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Synthesis and Spectroscopic Investigations of Organoaluminum Derivatives of ((Dimethylamino)methyl)ferrocene. Crystal and Molecular Structures of $Me_3Al{\cdot}N(Me_2)CH_2C_5H_4FeCp$ and $[(2\text{-}C_4H_3S)_2Al{\cdot}N(Me_2)CH_2C_5H_4FeCp]_2O$

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The reaction of organoaluminum derivatives, R_3Al (R = Me, Et, Ph), with ((dimethylamino)methyl)ferrocene yields $R_3Al{\cdot}N(Me_2)CH_2C_5H_4FeCp$ (R = Me (**1a**), Et (**1b**), Ph (**1c**); Cp = C_5H_5) quantitatively. The alkoxo and thiolato complexes, $[Me_2Al(\mu\text{-}OC_6F_5)]_2$ and $[Me_2Al(\mu\text{-}C_{10}H_7\text{-}2\text{-}S)]_n$, also react with ((dimethylamino)methyl)ferrocene to give $Me_2(C_6F_5O)Al{\cdot}N(Me_2)CH_2C_5H_4FeCp$ (**2**) and $Me_2(C_{10}H_7\text{-}2\text{-}S)Al{\cdot}N(Me_2)CH_2C_5H_4FeCp$ (**3**), respectively. Under similar reaction conditions ((dimethylamino)methyl)ferrocene does not react with tris(2,4,6-trimethylphenyl)aluminum (Mes_3Al). The reaction of $(2\text{-}C_4H_3S)_3Al{\cdot}OEt_2$ with the hydrated amine gives an aluminoxane $[(2\text{-}C_4H_3S)_2Al{\cdot}N(Me_2)CH_2C_5H_4FeCp]_2O$ (**4**). The resulting compounds have been characterized by ^1H and ^{13}C NMR spectroscopy. A single-crystal X-ray study of **1a** established that it crystallizes in the monoclinic cell system, space group $P2_1/a$ (No. 14), with cell constants of $a = 12.969(2)$ Å, $b = 13.103(2)$ Å, $c = 20.411(3)$ Å, $\beta = 91.45(2)°$, and $Z = 8$; $R = 5.4\%$ and $R_w = 3.7\%$, based on 2798 observed reflections ($I_o \geq 2.5\sigma(I)$). The molecular unit is monomeric with an Al–N bond distance of 2.06 Å. Compound **4** crystallizes in the monoclinic space group $P2_1/n$ (No. 14), with cell constants of $a = 11.518(2)$ Å, $b = 13.126(2)$ Å, $c = 13.839(3)$ Å, $\beta = 96.14(1)°$, and $Z = 2$; $R = 5.1\%$ and $R_w = 5.0\%$, based on 2445 observed reflections ($I_o \geq 2.5\sigma(I)$). The molecular unit consists of two ferrocene moieties connected via an N–Al–O–Al–N linkage with Al–N and Al–O bond distances of 2.024 and 1.690 Å, respectively. The NMR spectra of **1a** and **4** are temperature dependent with significant changes occurring for the resonances associated with the $Me_2NCH_2C_5H_4FeCp$ group.

Introduction

Compounds which contain a main group metal and a transition metal in the same molecular unit are of major interest because of the differing reactivities of the metal centers as well as their relationship to materials and solid-state chemistry.[1] The mode of incorporation of the metal centers into a single molecule may involve direct metal–metal bonds,[2–6] simple M–E–M bridge bonds,[7–10] or more complex molecular structures. We believe that such heterobimetallic molecular systems may exhibit combined and/or enhanced reactivity and selectivity as has been demonstrated by Tebbe's reagent[11] and the Ziegler–Natta polymerization catalysts.[12] Furthermore, such bimetallic systems may be used to provide specific mechanistic or structural information on their material counterparts since they are amenable to precise characterization using a variety of spectroscopic and structural techniques.

The present work focuses on the interaction between the much studied ferrocene derivatives and group 13 organometallic compounds. To our knowledge, the only other structural studies reported of the ((dimethylamino)methyl)ferrocene ligand with group 13 elements are of $H_3B{\cdot}N(Me_2)CH_2C_5H_4FeCp$[13] and the related hydrolyzed adduct $(OH)_2FB{\cdot}N(Me_2)CH(CH_3)C_5H_4FeCp$.[14]

In this paper we report the synthesis and characterization of heterobimetallic complexes formed by the interaction of the ((dimethylamino)methyl)ferrocene molecule through the amine moiety with various simple alkyl and aryl aluminum derivatives. The crystal and molecular structures of $Me_3Al{\cdot}N(Me_2)CH_2C_5H_4FeCp$ and $[(2\text{-}C_4H_3S)_2Al{\cdot}N(Me_2)CH_2C_5H_4FeCp]_2O$ are reported.

Experimental Section

General Experimental Procedures. All solvents were purified and dried by standard techniques.[15] Argon gas was purified by passing it through a series of columns containing Deox catalyst (Alfa), phosphorus pentoxide, and calcium sulfate. Aluminum alkyls (Aldrich, Me_3Al, 2 M solution in toluene, and Et_3Al, 1.9 M solution in toluene), 2-naphthalenethiol (Aldrich), pentafluorophenol (Aldrich) and ((dimethylamino)methyl)ferrocene (Strem) were used as received. Mes_3Al,[16] Ph_3Al,[17] $(2\text{-}C_4H_3S)_3Al{\cdot}OEt_2$,[18] and $[Me_2Al(\mu\text{-}OC_6F_5)]_2$[19] were prepared as described previously. All of the glassware used in the synthetic work was oven and/or flame dried. The compounds are both oxygen and water sensitive so standard Schlenk line techniques were employed. ^1H and ^{13}C NMR spectra were recorded either on a General Electric QE-300 NMR or on a GN-300 NMR spectrometer. The chemical shifts were referenced to the residual proton line from benzene-d_6 ($\delta = 7.15$ ppm for ^1H; $\delta = 128.0$

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ppm for ^{13}C). The variable-temperature NMR spectra were obtained from toluene-d_8 solutions and were referenced to the methyl resonance of toluene ($\delta = 2.09$ ppm). The infrared spectra were obtained on either a Nicolet DX20 FTIR or an FX FTIR spectrometer. The mass spectral data were obtained on a Kratos MS 80 RFA mass spectrometer operating in the electron impact mode with a 70-eV ionization potential.

Preparation of $Me_3Al\cdot N(Me_2)CH_2C_5H_4FeCp$ (1a). ((Dimethylamino)methyl)ferrocene (1.00 mL, 5.05 mmol) was stirred in pentane (60 mL), and Me_3Al (2.52 mL, 5.05 mmol) was added over a period of 10 min. The reaction appeared to be instantaneous, but to ensure complete reaction the solution was stirred for 2 h. The volume of the reaction mixture was reduced to half under vacuum, resulting in the precipitation of an orange-yellow solid. This precipitate was isolated, washed with 10–15 mL of very cold pentane, and dried under vacuum. The product was purified by dissolving it in the minimum amount of pentane and then recrystallizing it from this solution by cooling it to −20 °C overnight. This solid was identified from its ^1H and ^{13}C NMR spectra as $Me_3Al\cdot N(Me_2)CH_2C_5H_4FeCp$. Yield: 80%. ^1H NMR (C_6D_6, δ, ppm): 3.85 (s, 5H, Cp); 3.88 (t, $J_{HH} = 2$ Hz, 2H), 3.73 (t, $J_{HH} = 2$ Hz, 2H) (C_5H_4); 3.58 (s, 2H, CH_2); 1.85 (s, 6H, NMe_2); −0.39 (s, 9H, $AlCH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, δ, ppm): 69.0 (s, Cp); 75.8, 71.7, 69.2 (C_5H_4); 56.9 (CH_2); 42.2 (NMe_2); −9.2 ($AlCH_3$). IR (Nujol, cm^{-1}): 3086 w, 3002 w, 2954 br, 2923 br, 1558 m, 1431 m, 1436 m, 1404 w, 1341 m, 1294 w, 1240 m, 1230 w, 1183 s, 1105 s, 1040 m, 1017 s, 1001 m, 971 s, 928 m, 841 m, 819 s, 798 s, 772 m, 700 br, 624 m, 607 w. Mass spectral data: *m/e* 300, 243, 228, 213, 199, 186, 163, 134, 121, 56 corresponding to fragments $Me_2AlN(Me_2)CH_2C_5H_4FeC_5H_5^{\bullet+}$, $Me_2NCH_2C_5H_4FeC_5H_5^{\bullet+}$, $MeNCH_2C_5H_4FeC_5H_5^{\bullet+}$, $NCH_2C_5H_4FeC_5H_5^{\bullet+}$, $CH_2C_5H_4FeC_5H_5^{\bullet+}$, $C_5H_4FeC_5H_5^{\bullet+}$, $MeNCH_2C_5H_4Fe^{\bullet+}$, $CH_2C_5H_4Fe^{\bullet+}$, $FeC_5H_5^{\bullet+}$, $Fe^{\bullet+}$.

Preparation of $Et_3Al\cdot N(Me_2)CH_2C_5H_4FeCp$ (1b). ((Dimethylamino)methyl)ferrocene (1.00 mL, 5.05 mmol) was dissolved in pentane (60 mL) and reacted with Et_3Al (2.66 mL, 5.05 mmol) following the procedure given for **1a**. The solid was identified as $Et_3Al\cdot N(Me_2)CH_2C_5H_4FeCp$ from its ^1H and ^{13}C NMR spectra. Yield: >90%. ^1H NMR (C_6D_6, δ, ppm): 3.88 (s, 5H, Cp); 3.91 (t, $J_{HH} = 2$ Hz, 2H), 3.75 (b, 2H) (C_5H_4); 3.58 (s, 2H, CH_2); 1.84 (s, 6H, NMe_2); 1.47 (t, $J_{HH} = 8.1$ Hz, 9H, $AlCH_2\mathit{CH_3}$); 0.19 (q, $J_{HH} = 8.1$ Hz, 6H, $Al\mathit{CH_2}CH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, δ, ppm): 69.1 (s, Cp); 75.1, 71.8, 69.3 (C_5H_4); 57.2 (CH_2); 42.4 (NMe_2); 10.9 ($AlCH_2\mathit{CH_3}$); −0.4 ($Al\mathit{CH_2}CH_3$).

Preparation of $Ph_3Al\cdot N(Me_2)CH_2C_5H_4FeCp$ (1c). To a toluene solution containing 0.50 g (1.94 mmol) of Ph_3Al was added 4.8 mL of a 0.40 M hexane solution of ((dimethylamino)methyl)ferrocene. Over a period of approximately 20 min, all of the Ph_3Al dissolved to give a clear solution. The reaction mixture was allowed to stir overnight. The solvent was then removed under vacuum. The compound was recrystallized from a toluene/hexane mixture at −20 °C, resulting in an orange microcrystalline product. The solid was identified from its ^1H and ^{13}C NMR spectra as $Ph_3Al\cdot N(Me_2)CH_2C_5H_4FeCp$. Yield: >70%. Mp: 189 °C. ^1H NMR (C_6D_6, δ, ppm): 7.38 (m, 9H, Ph), 8.15 (m, 6H, Ph), 3.78 (s, 5H, Cp); 3.53 (t, $J_{HH} = 2$ Hz, 2H), 3.77 (t, $J_{HH} = 2$ Hz, 2H) (C_5H_4); 3.92 (s, 2H, CH_2); 2.06 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR (C_6D_6, δ, ppm): 147.6, 139.7, 127.8 (Ph); 69.0 (Cp); 74.8, 71.9, 69.3 (C_5H_4); 57.9 (CH_2); 43.2 (NMe_2). IR (Nujol, cm^{-1}): 3056 w, 3048 w, 3042 w, 2987 w, 2954 br, 2923 br, 1558 m, 1480 m, 1429 m, 1417 s, 1498 vw, 1351 m, 1298 w, 1240 m, 1192 m, 1154 m, 1105 m, 1084 s, 1044 m, 1012 m, 995 m, 969 s, 929 m, 856 w, 835 m, 816 m, 794 s, 773 w, 729 s, 704 s, 676 s, 652 w, 562 s, 501 m, 473 s, 467 s, 429 m, 410 m, 397 w, 384 w, 375 w, 352 s. Mass spectral data: *m/e* 243, 228, 213, 199, 186, 163, 134, 121, 56 corresponding to fragments $Me_2NCH_2C_5H_4FeC_5H_5^{\bullet+}$, $MeNCH_2C_5H_4FeC_5H_5^{\bullet+}$, $NCH_2C_5H_4FeC_5H_5^{\bullet+}$, $CH_2C_5H_4FeC_5H_5^{\bullet+}$, $C_5H_4FeC_5H_5^{\bullet+}$, $MeNCH_2C_5H_4Fe^{\bullet+}$, $CH_2C_5H_4Fe^{\bullet+}$, $FeC_5H_5^{\bullet+}$, $Fe^{\bullet+}$.

Preparation of $Me_2(C_6F_5O)Al\cdot N(Me_2)CH_2C_5H_4FeCp$ (2). $[Me_2Al(\mu\text{-}OC_6F_5)]_2$ was prepared by reported methods[19] from pentafluorophenol (1.562 g, 8.49 mmol) in pentane (60 mL) and Me_3Al (4.24 mL, 8.49 mmol). The solvent was removed under vacuum to leave crystalline $[Me_2Al(\mu\text{-}OC_6F_5)]_2$, which was dissolved in pentane (50 mL), and ((dimethylamino)methyl)ferrocene (1.68 mL, 8.49 mmol) was slowly added. The reaction was allowed to stir for 24 h. The solvent was completely removed under vacuum to give a yellow solid. The product was dissolved in hot toluene from which a crystalline solid deposited upon cooling to 25 °C. The solid was identified from its ^1H and ^{13}C NMR spectra as $Me_2(C_6F_5O)Al\cdot N(Me_2)CH_2C_5H_4FeCp$. Yield: >90%. ^1H NMR (C_6D_6, δ, ppm): 3.89 (s, 5H, Cp); 3.92 (t, $J_{HH} = 2$ Hz, 2H), 3.82 (t, $J_{HH} = 2$ Hz, 2H) (C_5H_4); 3.65 (s, 2H, CH_2); 1.91 (s, 6H, NMe_2); −0.48 (s, 6H, $AlCH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, δ, ppm): 68.7 (s, Cp); 74.8, 71.4, 69.0 (C_5H_4); 56.6 (CH_2); 41.5 (NMe_2); −12.3 ($AlCH_3$). IR (Nujol, cm^{-1}): 3082 w, 3077 w, 3002 w, 2923 br, 1654 m, 1558 m, 1521 s, 1507 s, 1437 m, 1418 vw, 1410 m, 1398 vw, 1348 m, 1313 m, 1296 vw, 1253 w, 1240 m, 1230 w, 1195 s, 1178 s, 1113 m, 1106 s, 1054 m, 1023 s, 994 s, 966 m, 929 m, 900 w, 861 w, 842 m, 819 s, 795 s, 772 m, 728 s, 714 s, 685 s, 665 s, 591 m, 571 m, 558 m. Mass spectral data: *m/e* 243, 228, 213, 199, 186, 184, 163, 134, 121, 56 corresponding to fragments $Me_2NCH_2C_5H_4FeC_5H_5^{\bullet+}$, $MeNCH_2C_5H_4FeC_5H_5^{\bullet+}$, $NCH_2C_5H_4FeC_5H_5^{\bullet+}$, $CH_2C_5H_4FeC_5H_5^{\bullet+}$, $C_5H_4FeC_5H_5^{\bullet+}$, $C_6F_5H^{\bullet+}$, $MeNCH_2C_5H_4Fe^{\bullet+}$, $CH_2C_5H_4Fe^{\bullet+}$, $FeC_5H_5^{\bullet+}$, $Fe^{\bullet+}$.

Preparation of $[Me_2Al(C_{10}H_7\text{-}2\text{-}S)]_n$. $[Me_2Al(C_{10}H_7\text{-}2\text{-}S)]_n$ was prepared by the reaction of 2-naphthalenethiol (1.0 g, 6.24 mmol) in pentane (100 mL) with Me_3Al (3.12 mL, 6.24 mmol). The reaction was stirred for 24 h, during which time a white microcrystalline material precipitated. The solvent was decanted to leave the product, $[Me_2Al(C_{10}H_7\text{-}2\text{-}S)]_n$. ^1H NMR (C_6D_6, δ, ppm): 7.09–8.09 (m, 7H, $C_{10}H_7$); −0.05 (s, 6H, $AlCH_3$).

Preparation of $Me_2(C_{10}H_7\text{-}2\text{-}S)Al\cdot N(Me_2)CH_2C_5H_4FeCp$ (3). $[Me_2Al(C_{10}H_7\text{-}2\text{-}S)]_n$ was isolated as described above and dissolved in toluene (50 mL). ((Dimethylamino)methyl)ferrocene (1.24 mL, 6.24 mmol) was added slowly. The reaction was stirred for 2 h. The solvent was completely removed under vacuum to give a yellow solid. The product was recrystallized as described for **2**. The solid was identified from its ^1H and ^{13}C NMR spectra as $Me_2(C_{10}H_7\text{-}2\text{-}S)Al\cdot N(Me_2)CH_2C_5H_4FeCp$. Yield: >90%. ^1H NMR (C_6D_6, δ, ppm): 8.26–7.10 (m, 7H, $C_{10}H_7$), 3.67 (s, 5H, Cp); 3.83 (t, $J_{HH} = 2$ Hz, 2H), 3.65 (t, $J_{HH} = 2$ Hz, 2H) (C_5H_4); 3.55 (s, 2H, CH_2); 1.87 (s, 6H, NMe_2); −0.29 (s, 6H, $AlCH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, δ, ppm): 136.9, 134.7, 133.9, 132.5, 131.6, 127.8, 126.9, 126.3, 124.9 ($C_{10}H_7$), 68.9 (s, 5H, Cp); 74.7, 71.7, 69.3 (C_5H_4); 56.9 (CH_2); 42.1 (NMe_2); −9.9 ($AlCH_3$). IR (Nujol, cm^{-1}): 3100 vw, 3081 w, 3046 w, 3008 w, 2994 vw, 2953 br, 2922 br, 1623 m, 1492 m, 1407 w, 1346 m, 1328 w, 1296 vw, 1266 w, 1238 m, 1195 s, 1189 s, 1149 vw, 1133 m, 1114 m, 1105 m, 1098 m, 1071 m, 1054 vw, 1041 m, 1030 w, 1013 m, 1002 m, 967 s, 941 m, 928 m, 895 s, 867 w, 858 m, 848 m, 838 m, 815 s, 794 s, 773 w, 765 w, 753 s, 738 vw, 703 s, 676 s, 641 m, 600 m, 572 m, 559 m, 502 s, 475 s, 442 m, 422 s, 387 s, 357 s. Mass spectral data: *m/e* 318, 243, 228, 213, 199, 186, 163, 159, 134, 127, 121, 56 corresponding to fragments $(C_{10}H_7)_2S_2^{\bullet+}$, $Me_2NCH_2C_5H_4FeC_5H_5^{\bullet+}$, $MeNCH_2C_5H_4FeC_5H_5^{\bullet+}$, $NCH_2C_5H_4FeC_5H_5^{\bullet+}$, $CH_2C_5H_4FeC_5H_5^{\bullet+}$, $C_5H_4FeC_5H_5^{\bullet+}$, $MeNCH_2C_5H_4Fe^{\bullet+}$, $C_{10}H_7S^{\bullet+}$, $CH_2C_5H_4Fe^{\bullet+}$, $C_{10}H_7^{\bullet+}$, $FeC_5H_5^{\bullet+}$, $Fe^{\bullet+}$.

Preparation of $[(2\text{-}C_4H_3S)_2Al\cdot N(Me_2)CH_2C_5H_4FeCp]_2O$ (4). $(2\text{-}C_4H_3S)_3Al\cdot OEt_2$ (1.5 g, 4.28 mmol) was dissolved in toluene (40 mL) and ((dimethylamino)methyl)ferrocene (0.85 mL, 4.28 mmol) was added dropwise. The reaction appeared to be instantaneous, but to ensure complete reaction, the solution was heated for 5 min and then stirred for 12 h. The volume of the solution was reduced to half under vacuum, and the solution was left undisturbed for 3 days at room temperature during which time orange-yellow crystals precipitated. The product was collected, washed with 20 mL of cold pentane, and dried under vacuum. This solid was identified from its ^1H and ^{13}C NMR spectra as $[(2\text{-}C_4H_3S)_2Al\cdot N(Me_2)CH_2C_5H_4FeCp]_2O$. Yield: 80%. Mp: 150 °C dec. ^1H NMR (C_6D_6, δ, ppm): 7.30–7.33 (m, 2H), 7.61–7.62 (m, 2H), 7.92–7.93 (m, 2H) ($2\text{-}C_4H_3S$) 3.87 (s, 5H, Cp); 3.78 (t, $J_{HH} = 2$ Hz, 2H), 3.58 (t, $J_{HH} = 2$ Hz, 2H) (C_5H_4); 3.96 (s, 2H, CH_2); 2.08 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR (C_6D_6, δ, ppm): 139.2, 131.5, 128.7, 125.2 (C_4H_3S); 69.1 (s, Cp); 76.1, 71.7, 69.2 (C_5H_4); 57.6 (CH_2); 42.8 (NMe_2). Anal. Calcd for $Fe_2S_4Al_2ON_2C_{42}H_{46}$: C, 56.76; H, 5.22. Found: C, 55.00; H, 5.62. IR (Nujol, cm^{-1}): 3093 w, 3082 w, 3066 w, 3056 w, 3042 w, 2954 br, 2924 br, 1652 m, 1558 m, 1427 vw, 1418 vw, 1394 m, 1344 m, 1313 w, 1296 vw, 1261 w, 1237 m, 1228 w, 1208 m, 1202 m, 1105 m, 1075 m, 1056 w, 1043 w, 1022 s, 969 m, 944 m, 931 m, 842 s, 823 m, 814 m, 793 s, 773 m, 742 m, 717 s, 705 s, 625 w, 578 m, 563 s, 502 m, 487 s, 447 m, 433 m, 410 w, 408 w, 397 m, 382 m, 352 m. Mass spectral data (EI mode): *m/e* 243, 199, 186, 163, 134, 121, 83 corresponding to fragments $Me_2NCH_2C_5H_4FeC_5H_5^{\bullet+}$, $CH_2C_5H_4FeC_5H_5^{\bullet+}$, $C_5H_4FeC_5H_5^{\bullet+}$, $MeNCH_2C_5H_4Fe^{\bullet+}$, $CH_2C_5H_4Fe^{\bullet+}$, $FeC_5H_5^{\bullet+}$, $SC_4H_3^{\bullet+}$. No aluminum-containing fragments were observed.

Reaction of Mes_3Al with ((Dimethylamino)methyl)ferrocene. The compound Mes_3Al was reacted with a 2-fold excess of ((dimethylamino)methyl)ferrocene in benzene-d_6 in a 5-mm NMR tube and monitored at intervals over a period of 24 h. No shifts in the proton resonances of either the ligand or the Mes_3Al were observed.

Attempted Metalation of the Cyclopentadienyl Ring of $Me_2NCH_2C_5H_4FeCp$. ((Dimethylamino)methyl)ferrocene (1.00 mL, 5.05 mmol) was stirred in heptane (60 mL), and Me_3Al (5.04 mL, 10.1 mmol) was added over a period of 5 min. The solution was stirred for 2 h and then refluxed for 15 h. The volume of the solution was reduced to half under vacuum,

Table 1. Experimental Parameters for the X-ray Diffraction Study of Compounds $Me_3Al\cdot N(Me_2)CH_2C_5H_4FeCp$ (**1a**) and $[(2\text{-}C_4H_3S)_2Al\cdot N(Me_2)CH_2C_5H_4FeCp]_2O$ (**4**)

compound	$Me_3Al\cdot N(Me_2)CH_2C_5H_4FeCp$ (**1a**)	$[(2\text{-}C_4H_3S)_2Al\cdot N(Me_2)CH_2C_5H_4FeCp]_2O$ (**4**)
formula	$C_{16}H_{26}AlFeN$	$C_{42}H_{46}AlFe_2ON_2S_4$
mol. wt	315.218	888.76
cryst color	yellow	yellow-orange
cryst system	monoclinic	monoclinic
space group	$P2_1/a$ (No. 14)	$P2_1/n$ (No. 14)
cell const obtained from 25 high angle reflcns		
a, Å	12.969(2)	11.518(2)
b, Å	13.1033(2)	13.126(2)
c, Å	20.411(3)	13.839(3)
β, deg	91.45(2)	96.14(1)
Z	8	2
V, Å^3	3467.5(8)	2080.2(0.6)
density(calcd), g cm^{-3}	1.208	1.419
radiation type	Mo K$\bar{\alpha}$ (λ = 0.710 73 Å), with a graphite monochromator	Mo K$\bar{\alpha}$ (λ = 0.710 73 Å), with a graphite monochromator
temp, °C	20	20
type of data collcn	$\theta/2\theta$ scan	$\theta/2\theta$ scan
2θ scan range, deg	6–50	6–50
octants used	+h, +k, ±l	+h, +k, ±l
scan rate, deg/min	variable, 4–12	variable, 3–15
scan range; deg	1.0 below Kα_1 to 1.1 above Kα_2	1.0 below Kα_1 to 1.2 above Kα_2
std. reflcns: 3 measd per every 97 reflcns	max dev from std less than 1%	max dev from std less than 2%
no. of data collcd	5783	4172
no. of unique reflcns	5279	3673
no. of obsd reflcns	2798 [$I_o \geq 2.5\sigma(I)$]	2445 [$I_o \geq 2.5\sigma(I)$]
linear abs coeff (μ), cm^{-1}	8.60 cm^{-1}	9.66 cm^{-1}
F(000)	1344	924
abs cor	applied, ψ scans	applied, ψ scans
no. of params refined	344 (block 1 and 2 with 172 in each block)	223
obsd/param ratio	8.13:1	11:1
$R(\Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert)$, %	5.42	5.1
R_w $([\Sigma(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2})$	3.71	5.0
max shift/esd	0.004	0.002
residual electron density, e/Å^3	0.296	0.42

resulting in the precipitation of an orange-yellow solid. The product was collected, washed with 10–15 mL of very cold pentane, and dried under vacuum. It was identified from its ^{1}H and ^{13}C NMR spectra as **1a**.

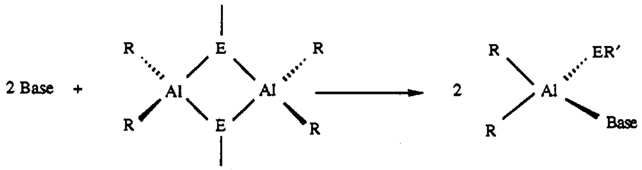
Metalation of $Me_2NCH_2C_5H_4FeCp$ was also attempted by its reaction with (i-Bu)$_2$AlH as follows. ((Dimethylamino)methyl)ferrocene (1.00 mL, 5.05 mmol) was stirred in heptane (60 mL), and (i-Bu)$_2$AlH (10.1 mL, 10.1 mmol) was added over a period of 5 min. The solution was stirred for two h and then refluxed for 15 h. During reflux, a shiny gray metallic material (presumably aluminum metal) appeared in the reaction mixture. The amount of this material increased as the reflux continued. On workup, unreacted $Me_2NCH_2C_5H_4FeCp$ was found, and all of the (i-Bu)$_2$AlH had decomposed.

X-ray Structure Determination of $Me_3Al\cdot N(Me_2)CH_2C_5H_4FeCp$ (1a) and $[(2\text{-}C_4H_3S)_2Al\cdot N(Me_2)CH_2C_5H_4FeCp]_2O$ (4). Crystals of $Me_3Al\cdot N(Me_2)CH_2C_5H_4FeCp$ (**1a**) were grown from a mixture of pentane and toluene in a 3:1 ratio at room temperature while crystals of $[(2\text{-}C_4H_3S)_2Al\cdot N(Me_2)CH_2C_5H_4FeCp]_2O$ (**4**) were obtained from a hot toluene solution by slow cooling to 25 °C. In each case a crystal suitable for X-ray diffraction studies was mounted in a thin-walled capillary tube as previously described[19] and placed on a Nicolet P2$_1$ diffractometer for data collection. Crystal structure parameters are presented in Table 1.

Data reduction and calculations were carried out using the SHELXTL program.[20] Direct method routines produced acceptable solutions for the structures, yielding positions for some of the non-hydrogen atoms while other atoms were located during subsequent refinement. Full-matrix least-squares refinement was carried out using SHELX-76.[21] The data were corrected for Lorentz and polarization effects, and scattering factors for neutral carbon, nitrogen, oxygen, sulfur, iron, and aluminum atoms were used.[22] Additional information concerning the refinement is included in the supplementary material. The only unusual feature in the structure is that one thiophene ligand on aluminum is sulfur/carbon disordered; therefore, the atom C19/S2 describes a position composed of 70% carbon and 30% sulfur and the atom S2/C19 describes a position composed of 70% sulfur and 30% carbon. Atomic coordinates and isotropic thermal parameters for the non-hydrogen atoms for **1a** and **4** are presented in Tables 2 and 3.

Results and Discussion

Reaction of R_3Al (R = Me, Et, Ph), $[Me_2Al(\mu\text{-}OC_6F_5)]_2$, $[Me_2Al(\mu\text{-}S\text{-}2\text{-}C_{10}H_7)]_n$, and $(2\text{-}C_4H_3S)_3Al\cdot OEt_2$ with ((Dimethylamino)methyl)ferrocene. The amine moiety of ((dimethylamino)methyl)ferrocene is a strong Lewis base which reacts rapidly at room temperature with simple electron deficient carbon bridged aluminum alkyls and aryls, R_3Al (R = Me, Et, Ph), in a 1:1 stoichiometry to form the corresponding adducts, $R_3Al\cdot N(Me_2)CH_2C_5H_4FeCp$ (R = Me (**1a**), Et (**1b**), Ph (**1c**)). This is shown by its ability to disrupt the oxygen and sulfur bridge bond in $[Me_2Al(\mu\text{-}OC_6F_5)]_2$ and $[Me_2Al(\mu\text{-}S\text{-}2\text{-}C_{10}H_7)]_n$ via the reaction shown in eq 1 to give $Me_2(C_6F_5O)Al\cdot N(Me_2)CH_2C_5H_4FeCp$ (**2**) and $Me_2(C_{10}H_7\text{-}2\text{-}S)Al\cdot N(Me_2)CH_2C_5H_4FeCp$ (**3**).



E = O, S (1)

Partially hydrated amine leads to the formation of $[(2\text{-}C_4H_3S)_2Al\cdot N(Me_2)CH_2C_5H_4FeCp]_2O$ (**4**) by its ligand displacement/

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Table 2. Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $Me_3Al{\cdot}N(Me_2)CH_2C_5H_4FeCp$ (**1a**)

atom	*x*	*y*	*z*	U_{eq},[a] Å^2
		Molecule 1		
Fe1	0.06171(7)	–0.05630(7)	0.74586(4)	0.0574(3)
Al1	0.1304(2)	–0.2240(1)	0.47565(8)	0.0546(8)
N1	0.1988(4)	–0.1664(4)	0.5601(2)	0.047(2)
C1	0.1639(5)	0.0081(5)	0.6855(3)	0.054(3)
C2	0.1545(4)	–0.0979(4)	0.6722(3)	0.044(2)
C3	0.1802(5)	–0.1526(5)	0.7305(3)	0.061(3)
C4	0.2065(5)	–0.0788(6)	0.7786(3)	0.074(3)
C5	0.1972(6)	0.0173(5)	0.7517(4)	0.070(3)
C6	0.1170(4)	–0.1437(4)	0.6087(3)	0.046(2)
C7	0.2734(5)	–0.2418(5)	0.5880(3)	0.071(3)
C8	0.2560(5)	–0.0715(5)	0.5433(3)	0.069(3)
C9	–0.0354(9)	–0.071(1)	0.8213(5)	0.146(7)
C10	–0.0439(8)	0.0229(9)	0.7942(6)	0.111(5)
C11	–0.0731(7)	0.0163(9)	0.7322(6)	0.107(5)
C12	–0.0821(7)	–0.080(1)	0.7178(6)	0.127(6)
C13	–0.059(1)	–0.1424(7)	0.770(1)	0.174(9)
C14	0.0627(5)	–0.3510(5)	0.5017(3)	0.087(3)
C15	0.0323(6)	–0.1182(5)	0.4479(3)	0.094(3)
C16	0.2432(6)	–0.2434(6)	0.4152(3)	0.093(3)
		Molecule 2		
Fe2	0.05352(7)	0.44073(7)	0.74996(4)	0.0485(3)
Al2	0.2361(2)	0.3577(2)	1.02003(8)	0.0579(8)
N2	0.1699(4)	0.2978(4)	0.9361(2)	0.052(2)
C17	–0.0178(5)	0.3498(4)	0.8143(3)	0.052(3)
C18	–0.0384(5)	0.3163(5)	0.7495(3)	0.067(3)
C19	0.0569(7)	0.2932(5)	0.7212(3)	0.070(3)
C20	0.1369(5)	0.3141(5)	0.7676(3)	0.056(3)
C21	0.0899(5)	0.3473(4)	0.8259(3)	0.041(2)
C22	0.1463(4)	0.3807(4)	0.8878(3)	0.047(2)
C23	0.2420(7)	0.2245(5)	0.9077(3)	0.104(4)
C24	0.0763(6)	0.2430(5)	0.9531(3)	0.092(3)
C25	0.023(2)	0.5841(9)	0.771(1)	0.17(1)
C26	0.125(2)	0.573(1)	0.7620(8)	0.17(1)
C27	0.1417(8)	0.5397(9)	0.704(1)	0.128(7)
C28	0.052(2)	0.5298(7)	0.6714(4)	0.115(6)
C29	–0.0225(9)	0.557(1)	0.711(1)	0.126(6)
C30	0.1263(5)	0.4435(6)	1.0558(3)	0.095(3)
C31	0.3514(5)	0.4385(5)	0.9895(3)	0.094(3)
C32	0.2764(6)	0.2376(6)	1.0723(3)	0.099(4)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*{\cdot}a_j^*\vec{a}_i{\cdot}\vec{a}_j$.

hydrolysis reaction with $(2\text{-}C_4H_3S)_3Al{\cdot}OEt_2$. Compounds **1a–c** and **2–4** have been isolated as orange-yellow, transparent crystals. The complexes are both air and moisture sensitive in the solid state, decomposing over a period of seconds on exposure to air. They are moderately soluble in pentane, benzene and toluene.

Attempted Metalation of the Cyclopentadienyl Ring of $Me_2NCH_2C_5H_4FeCp$. The direct metalation of the cyclopentadienyl ring in ((dimethylamino)methyl)ferrocene occurs readily with lithium alkyls. Derivatives containing aluminum bound to the cyclopentadienyl ring have been prepared by metal displacement, reacting mercurated ferrocene derivatives with alkylaluminum halides.[23-26] Furthermore, it has been shown that transition metal alkyls such as $MeM(CO)_5$ (M = Mn or Re) can be used to metallate either the cyclopentadienyl ring or the methyl groups of the ((dimethylamino)methyl)ferrocene ligand.[27] With this information in hand, we attempted to take advantage of the activation of the aluminum alkyls or alkylaluminum hydrides to carry out internal metalation processes but obtained only the addition compound with Me_3Al and decomposition products when diisobutylaluminum hydride was employed.

Table 3. Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $[(2\text{-}C_4H_3S)_2Al{\cdot}N(Me_2)CH_2C_5H_4FeCp]_2O$ (4)

atom	*x*	*y*	*z*	U_{eq},[a] Å^2
Fe1	–0.00372(6)	0.41198(6)	0.68674(5)	0.0416(3)
C1	0.0042(4)	0.5658(3)	0.7099(3)	0.065(2)
C2	–0.0735(4)	0.5195(3)	0.7697(3)	0.063(2)
C3	–0.0095(4)	0.4466(3)	0.8297(3)	0.064(2)
C4	0.1078(4)	0.4478(3)	0.8069(3)	0.065(2)
C5	0.1163(4)	0.5215(3)	0.7328(3)	0.067(3)
C6	–0.0626(3)	0.3887(2)	0.5442(2)	0.045(2)
C7	0.0474(3)	0.3406(2)	0.5663(2)	0.056(2)
C8	0.0369(3)	0.2689(2)	0.6417(2)	0.056(2)
C9	–0.0797(3)	0.2727(2)	0.6662(2)	0.046(2)
C10	–0.1412(3)	0.3468(2)	0.6059(2)	0.037(2)
C11	–0.2647(4)	0.3819(4)	0.6107(4)	0.039(2)
N1	–0.3570(3)	0.3204(3)	0.5507(3)	0.037(1)
C12	–0.3339(4)	0.3194(4)	0.4467(4)	0.052(2)
C13	–0.3575(5)	0.2135(4)	0.5882(4)	0.055(2)
Al1	–0.5127(1)	0.3892(1)	0.5602(1)	0.0361(5)
C14	–0.6281(4)	0.2892(4)	0.5024(4)	0.042(2)
C15	–0.6630(4)	0.1938(4)	0.5415(3)	0.038(2)
C16	–0.7513(5)	0.1471(4)	0.4772(5)	0.066(3)
C17	–0.7856(5)	0.2012(5)	0.3971(4)	0.063(2)
S1	–0.7092(1)	0.3106(1)	0.3947(1)	0.0631(6)
C18	–0.5275(4)	0.4083(4)	0.7003(3)	0.039(2)
C/S	–0.5888(3)	0.3339(3)	0.7707(2)	0.057(1)
C20	–0.5763(5)	0.3950(5)	0.8643(4)	0.066(3)
C21	–0.5266(5)	0.4864(5)	0.8620(4)	0.067(3)
S/C	–0.4852(2)	0.5152(2)	0.7556(2)	0.0747(9)
O1	–0.50000	0.50000	0.50000	0.044(2)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*{\cdot}a_j^*\vec{a}_i{\cdot}\vec{a}_j$.

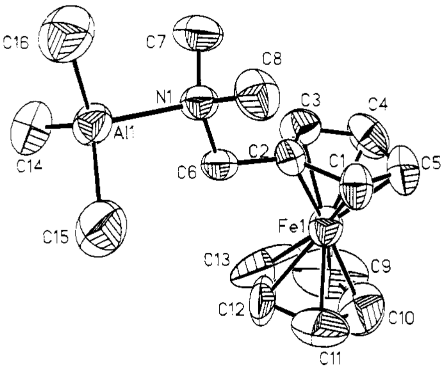

Figure 1. ORTEP diagram (50% thermal ellipsoids) of $Me_3Al{\cdot}N(Me_2)CH_2C_5H_4FeCp$ (**1a**) showing the atom labeling scheme. Hydrogen atoms have been omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $Me_3Al{\cdot}N(Me_2)CH_2C_5H_4FeCp$ (**1a**)

	Molecule 1		
	Bond Distance		
Al1–N1	2.062(5)	Al1–C15	1.956(7)
Al1–C14	1.961(7)	Al1–C16	1.955(7)
	Bond Angle		
N1–Al1–C14	105.7(2)	C14–Al1–C15	112.8(3)
N1–Al1–C15	104.2(2)	C15–Al1–C16	113.6(3)
N1–Al1–C16	105.2(3)	C14–Al1–C16	114.1(3)
	Molecule 2		
	Bond Distance		
Al2–N2	2.053(5)	Al2–C31	1.947(7)
Al2–C30	1.970(7)	Al2–C32	1.964(7)
	Bond Angle		
N2–Al2–C30	103.7(2)	C30–Al2–C31	112.1(3)
N2–Al2–C31	104.4(2)	C31–Al2–C32	114.4(3)
N2–Al2–C32	104.3(3)	C30–Al2–C32	116.1(3)

Crystal Structures of $Me_3Al{\cdot}N(Me_2)CH_2C_5H_4FeCp$ (1a) and $[(2\text{-}C_4H_3S)_2Al{\cdot}N(Me_2)CH_2C_5H_4FeCp]_2O$ (4). The ORTEP diagram of $Me_3Al{\cdot}N(Me_2)CH_2C_5H_4FeCp$, **1a**, is presented in

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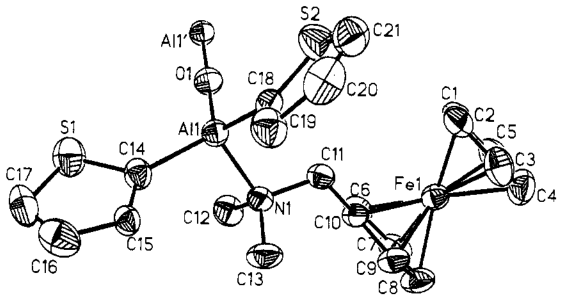

Figure 2. ORTEP diagram (50% thermal ellipsoids) of $[(2\text{-}C_4H_3S)_2Al{\cdot}N(Me_2)CH_2C_5H_4FeCp]_2O$ (**4**), showing half of the molecule with the atom labeling scheme. The remainder of the atoms are related to those shown through an inversion center located at O1. Hydrogen atoms have been omitted for clarity.

Table 5. Selected Bond Distances (Å) and Angles (deg) for $[(2\text{-}C_4H_3S)_2Al{\cdot}N(Me_2)CH_2C_5H_4FeCp]_2O$ (**4**)

	Bond Distance		
Al1–N1	2.024(4)	Fe1–Cp1	1.647(3)
Al1–O1	1.690(1)	Fe1–Cp2	1.645(3)
Al1–C14	1.975(5)	Fe···Al	5.944(1)
Al1–C18	1.980(4)		
	Bond Angle		
C14–Al1–O1	117.5(2)	N1–Al1–C18	106.9(2)
C14–Al1–C18	110.9(2)	N1–Al1–O1	103.1(1)
C18–Al1–O1	113.3(2)	Cp1–Fe1–Cp2	178.5(2)
N1–Al1–C14	103.8(2)		

Figure 1. Selected bond distances and bond angles are presented in Table 4. There are two molecules of $Me_3Al{\cdot}N(Me_2)CH_2C_5H_4FeCp$ in the asymmetric unit. The gross features of the molecular structure around the aluminum center of molecule 1 are normal. The coordination geometry around the aluminum is distorted tetrahedral. The Al–N distance of 2.06 Å is similar to that of other nitrogen adducts and greater than the Al–N distance observed in amido or imido complexes.[28] The Al–C distances ranging from 1.955 to 1.961 Å are clearly within the range expected for Al–C terminal bond distances.[29,30] The cyclopentadienyl rings in the ferrocene moiety are in the eclipsed conformation.

The ORTEP diagram of $[(2\text{-}C_4H_3S)_2Al{\cdot}N(Me_2)CH_2C_5H_4FeCp]_2O$ (**4**) is presented in Figure 2. Selected bond distances and bond angles are presented in Table 5. The general features of the molecular structure are similar to **1a**. The linear geometry around the oxygen atom with a Al–O–Al bond angle of 180° is crystallographically imposed since O1 occupies a crystallographic inversion center. A similar geometry is found in oxo-bridged complexes $[(2\text{-methyl-8-quinolinolato})_2Al]_2O$[31] and ($\mu$-oxo)bis[(phthalocyaninato)aluminum(III)].[32] However, a significant deviation of 18° in Al–O–Al bond angle was reported in an analogous complex, $\{[Al(salen)]_2(\mu\text{-}O)\}{\cdot}MeCN$.[33] The Al–O bond distance is 1.69 Å. A similarly short distance of 1.677 Å has been reported for $[(2\text{-methyl-8-quinolinolato})_2Al]_2O$[31] and ($\mu$-oxo)bis[(phthalocyaninato)aluminum(III)][32] which have five-coordinate aluminum centers. Furthermore, it has been shown that the terminal Al–O bond distance is of similar order (1.69 Å) in some aluminum alkoxides, $(RO)_2Al(\mu\text{-}OR)Al(OR)_2$.[34] However, this bond distance is substantially shorter than those found in ether adducts of simple trialkylaluminums, $R_3Al{\cdot}ER'_2$, or in alkoxides or aluminoxanes containing three-coordinate oxygen atoms[35,36] but is comparable to bond distances found in other compounds containing three-coordinate oxygen. The presence of a relatively short Al–O bond distance in **4**, where neither a vacant p orbital nor an energetically accessible aluminum d orbital is available for π-bonding, led to the proposal that π-donation from the oxygen lone pair to the Al–C and Al–E σ antibonding orbitals occurs. This hypothesis was later supported by using *ab initio* molecular orbital calculations and photoelectron spectroscopic data on some model and known compounds.[34,37,38] This has also been discussed by Haaland,[39] who attributes the large variation in Al–O bond distances observed to the mix of "normal" and "dative" bonds.

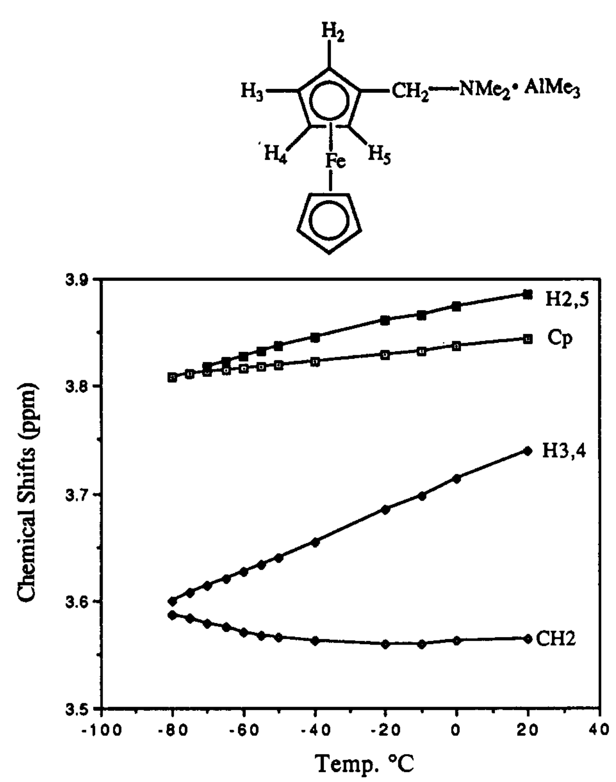

Figure 3. Plot of the ^1H NMR chemical shifts of the 2,5- and 3,4-protons of the C_5H_4 and CH_2 groups in $Me_3Al{\cdot}N(Me_2)CH_2C_5H_4FeCp$ (**1a**) as a function of temperature.

Compound **4** crystallizes with an eclipsed Cp ring conformation. Other structural features of the ferrocene moiety, such as the Fe–(Cp) bond distances, the carbon-carbon distances and the C–C–C bond angles within the two cyclopentadienyl rings, are similar to those found in **1a**. The ferrocene moiety is slightly bent with a Cp–Fe–Cp angle of 178.5°.

NMR Studies. The ^1H and ^{13}C NMR spectral data for the adducts, $R_3Al{\cdot}N(Me_2)CH_2C_5H_4FeCp$ (R = Me (**1a**), Et (**1b**), Ph (**1c**)), $Me_2(C_6F_5O)Al{\cdot}N(Me_2)CH_2C_5H_4FeCp$ (**2**), $Me_2(C_{10}H_7\text{-}2\text{-}S)Al{\cdot}N(Me_2)CH_2C_5H_4FeCp$ (**3**), and $[(2\text{-}C_4H_3S)_2Al{\cdot}N(Me_2)CH_2C_5H_4FeCp]_2O$ (**4**) are presented in the Experimental Section. The proton resonance for the NMe_2 group is a singlet and is shifted upfield with respect to the that of free ligand for **1a** and **1b** and is relatively unaffected for **1c** and **4**. The CH_2 protons also resonate as a singlet and are shifted downfield in comparison to that of the free ligand with a pronounced $\Delta\delta$ of

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0.8 ppm observed for **1c** and **4**. The large downfield shift of the CH_2 resonance is due either to magnetic anisotropy or to the inductive effect of the organic groups on the aluminum atom. The 2,5- and 3,4-protons of the substituted cyclopentadienyl ring appear as a pair of pseudotriplets. This pattern is consistent with an AA′BB′ spin system where J_{AB} and $J_{A'B}$ (or $J_{AB'}$) are approximately 2 Hz. The 2,5-protons and, to a lesser extent, the 3,4-protons are shifted upfield relative to the free ligand. These shift effects become slightly more pronounced at low temperature for **1a** and **4**. A plot of the chemical shifts of the CH_2 group, the 2,5- and 3,4-protons of the substituted Cp ring and the Cp ring as a function of temperature is presented in Figure 3. These changes in chemical shifts can be attributed to the formation of the Fe–Al adduct, the concentration of which increases with decreasing temperature, consistent with the equilibrium described by eq 2.

$$R_3Al + Base \rightleftharpoons R_3Al{\cdot}Base \qquad (2)$$

Under similar NMR conditions we did not observe any temperature dependence of the chemical shifts of the authentic $Me_2NCH_2C_5H_4FeCp$ ligand. Furthermore, no reaction of this ligand with the sterically hindered Mes_3Al was observed which further supports the presence of dissociation/association equilibria in solution for such complexes.

Finally, the ^{13}C NMR spectra of these compounds need a special comment. Examination of the ^{13}C NMR spectra of all of the complexes shows that the CH_2 and the NMe_2 carbon resonances are shifted upfield slightly while the *ipso* carbon atoms of the substituted cyclopentadienyl ring undergo the largest chemical shift variation and are shifted upfield from the ligand ($\Delta\delta = 7$–9 ppm). However, the 2,5- and 3,4-carbons and the carbon atoms of the unsubstituted cyclopentadienyl ring are shifted downfield only slightly. These NMR results further demonstrate that the coordination of the nitrogen atom of the ((dimetylamino)methyl)-ferrocene ligand to organoaluminum makes a considerable contribution to the electron density redistribution over the unsubstituted cyclopentadienyl ring.

Supplementary Material Available: Complete listings of bond distances and bond angles, anisotropic thermal parameters for the heavy atoms, and hydrogen atom positional parameters for **1a** and **4** and least-squares planes for **4** (14 pages). Ordering information is given on any current masthead page.