_2$: C, 51.29; H, 11.84; N, 7.48. Found: C, 50.99; H, 11.86; N, 7.36. Nine determinations were made, and the greatest deviations from the average were as follows: C, 0.43; H, 0.60; N, 0.70. IR (Nujol, 400–4000 cm^{-1}): 468 (w, br), 497 (m), 565 (m), 670 (s), 721 (s), 763 (s), 795 (s), 820 (s), 955 (m), 1000 (s) (ν(Si–N)[9]), 1070 (sh), 1100 (s), 1185 (s), 1225 (m), 1250 (m), 1400 (m), 3200 (w) (ν(N–H)[11]) cm^{-1}. ^1H NMR (C_6D_6 25 °C): δ 0.90 (t, J = 7.9 Hz, 9 H, $-CH_2CH_3$); 0.63, 0.62 (q, J = 8.0 Hz, 6 H, $-CH_2CH_3$); 0.32, 0.31 (s, 1 H, N–H); −0.34, −0.46 (s, 3 H each, Al–CH_3, cis isomer); −0.41 (s, 6 H, Al–CH_3, trans isomer). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 7.33 (s, $-CH_2CH_3$); 6.73, 6.69 (s, CH_2CH_3); −6.06 (s, fwhm = 27.2 Hz, $AlCH_3$). MS (EI, 70 eV): 373 amu (M − 1).

Preparation of $[Me_2AlN(H)SiMe_3]_2$ (3). To a stirred solution of $[Cl_2AlN(H)SiMe_3]_2$ (2.25 g, 6.05×10^{-3} mol) at −10 °C in 40 mL of diethyl ether was added Me_2Mg (0.83 M in ether, 14.5 mL, 12.1×10^{-3} mol) via syringe. A white precipitate formed immediately, and the solution was stirred for 15 min at −10 °C. The solution was stirred for an additional 45 min at room temperature.

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The ether was removed in vacuo and the white powder rigorously dried under vacuum. The product was sublimed away from the $MgCl_2$ (0.1 Torr, 70 °C) to yield 0.47 g of product (27%, 1.62×10^{-3} mol, mp 82–84 °C). Anal. Calcd for $C_6H_{20}Al_2Cl_4N_2Si_2$: C, 19.36; H, 5.42; N, 7.53. Found: C, 18.89; H, 5.23; N, 7.06. IR (Nujol, 400–4000 cm^{-1}): 480 (m), 510 (m), 580 (m), 680 (s), 765 (s), 850 (s), 1120 (m), 1195 (m), 1260 (s), 1380 (m), 1460 (s), 2950 (s), 3240 (m) cm^{-1}. ^1H NMR (C_6D_6, 25 °C): δ −0.55, −0.39 (s, 3 H each, $Al{-}CH_3$); −0.48 (s, 6 H, $Al{-}CH_3$); 0.045 (s, 9 H, $Si{-}CH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 1.88 (s, $Si{-}CH_3$); −6.59 (s, br, $Al{-}CH_3$).

Preparation of [*i*-Bu$_2$AlN(H)SiPh$_3$]$_2$ (4). Triisobutylaluminum in hexane (11.10 mL of a 0.67 M solution, 7.45×10^{-3} mol) was added to (triphenylsilyl)amine (2.05 g, 7.45×10^{-3} mol) in hexane (35 mL) with stirring. The colorless solution was refluxed for ca. 20 h. Hexane was removed under reduced pressure to yield a white crystalline solid. The compound was purified by recrystallization from hexane at −30 °C. A 2.47-g (80%, 5.95×10^{-3} mol, mp 130–190 °C dec) yield of colorless prisms was obtained. Anal. Calcd for $C_{52}H_{68}Al_2N_2Si_2$: C, 75.14; H, 8.25; N, 3.37. Found: C, 74.52; H, 8.12; N, 3.04. Three determinations were made, and the greatest deviations from the average were as follows: C, 0.59; H, 0.26; N, 0.11. IR (Nujol mull, 400–4000 cm^{-1}): 505 (m), 535 (s), 603 (m), 640 (sh), 660 (s), 695 (s), 705 (s), 730 (s), 765 (s), 805 (s), 820 (m), 995 (w), 1060 (m), 1113 (s), 1155 (m), 1360 (sh), 1365 (s), 1430 (s), 1465 (s), 1590 (w), 1770 (w), 1820 (w), 1885 (w), 1960 (w), 2860 (s), 2940 (s, br), 3220 (w) cm^{-1}. ^1H NMR (C_6D_6, 25 °C): δ 0.86, 0.95 (d, 12 H each, $-CHCH_3$, trans isomer); 0.68, 1.13 (d, 12 H each, $-CHCH_3$, cis isomer); −0.03, 0.52 (d, 4 H each, $Al{-}CH_2$, cis isomer); 0.09, 0.11 (d, 4 H each, $Al{-}CH_2$, trans isomer); 1.34, 2.08 (nonet, 2 H each, $-CH(CH_3)_2$, cis isomer); 1.75 (nonet, 4 H, $-CH(CH_3)_2$, trans isomer); 1.84, 1.89 (s, 2 H, N–*H*); 7.16–7.19 (m, Ph–*H*); 7.72–7.78 (m, Ph *H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 24.85, 27.69 (br s, $Al{-}CH_2$); 25.75, 26.60, 28.04, 29.19 (s, $Al{-}CH_2CH(CH_3)_2$); 26.21, 28.30, 28.77 (s, $Al{-}CH_2CH(CH_3)_2$); 129.68, 130.48, 135.06, 135.16, 135.58, 136.05, 136.38, 136.75 (s, C_6H_5). MS (EI, 70 eV): 774 ($M - C_4H_{10}$).

Preparation of [*i*-Bu$_2$AlN(H)Si(H)-*t*-Bu$_2$]$_2$ (5). A freshly prepared solution of triisobutylaluminum in hexane (9.6 mL of a 0.655 M solution, 0.0063 mol) was added to (di-*tert*-butylsilyl)amine (0.95 mL, 0.0063 mol) in hexane (30 mL) with stirring. The colorless solution was refluxed for ca. 24 h. The hexane was removed under vacuum to yield a sticky, white crystalline solid, which was recrystallized from hexane at −78 °C. A 1.32-g (70%, 0.0044 mol, mp 165–170 °C) yield of colorless needles was obtained. IR (Nujol mull, 400–4000 cm^{-1}): 655 (m, br), 670 (m, br), 750 (s), 815 (s), 870 (m), 1005 (m), 1060 (m), 1135 (m), 1365 (m), 1375 (m), 1465 (s), 2100 (s), 2860 (s), 2940 (s, br), 3220 (w) cm^{-1}. ^1H NMR (C_6D_6, 25 °C): δ 0.46, 0.56 (dd, 4 H, $-CH_2$), 0.42, 0.60 (dd, 4 H, $-CH_2$), 0.78 (s, 2 H, N–*H*), 1.11 (s, 36 H, $Si{-}C(CH_3)_3$), 1.24 (d, 12 H, $-CHCH_3$), 2.19 (nonet, 4 H, –C*H*), 4.27 (s, 2 H, Si–*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 29.26; 29.06, 29.03; 28.79 (s, $Si{-}C(CH_3)_3$); 28.75; 28.38; 26.81; 26.15 (s, br, $Al{-}CH_2$); 19.98, 19.71. MS (CI, CH_5^+): 541 amu ($M - C_4H_{10}$).

Preparation of *i*-Bu$_2$(4-Me-py)AlN(H)SiPh$_3$ (7). Freshly distilled 4-methylpyridine (0.06 mL, 6.16×10^{-4} mol) was added to [*i*-Bu$_2$AlN(H)SiPh$_3$]$_2$ (0.25 g, 3.01×10^{-4} mol) in hexane (10 mL). After 24 h at room temperature, the hexane was removed under vacuum to yield a yellow oil. The oil was taken up in hexane (5 mL) and cooled to −30 °C, whereupon a white crystalline solid was isolated (0.069 g, 45%, mp 156–160 °C). Anal. Calcd for $C_{32}H_{41}AlN_2Si$: C, 75.55; H, 8.12; N, 5.51. Found: C, 75.03; H, 8.01; N, 5.26. IR (Nujol mull, 400–4000 cm^{-1}): 500 (s), 510 (sh, s), 655 (m), 700 (s), 735 (m), 805 (m), 925 (s), 1030 (m), 1105 (s), 1380 (m), 1430 (s), 1465 (s), 1630 (s), 1770 (w), 1825 (w), 1890 (w), 1960 (w), 2860 (s), 2940 (br, s), 3040 (m), 3400 (w) cm^{-1}. ^1H NMR (C_6D_6, 25 °C): δ 0.24 (d, 4 H, $Al{-}CH_2$); 1.21 (d, 12 H, $-CH(CH_3)_2$); 0.66 (s, 1 H, N–*H*); 1.45 (s, 3 H, $py{-}CH_3$); 2.08 (nonet, 2 H, $Al{-}CH_2CH$); 7.16–7.84 (m, Ph *H*); 6.14, 8.13 (d, 4 H, Ar *H*, for 4-Me-py). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 151.8, 147.14, 125.42 (s, py C_5H_4); 140.55, 135.94, 135.57, 129.73, 128.91 (s, $Si{-}C_6H_5$); 28.87 (s, $Al{-}CH_2CH(CH_3)_2$); 27.16 (s, $Al{-}CH_2CH(CH_3)_2$); 24.14 (s, br, $Al{-}CH_2$); 20.57 (s, $py{-}CH_3$).

Reactions of [R′$_2$AlN(H)SiR$_3$]$_2$ with 4-Methylpyridine. A large-scale reaction of 4 with 4-methylpyridine is described above. The reactions of 1, 3, 5, and 7 with 4-methylpyridine were done in NMR tubes in C_6D_6. To ca. 25 mg of the corresponding compound were added ca. 1, 2, and 3 equiv of 4-methylpyridine in succession, and the reaction was monitored by ^1H NMR spectroscopy. Compounds **1**, **3**, and **5** exhibited a decrease in the intensity of the dimer $Al{-}CH_3$ or $Al{-}CH_2$ resonances and broadening of these same resonances. At the same time, new resonances were observed which represent the 4-methylpyridine adduct. Some of the characteristic ^1H NMR resonances (all in C_6D_6 at 25 °C) corresponding to the 4-methylpyridine adducts for **1**, **3**, **5** and **7** are as follows. Me$_2$(4-Me-py)AlN(H)SiPh$_3$: δ −0.33 (s, 6 H, $Al{-}CH_3$); 0.65 (s, 1 H, N–*H*); 1.49 (s, 3 H, $py{-}CH_3$). Me$_2$(4-Me-py)AlN(H)SiMe$_3$: δ −0.50 (s, 6 H, $Al{-}CH_3$); 1.74 (s, 3 H, $py{-}CH_3$). *i*-Bu$_2$(4-Me-py)AlN(H)Si-*t*-Bu$_2$H: δ −0.43 (d, 1 H, N–*H*); 0.48 (d, 4 H, $Al{-}CH_2$); 1.21 (s, 18 H, $Si{-}C(CH_3)_3$); 1.27 (d, 12 H, $Al{-}CH_2CH(CH_3)_2$); 1.48 (s, 3 H, $py{-}CH_3$); 4.29 (d, 1 H, Si–*H*); 2.18 (nonet, 2 H, $Al{-}CH_2CH(CH_3)_2$). Cl$_2$(4-Me-py)AlN(H)SiMe$_3$: δ 0.09 (s, 9 H, $Si{-}(CH_3)_3$); 1.36 (s, 3 H, $py{-}CH_3$).

Attempted Reactions of 2,6-Di-*tert*-butylpyridine with 1 and 4 and of 2,6-Dimethylpyridine with 2 and 4. These reactions were run in NMR tubes in C_6D_6 as above. There was no observable effect on the isomerization of these compounds when up to 3 equiv of either 2,6-di-*tert*-butylpyridine or 2,6-dimethylpyridine was added to the NMR samples, over a period of 3 h. The $Al{-}CH_3$ dimer resonances did not broaden, and the corresponding pyridine adducts were not formed.

Attempted Crossover Reaction of 2 and 3. A ^1H NMR sample containing ca. 25 mg each of **2** and **3** in 1.5 mL of C_6D_6 was prepared and measured after 24 min at 25 °C. Only the trans isomers of **2** and **3** were observed. After 185 min the spectrum was identical except for traces of the cis isomers. Approximately 1 equiv of 4-methylpyridine was added, the tube was warmed to 80 °C for 30 min under nitrogen, and the spectrum was remeasured. Equilibrium amounts of cis and trans isomers of **2** and **3** were observed, but no other signals were present.

X-ray Crystallography of 1 and 2. Under a nitrogen atmosphere, crystals were mounted in glass capillaries, which were then flame-sealed. Cell constants and the orientation matrix for intensity data collection were based on the setting angles of more than 16 centered reflections. ω scans of several strong low-angle reflections were acceptable. The structures were solved by direct methods (Siemens SHELXTL PLUS crystallographic package). Full-matrix least-squares refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. Both molecules possess a crystallographic inversion center. The hydrogen atoms attached to N were located in the difference Fourier map and refined isotropically. In compound **1**, the N–H bond length was constrained at 0.90 (1) Å. The remaining hydrogen atoms were placed in calculated positions. Crystallographic data are presented in Table I. Selected bond distances and angles are given in Table II. Full structure data are given in the supplementary material.

Results and Discussion

Synthesis and Characterization. The aluminum amides were prepared as follows, except for [Me$_2$AlN(H)SiMe$_3$]$_2$ (**3**):

$$R_3SiNH_2 + AlR'_3 \xrightarrow[\text{reflux}]{\text{hexane}} \tfrac{1}{2}[R'_2AlN(H)SiR_3]_2 + R'H \qquad (1)$$

$$\mathbf{1, 2, 4, 5}$$

1, $R_3 = Ph_3$, $R' = Me$; **2**, $R_3 = Et_3$, $R' = Me$;
4, $R_3 = Ph_3$, $R' = i\text{-Bu}$; **5**, $R_3 = t\text{-Bu}_2H$, $R' = i\text{-Bu}$

These reactions presumably occur via amine adducts $R_3Al{\leftarrow}NH_2SiR_3$, but none of these have been isolated. Alkylation of [Cl$_2$AlN(H)SiMe$_3$]$_2$ (**6**) with Me$_2$Mg gave **3**, while the reported[12] alkylation using MeLi gave only methane and [MeAlNSiMe$_3$]$_4$[13] as isolable products. The compounds are very moisture-sensitive but are unchanged

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[12] Schmidbaur, H. *Angew. Chem.* **1961**, *73*, 257.

[13] This new compound will be discussed in a future publication. See also: Timm, M. J. M.S. Thesis, University of New Hampshire, May 1990.

Table I. Summary of Crystallographic Data for $[Me_2AlN(H)SiPh_3]_2$ (1) and $[Me_2AlN(H)SiEt_3]_2$ (2)

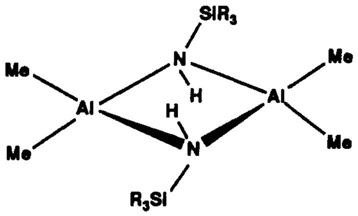
	1	2
empirical formula	$C_{40}H_{44}N_2Al_2Si_2$	$C_{16}H_{44}N_2Al_2Si_2$
mol wt	662.96	374.6
a, Å	8.821 (2)	7.095 (3)
b, Å	9.435 (3)	11.452 (5)
c, Å	13.342 (4)	15.467 (5)
α, deg	70.97 (3)	90
β, deg	74.23 (2)	96.83 (3)
γ, deg	66.02 (2)	90
Z	1	2
V, Å^3	946.6 (5)	1247.9 (8)
space group	$P\bar{1}$	$P2_1/n$
d_{calcd}, g cm^{-3}	1.16	0.997
radiation	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
diffractometer	Nicolet R3m/V four circle	Nicolet R3m/V
temp, °C	23	20
scan width, deg	1.4 + Kα separation	0.6 + Kα separation
scan speed, deg min^{-1}	3.5–15.0	3.0–15.0
scan type	θ–2θ	θ–2θ
data collcn range, deg	4.5–55.0	3.0–55.0
no. of unique data	3361 (R_{int} = 0.013)	1646 (R_{int} = 0.011)
no. of obsd data	2237 ($I > 3\sigma(I)$	1204 ($I > 3\sigma(I)$)
rfln/param ratio	10.6	12.0
R^a	0.0412	0.0546
$R_w{}^b$	0.0425	0.0515
goodness of fit	1.53	1.69

[a] $R = \sum||F_o| - |F_c|| / \sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|) + 0.0004(|F_o|^2)$.

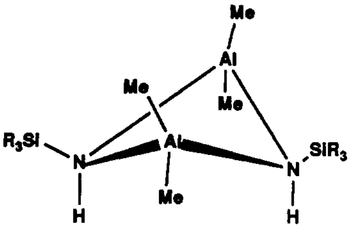
after exposure to dry air for 30 s.

All of the dimers **1–6** may be cleaved to monomeric adducts by addition of 4-methylpyridine, as observed by ^1H NMR spectroscopy. The adduct $(i\text{-}Bu)_2(4\text{-}Mepy)AlN(H)SiPh_3$ (**7**) has been isolated and fully characterized.

Compounds **1–3** and **6** have a trans structure when in the solid state (see below) and when initially dissolved in C_6D_6, but they isomerize to a ca. 50/50 cis/trans mixture over 24 h.



trans



cis

Thus, the ^1H NMR spectrum of *trans*-$[Me_2AlN(H)SiEt_3]_2$ initially shows a singlet at −0.41 ppm (trans Al–CH_3). Two additional peaks appear at −0.34 and −0.46 ppm (cis Al–CH_3). The only other reasonable solution structure with two Me–Al ^1H NMR signals would be the cis-trimer structure, assumed, for example, by $[Me_2AlN(H)Me]_3$.[14] This would imply a dimer–trimer equilibrium (cf. $2(Me_2AlNH_2)_3 \rightleftarrows 3(Me_2AlNH_2)_2$).[15] However, the lack of concentration dependence of the spectra rules this out. Similar cis/trans mixture have been observed for $[Me_2AlN(H)\text{-}i\text{-}Pr]_2$,[16] $[Et_2AlN(H)\text{-}t\text{-}Bu]_2$,[17] and $[Et_2AlN(Me)(SiMe_3)]_2$.[2a]

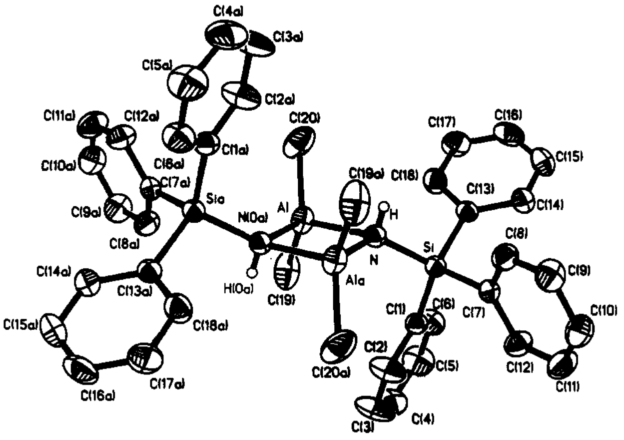


Figure 1. ORTEP plot of the molecular structure of $[Me_2AlN(H)SiPh_3]_2$ (**1**).

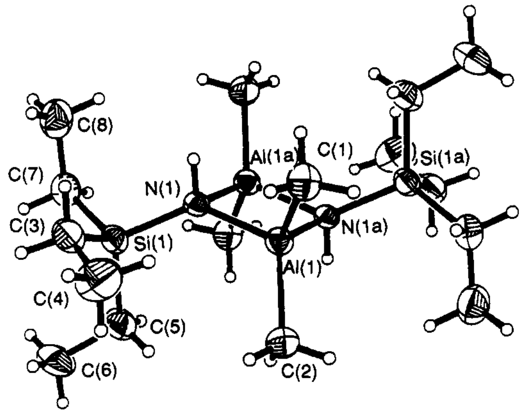


Figure 2. ORTEP plot of the molecular structure of $[Me_2AlN(H)SiEt_3]_2$ (**2**).

At least in the case of $[Me_2AlN(H)SiEt_3]_2$, the two isomers are in equilibrium at room temperature. Cooling a toluene solution of compound **2** to −30 °C precipitates the trans isomer. The supernatant containing the cis isomer may be warmed to room temperature, giving the 50/50 cis/trans mixture again.

Isomer distributions of **4** and **5** are different from those of **1–3**. $[i\text{-}Bu_2AlN(H)SiPh_3]_2$ is largely the cis form when initially dissolved in benzene (ratio cis/trans ≈ 80/20), while $[i\text{-}Bu_2AlN(H)Si\text{-}t\text{-}Bu_2H]_2$ appears to be largely in the trans form (ratio cis/trans ≈ 10/90). These are not equilibrium distributions, however. As the solution is warmed, these proportions change, but a competing decomposition reaction occurs, making it impossible to determine final isomer distributions. Compounds **4** and **5** have a similar degree of steric hindrance at silicon, so the reason one prefers trans and the other cis is not understood. The reasons these compounds fail to isomerize are discussed below.

Structural Studies. Single-crystal X-ray studies of $[Me_2AlN(H)SiPh_3]_2$ and $[Me_2AlN(H)SiEt_3]_2$ reveal a crystallographically centrosymmetric Al_2N_2 ring with trans silyl groups about the ring (Figures 1 and 2), consistent

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[14] Alford, K. J.; Gosling, K.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1972**, 2203.

[15] Sauls, F. C.; Czekaj, C. L.; Interrante, L. V. *Inorg. Chem.* **1990**, *29*, 4688.

[16] Amirkhalili, S.; Hitchcock, P. B.; Jenkins, A. D.; Nyathi, J. Z.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1981**, 377.

[17] Gosling, K.; Smith, J. D.; Wharmby, D. H. W. *J. Chem. Soc. A* **1969**, 1738.

Table II. Selected Bond Distances (Å) and Bond Angles (deg) in $[Me_2AlN(H)SiPh_3]_2$ (1) and $[Me_2AlN(H)SiEt_3]_2$ (2)

	$[Me_2AlN(H)SiPH_3]_2$		
Si–N	1.765 (2)	C(19)–Al–C(20)	118.3 (2)
Si–C(1)	1.867 (4)	N–Al–AlA	44.1 (1)
Si–C(7)	1.875 (3)	C(19)–Al–AlA	121.1 (1)
Si–C(13)	1.873 (3)	C(20)–Al–AlA	120.6 (2)
Al–N	1.971 (3)	N–Al–NA	88.2 (1)
Al–C(19)	1.952 (6)	C(19)–Al–NA	109.5 (1)
Al–C(20)	1.951 (4)	C(20)–Al–NA	114.3 (1)
Al–AlA	2.832 (2)	Si–N–Al	127.9 (2)
Al–NA	1.971 (3)	Si–N–AlA	126.9 (1)
		Al–N–AlA	91.8 (1)
N–Si–C(1)	112.0 (1)	Si–C(1)–C(6)	121.0 (2)
N–Si–C(7)	109.6 (1)	Si–C(1)–C(2)	122.8 (3)
C(1)–Si–C(7)	109.9 (1)	C(13)–C(14)–C(15)	121.1 (3)
N–Si–C(13)	106.8 (1)	Si–(7)–C(8)	121.4 (2)
C(1)–Si–C(13)	109.1 (1)	Si–C(7)–C(12)	122.3 (3)
C(7)–Si–C(13)	109.4 (1)	Si–C(13)–C(18)	120.7 (2)
N–Al–C(19)	114.0 (1)	Si–C(13)–C(14)	122.6 (2)
N–Al–C(20)	108.7 (2)		
	$[Me_2AlN(H)SiEt_3]_2$		
Al(1)–N(1)	1.965 (3)	C(2)–Al(1)–N(1A)	107.8 (2)
Al(1)–C(2)	1.957 (5)	N(1)–Si(1)–C(3)	109.1 (2)
Al(1)–N(1A)	1.969 (3)	C(3)–Si(1)–C(5)	112.0 (2)
Si(1)–C(3)	1.851 (5)	C(3)–Si(1)–C(7)	107.3 (2)
Si(1)–C(7)	1.871 (5)	Al(1)–N(1)–Si(1)	128.0 (2)
C(3)–C(4)	1.497 (7)	Si(1)–N(1)–Al(1A)	124.0 (2)
C(7)–C(8)	1.498 (8)	Si(1)–C(5)–C(6)	116.1 (4)
Al(1)–C(1)	1.959 (4)	N(1)–Al(1)–C(2)	116.0 (2)
Al(1)–Al(1A)	2.802 (3)	N(1)–Al(1)–Al(1A)	44.6 (1)
Si(1)–N(1)	1.778 (3)	C(2)–Al(1)–Al(1A)	121.5 (2)
Si(1)–C(5)	1.845 (5)	C(1)–Al(1)–N(1A)	114.0 (2)
N(1)–Al(1A)	1.969 (3)	Al(1A)–Al(1)–N(1A)	44.5 (1)
C(5)–C(6)	1.505 (7)	N(1)–Si(1)–C(5)	110.1 (2)
		N(1)–Si(1)–C(7)	109.2 (2)
N(1)–Al(1)–C(1)	107.5 (2)	C(5)–Si(1)–C(7)	109.0 (2)
C(1)–Al(1)–C(2)	118.8 (2)	Al(1)–N(1)–Al(1A)	90.8 (1)
C(1)–Al(1)–Al(1A)	119.7 (2)	Si(1)–C(3)–C(4)	117.7 (4)
N(1)–Al(1)–N(1A)	89.2 (1)	Si(1)–C(7)–C(8)	116.5 (3)

with ^1H NMR spectroscopy immediately upon dissolving in C_6D_6. Preference for the dimer over the Al_3N_3 trimer (e.g., in $[t\text{-}Bu_2AlNH_2]_3$[7b]) occurs when the N and Al substituents are bulkier.[18] There are no other primary silylamides of aluminum to compare with;[19] however, the bond distances of 1 and 2 are comparable and are similar to those of alkylaluminum amides such as *trans*-$[Me_2AlN(H)\text{-}i\text{-}Pr]_2$.[20]

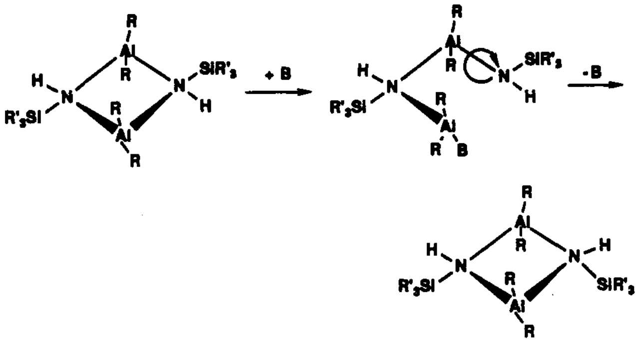
The most striking feature of the structures of 1 and 2 is a distortion of the amide nitrogen whereby the N-Si bond vector is moved toward the plane of the Al_2N_2 ring, while the N-H bond vector shifts to a position nearly perpendicular to the Al_2N_2 plane. This removes steric hindrance between SiR_3 and substituents on aluminum, so the average Al-N bond distances of 1.971 (3) and 1.967 (3) Å in 1 and 2 do not differ appreciably even though the $SiPh_3$ group is bulkier than the $SiEt_3$ group. Thus, $[Me_2AlN(H)SiPh_3]_2$ is simply more distorted at nitrogen than $[Me_2AlN(H)SiEt_3]_2$. This distortion is quantitated in Table III in terms of the dihedral angle between the Al_2N_2 plane and the N-Si (or C) bond vector. The influence of the substituent group on the magnitude of distortion is clearly determined by the following series of steric effects, from most distorted to least: $SiPh_3 > SiEt_3 > SiMe_3 > i\text{-Pr}$. Structural data are also available for $[Me_2Al\overline{NSi(Me)_2CH_2CH_2Si}(Me)_2]_2$ and $[Me_2AlN(SiMe_2H)_2]_2$,[21] which both have longer Al-N distances (in the range 1.992 (3)–2.005 (3) Å) than 1 and 2. Because this distortion is not available to these disilylamido compounds (Table III shows the angle for $[Me_2AlN(SiMe_2H)_2]_2$ is close to the ideal of 54.75°, assuming tetrahedral geometry), steric interactions between substituents on Al and N are greater, lengthening the Al-N bond.

Table III. Structural Parameters of Aluminum Amides

compd	av d(Al–N), Å	dihedral angle between Al_2N_2 plane and N–Si or N–C bond vector, deg
$[Me_2AlN(H)SiPh_3]_2$	1.971 (3)	29.3 (1)
$[Me_2AlN(H)SiEt_3]_2$	1.967 (3)	33.2 (1)
$[Cl_2AlN(H)SiMe_3]_2$[a]	1.914 (4)	36.4 (1)
$[Me_2AlN(H)\text{-}i\text{-}Pr]_2$[b]	1.958 (5)	43.0 (2)
$[Me_2AlN(SiMe_2H)_2]_2$[c]	1.992 (3)	58.6 (1)

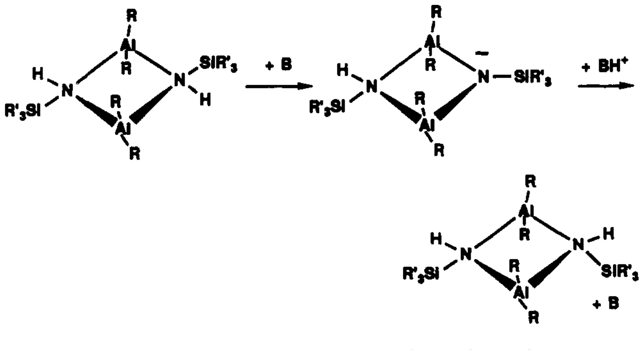
[a] Reference 24. [b] Reference 20. [c] Reference 21.

Mechanistic Studies. The mechanism of cis–trans isomerization of aluminum amido dimers has been proposed to involve catalytic Lewis base attack at aluminum,[22] because pyridine accelerates isomerization in $[Me_2AlN(CH_3)(Ph)]_2$:



Systematically varying steric hindrance of the Lewis base and of the aluminum site of attack has provided further support for this mechanism. The cis–trans isomerization of 1–3 and 6, but not 4 and 5, is catalyzed by 4-methylpyridine. Hindered pyridines (2,6-dimethylpyridine and 2,6-di-*tert*-butylpyridine) have no effect. The dependence of isomerization on accessibility of the aluminum center (4 and 5, being $i\text{-}Bu_2Al$ compounds, have the more hindered aluminum center and do not isomerize at all, while 1–3 and 6 have more accessible Me_2Al and Cl_2Al groups) and on steric hindrance of the pyridine nitrogen further supports the proposed mechanism.

Certain other mechanisms of isomerization may be ruled out. The deprotonation mechanism



is excluded because 2,6-Me_2py and 4-Mepy have very

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(18) Beachley, O. T.; Coates, G. E. *Inorg. Chem.* **1965**, *5*, 3241.

(19) $[Et_2AlN(H)SiEt_3]_x$ has been briefly reported, but no spectroscopic properties have been given: Zhinkin, D. Y.; Korneeva, G. K.; Korneev, N. N.; Sobolevskii, M. V. *Zh. Obshch. Khim.* **1966**, *36*, 360.

(20) Al-Wassail, A. I.; Hitchcock, P. B.; Sarisaban, S.; Smith, J. D.; Wilson, C. L. *J. Chem. Soc., Dalton Trans.* **1985**, 1929.

(21) Byers, J. J.; Pennington, W. T.; Robinson, G. H.; Hrncir, D. C. *Polyhedron* **1990**, *9*, 2205.

(22) Wakatsuki, K.; Tanaka, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1475.

similar basicity,[23] but 2,6-Me_2py does not cause isomerization. Examination of models suggests the N–H proton in $[Me_2AlN(H)SiEt_3]_2$ should be readily available to 2,6-dimethylpyridine. Another possibility is cleavage of two Al–N bonds in $[R'_2AlN(H)SiR_3]_2$, giving monomers $R'_2AlN(H)SiR_3$, which then recombine, giving both cis and trans dimers. Because a mixture of $[Me_2AlN(H)SiMe_3]_2$ and $[Me_2AlN(H)SiEt_3]_2$ showed no crossover (i.e., the mixed dimer $[Me_2AlN(H)SiEt_3][Me_2AlN(H)SiMe_3]$ was not formed), this mechanism may also be excluded.

Future plans include thermal decomposition studies and structural studies to determine the degree of distortion in the isobutylaluminum compounds and the factors governing cis vs trans isomerism in these compounds.

Acknowledgment. Partial support from the donors of the Petroleum Reseach Fund, administered by the American Chemical Society, is gratefully acknowledged. The NSF (VT-EPSCoR program, Grant No. RII8610679) funded the X-ray diffractometer used in this study. Ethyl Corp. is acknowledged for a gift of alkylaluminums. We thank Prof. Guy Rosenthal for crystallographic studies on $[Me_2AlN(H)SiEt_3]_2$ and Dr. Fred Tebbe for useful discussions.

Supplementary Material Available: Tables IVS and VS (bond distances and angles for **1** and **2**), VIS and VIIS (final fractional coordinates for **1** and **2**), VIIIS and IXS (thermal parameters for **1** and **2**), and XIIS and XIIIS (H atom coordinates for **1** and **2**) (8 pages); Tables XS and XIS (F_o vs F_c for **1** and **2**) (19 pages). Ordering information is given on any current masthead page.

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[23] $pK_a(4\text{-MepyH}^+) = 6.02$, $pK_a(2,6\text{-Me}_2\text{pyH}^+) = 6.77$: Clarke, K.; Rothwell, K. *J. Chem. Soc.* **1960**, 1885.

[24] Structural data for $[Cl_2AlN(H)SiMe_3]_2$: $M_r = 372.2$, orthorhombic, *Pcab*, $a = 11.336$ (3) Å, $b = 9.192$ (2) Å, $c = 18.346$ (7) Å, $Z = 4$, $R = 0.048$, $R_w = 0.057$. Full details will be provided in a forthcoming publication.

Synthesis of ((Dimethylamino)alkyl)zirconocene Complexes and Their Dynamic Behavior

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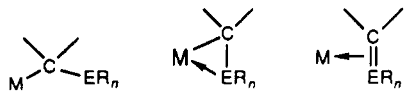
$PhCH(K)NMe_2$ and $LiCH_2NMe_2$ react with zirconocene or hafnocene chlorides in THF to give satisfactory yields of their (dimethylamino)alkyl derivatives. $Cp_2Zr(R)CH(Ph)NMe_2$ (R = Cl, **5**; R = Me, **6**) was prepared by treating $Cp_2Zr(R)Cl$ with $PhCH(K)NMe_2$. $Cp(\eta^5\text{-}C_5H_4R)M(Cl)CH_2N(CH_3)_2$ (M = Zr, X = Cl, R = H, **7**; M = Hf, X = Cl, R = H, **8**; M = Zr, X = Cl, R = $CPh(CH_3)_2$, **11**) was prepared by treating the appropriate metallocene dichloride with $LiCH_2N(CH_3)_2$. Acidic reagents (CF_3CO_2H, $CpMo(CO)_3H$, $[n\text{-}Bu_3NH][BPh_4]$) cleaved the methyl ligand from **6** and gave the $^-O_2CCF_3$ complex (**10**), the $^-(\mu\text{-}OC)Mo(CO)_2Cp$ complex (**12**), or the solvated cation (**13**). Complex **7** did not react with excess $LiCH_2N(CH_3)_2$, LiPh, MeI, CO(g) (1 atm), or Na(Hg), but a low yield of its methyl derivative was obtained by treating it with $LiCH_3$. The inequivalence of the *N*-methyl groups in the ^1H NMR spectra of complexes **5**, **6**, and **10**–**13** at low temperatures showed that the $CH(R)NMe_2$ ligands were bound in an η^2 fashion. Simulation of the temperature-dependent ^1H NMR spectra of $CDCl_3$ solutions of **11** gave $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values of 17.1 ± 0.8 kcal/mol and 2.3 ± 2.7 eu, respectively, for *N*-methyl exchange. The Zr–N interaction energy in **11** can thus be estimated at 8 kcal/mol.

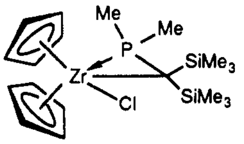
Introduction

Alkyl ligands with heteroatom substituents E on the α carbon can bind to transition metals in either an η^1 (A) or an η^2 (B) manner; the η^2 form can also be described as a π ligand (C).



A B C

Alkyl zirconocene complexes with α-phosphorus substituents generally do not exhibit η^2 interactions,[1] although an exception, $Cp_2Zr(Cl)[CH(SiMe_3)_2PMe_2]$ (**1**), has recently been reported by Karsch,[2] and Hückel calculations suggest that the η^2 form of a $-CH_2PH_2$ complex should be substantially more stable than the η^1 form.[3] Sulfur coordination has been suggested in certain zirconocene thioether derivatives, **2**, from their NMR behavior; in others there



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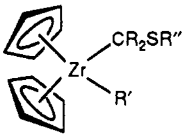
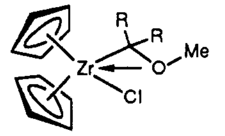


2



3a (R = H)
b (R = Ph)

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[1] (a) Schore, N. E.; Hope, H. *J. Am. Chem. Soc.* **1980**, *102*, 4251. (b) Schore, N. E.; Young, S. J.; Olmstead, M.; Hofmann, P. *Organometallics* **1983**, *2*, 1769. (c) Young, S. J.; Olmstead, M. M.; Knudsen, M. J.; Schore, N. E. *Organometallics* **1985**, *4*, 1432. (d) Karsch, H. H.; Müller, G.; Krüger, C. *J. Organomet. Chem.* **1984**, *273*, 195. (e) Engelhardt, L. M.; Jacobsen, G. E.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1984**, 220.

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[3] Hofmann, P.; Stauffert, P.; Schore, N. E. *Chem. Ber.* **1982**, *115*, 2153.

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