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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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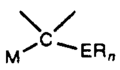
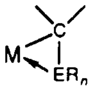
$PhCH(K)NMe_2$ and $LiCH_2NMe_2$ react with zirconocene or hafnocene chlorides in THF to give satisfactory yields of their (dimethylamino)alkyl derivatives. $Cp_2Zr(R)CH(Ph)NMe_2$ (R = Cl, **5**; R = Me, **6**) was prepared by treating $Cp_2Zr(R)Cl$ with $PhCH(K)NMe_2$. $Cp(\eta^5\text{-}C_5H_4R)M(Cl)CH_2N(CH_3)_2$ (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

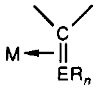
Alkyl ligands with heteroatom substituents E on the α carbon can bind to transition metals in either an η^1 (A) or an η^2 (B) manner; the η^2 form can also be described as a π ligand (C).



A

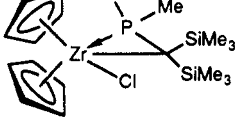


B

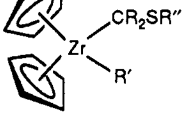


C

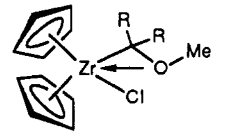
Alkyl zirconocene complexes with α-phosphorus substituents generally do not exhibit η^2 interactions,[1] although an exception, $Cp_2Zr(Cl)[CH(SiMe_3)_2PMe_2]$ (**1**), has recently been reported by Karsch,[2] and Hückel calculations suggest that the η^2 form of a $-CH_2PH_2$ complex should be substantially 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



1



2



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

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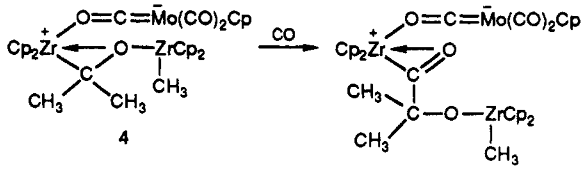
(1) (a) Schore, N. E.; Hope, H. *J. Am. Chem. Soc.* **1980**, *102*, 4251. (b) Schore, N. E.; Young, S. J.; Olmstead, M.; Hofmann, P. *Organometallics* **1983**, *2*, 1769. (c) Young, S. J.; Olmstead, M. M.; Knudsen, M. J.; Schore, N. E. *Organometallics* **1985**, *4*, 1432. (d) Karsch, H. H.; Müller, 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.

(2) Karsch, H. H.; Deubelly, B.; Hofmann, J.; Pieper, U.; Müller, G. *J. Am. Chem. Soc.* **1988**, *110*, 3654.

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

0276-7333/92/2311-0534$03.00/0

is no evidence that the sulfur is coordinated.[4,5] Analogous oxygen substituents generally are coordinated; examples can be seen in **3a,b**[6] and in **4**, which can be carbonylated under mild conditions (eq 1).[7]



(1)

The fact that analogous nitrogen compounds were unknown aroused our interest in their synthesis and reactivity. Previous syntheses of aminomethyl complexes had involved the reaction of electrophilic reagents with nucleophilic metal complexes.[8] However, an alternative method was obviously required in order to introduce an aminomethyl alkyl ligand into a high-valent (and therefore electrophilic) metal complex such as Cp_2MX_2 (M = Zr, Hf). The successful synthesis of other α-heteroatom-substituted metal alkyls (e.g., **1**–**3**) with $LiCR_2ER_n$ (E = O, S, n = 1; E = P, n = 2)[1,2,4–6a] suggested that $LiCH_2NMe_2$[9] and $PhCH(K)NMe_2$[10] might be used for the same purpose.

We now report the successful syntheses of $-CH_2NMe_2$ and $-CH(Ph)NMe_2$ derivatives of zirconocene and hafnocene dichlorides and also of $Cp_2Zr(CH_2SMe)_2$. We have inferred the strength of the interaction between the dimethylamino nitrogens and zirconium from the variable-temperature ^1H NMR spectra of derivatives in which the N-methyl groups are diastereotopic.

Experimental Section

All operations were performed under a nitrogen or argon atmosphere or under vacuum by Schlenk, inert-atmosphere-box, and vacuum-line techniques. Most of the solvents employed were distilled under N_2 from sodium benzophenone ketyl; the ether used for compounds **7**–**9**, **11**, and **14** was distilled from CaH_2, and the hexanes used for compounds **7**–**9**, **11**, and **14** were stirred over H_2SO_4 and distilled from sodium. Cp_2ZrMe_2,[11] $Cp_2ZrMeCl$,[12] $CpMo(CO)_3H$,[13] $Bu_3SnCH_2NMe_2$,[14] Cp_2HfCl_2,[15] ((methylthio)methyl)lithium,[16] and $Cp[\eta^5\text{-}C_5H_4(CMe_2Ph)]ZrCl_2$[17] were synthesized according to literature procedures. Some of the Cp_2ZrCl_2 employed was a gift from Boulder Scientific, Inc.

The ^1H NMR data for compounds **5**, **6**, **10**, **12**, and **13** were collected on a Bruker WP200 spectrometer; residual solvent proton shifts were used as internal standards. The NMR spectra of compounds **7**–**9**, **11**, and **14** were obtained on a Varian T-60 or a Bruker WNX 300-MHz FT spectrometer, with tetramethylsilane as an internal standard. IR data were collected on a Perkin-Elmer 983 spectrometer and processed on a IBM PC-AT computer with software from On-Line Instrument Systems, Inc. Elemental analyses were performed by Analytische Laboratorien, Gummersbach, Germany. Electron-impact (EI) and chemical-ionization (CI) mass spectra were obtained with a Varian MAT-112S spectrometer.

Bis(η^5-cyclopentadienyl)chloro[η^2-α-(dimethylamino)benzyl]zirconium(IV) (5). To prepare $PhCH(K)NMe_2$,[10] a 2.5 M solution of n-BuLi in hexane (6.5 mL, 16.25 mmol) was diluted with an additional 20 mL of hexane and cooled to −95 °C. After 16.3 mL of 1 M KO^tBu/THF (16.3 mmol) was added, the solution was stirred for 15 min (still at −95 °C) as it turned yellow. A cold (−78 °C) solution of 2.4 mL of $PhCH_2NMe_2$ (16.8 mmol) in 10 mL THF was then added; the color changed immediately to a deep red. The mixture was stirred for 30 min and allowed to warm to −78 °C.

When this solution of $PhCH(K)NMe_2$ was treated with a cold (−78 °C) solution of 4.7 g of Cp_2ZrCl_2 (16.1 mmol) in 70 mL of THF, its color changed to a light brown. After the reaction was stirred for 4 h and allowed to warm to 0 °C, the solvent was removed under reduced pressure. The product was extracted by treating the beige residue with 50 mL of toluene for ~30 min. The resulting solution was filtered through a D frit and the gel-like precipitate washed twice with 30 mL of toluene. The combined filtrates were concentrated to ~50 mL and overlayered with 50 mL of hexane. Cooling to −20 °C resulted in 3 g (48%) of off-white **5**, which was collected by filtration, washed twice with 10 mL of hexane, and dried under vacuum. ^1H NMR (C_6D_6): δ 7.5–6.8 (m, 5 H, Ph), 5.64 (s, 5 H, Cp), 5.48 (s, 5 H, Cp), 3.06 (s, 1 H, CH), 2.42 (s, 3 H, NMe), 2.40 (s, 3 H, NMe). Anal. Calcd for $C_{19}H_{22}NClZr$: C, 58.35; H, 5.63; N, 3.58; Cl, 9.09. Found: C, 58.15; H, 5.69; N, 3.34; Cl, 8.87.

Bis(η^5-cyclopentadienyl)[η^2-α-(dimethylamino)benzyl]methylzirconium(IV) (6). A red solution of $PhCH(K)NMe_2$ prepared as in the previous section was treated with a cold solution (−78 °C) of 4.3 g of $Cp_2ZrMeCl$ (15.8 mmol) in 50 mL of THF; its color changed to a light brown. After the reaction was stirred for 4 h and allowed to warm to 0 °C, the solvent was removed under reduced pressure. The product was extracted by treating the beige residue with 100 mL of toluene for ~30 min. The resulting solution was filtered through a D frit and the gel-like precipitate washed twice with 50 mL of toluene. The combined filtrates were concentrated until they became cloudy and then cooled to −20 °C. After 12 h, the solution was decanted and 2.2 g of yellow needles was dried under vacuum. The decanted solution was concentrated to ~20 mL, then overlayered with 10 mL of pentane, and again cooled to −20 °C. Another 2 g of **6** was isolated, giving a total yield of 4.2 g (70%). ^1H NMR (C_6D_6, 25 °C): δ 7.21 (m, 5 H, Ph), 5.42 (s, 5 H, Cp), 5.28 (s, 5 H, Cp), 2.7 (s, 1 H, CH), 2.15 (s, 6 H, NMe_2), −0.05 (s, 3 H, ZrMe). ^1H NMR (CD_2Cl_2, −20 °C): δ 7.21 (m, 5 H, Ph), 5.7 (s, 5 H, Cp), 5.42 (s, 5 H, Cp), 2.97 (s, 1 H, CH), 2.61 (s, 3 H, NMe), 2.52 (s, 3 H, NMe), −0.33 (s, 3 H, ZrMe). Anal. Calcd for $C_{20}H_{25}NZr$: C, 64.82; H, 6.75; N, 3.78. Found: C, 64.62; H, 6.71; N, 3.64.

$LiCH_2NMe_2$.[9] A THF solution (20 mL) of freshly distilled $Bu_3SnCH_2NMe_2$[14] (1.19 g, 3.42 mmol) at −78 °C was treated, dropwise, with n-BuLi/hexane (2.74 mL of a 1.31 M solution). After complete addition, the solution was allowed to stir for 5 min before use. Note: The tin reagent is air and moisture sensitive and should be stored under nitrogen. The quality of the tin reagent and the accuracy of the n-BuLi titer (solutions were standardized by the method of Kofron and Baclawski[18]) are extremely important in obtaining maximum conversions to $LiCH_2NMe_2$.

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(4) Ward, A. S.; Mintz, E. A.; Ayers, M. R. *Organometallics* **1986**, *5*, 1585.

(5) Buchwald, S. L.; Nielsen, R. B.; Dewan, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 1590.

(6) (a) Erker, G.; Dorf, U.; Atwood, J. L.; Hunter, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 2251. (b) Erker, G.; Schlund, R.; Krüger, C. *J. Chem. Soc., Chem. Commun.* **1986**, 1403. (c) Buchwald, S. L.; Nielsen, R. B.; Dewan, J. C. *Organometallics* **1988**, *7*, 2324.

(7) Matchett, S. A.; Norton, J. R.; Anderson, O. P. *Organometallics* **1988**, *7*, 2228.

(8) (a) Sepelak, D. J.; Pierpont, C. G.; Barefield, E. K.; Budz, J. T.; Poffenberger, C. A. *J. Am. Chem. Soc.* **1978**, *98*, 6178. (b) Barefield, E. K.; Sepelak, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 6542. (c) Barefield, E. K.; Carrier, A. M.; Sepelak, D. J.; Van Derveer, D. G. *Organometallics* **1982**, *1*, 103. (d) Abel, E. W.; Rowley, R. J. *J. Chem. Soc., Dalton Trans.* **1975**, 1096. (e) Fong, C. W.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1975**, 1100.

(9) Peterson, D. J. *J. Am. Chem. Soc.* **1971**, *93*, 4027.

(10) Brandsma, L.; Verkruijsse, H. *Preparative Polar Organometallic Chemistry*; Springer: New York, 1987; Vol. 1, p 201.

(11) (a) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1972**, *34*, 155. (b) Dimethylzirconocene was also prepared by treating Cp_2ZrCl_2 with an excess of MeLi followed by an excess of Me_3SiCl (Buchwald, S. L. Personal communication to J.R.N.).

(12) (a) Jordan, R. F. *J. Organomet. Chem.* **1985**, *294*, 321. (b) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729.

(13) King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 99.

(14) Peterson, D. J. *J. Organomet. Chem.* **1970**, *21*, P63.

(15) Druse, P. M.; Kinston, B. M.; Lappert, M. F.; Spalding, T. R.; Srivastava, R. C. *J. Chem. Soc. A* **1969**, 2106.

(16) Peterson, D. J. *J. Org. Chem.* **1967**, *32*, 1717.

(17) Renaut, P.; Tainturier, G.; Gautheron, B. *J. Organomet. Chem.* **1978**, *148*, 35.

(18) Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.

Cp$_2$M(Cl)CH$_2$NMe$_2$ (M = Zr, 7; M = Hf, 8). To a THF solution (20 mL) of LiCH$_2$NMe$_2$ (3.42 mmol) was added a THF solution (15 mL) of Cp$_2$ZrCl$_2$ (1.00 g, 3.42 mmol) via cannula. The light yellow solution that resulted was maintained at −78 °C for 2 h and then allowed to warm slowly to room temperature over 30 min. The solvent was removed under vacuum, the yellow residue was extracted with benzene, and the extract was filtered through Celite. The filtrate was concentrated and treated with a small amount of hexane to give 0.50 g of the desired product. Further concentration gave an additional 0.15 g. Yield: 0.65 g or 60%. Mass spectrum (EI) (*m*/*e*): 313 (0.2%), parent (P); 279 (1.9%), P − Cl; 248 (0.1%), P − C$_5$H$_5$; 58 (100%), CH$_2$NMe$_2^+$. ^{1}H NMR (C$_6$D$_6$): δ 1.47 (s, 2 H, CH$_2$), 2.20 (s, 6 H, NMe$_2$), 5.55 (s, 10 H, Cp$_2$). Cp$_2$Hf(Cl)(CH$_2$NMe$_2$) (8) was prepared in 41% yield on a 1.32-mmol scale by an identical procedure. Mass spectrum (EI) (*m*/*e*): 403 (0.4%), parent (P); 345 (2.3%), P − CH$_2$NMe$_2$; 58 (100%), CH$_2$NMe$_2^+$. ^{1}H NMR (C$_6$D$_6$): δ 1.47 (s, 2 H, CH$_2$), 2.20 (s, 6 H, NMe$_2$), 5.50 (s, 10 H, Cp$_2$).

Cp$_2$Zr(Me)CH$_2$NMe$_2$ (9). A THF solution (15 mL) of Cp$_2$ZrCl(CH$_2$NMe$_2$) (7) (0.50 g, 1.59 mmol) was treated with an equimolar amount of CH$_3$Li/Et$_2$O at room temperature. The solution was allowed to stand overnight, after which the solvent was removed under vacuum, the off-white residue extracted with hexane (15 mL), and the extract filtered. The colorless filtrate was reduced in volume to 5 mL and cooled to −20 °C. The microcrystalline product that formed was filtered while cold and dried under vacuum. Yield: 0.17 g or 36%. Mass spectrum (EI) (*m*/*e*): 293 (0.89%), parent (P); 278 (29.07%), P − CH$_3$; 235 (6.88%), P − CH$_2$NMe$_2$; 220 (32.36%), Cp$_2$Zr$^+$; 58 (100%), CH$_2$NMe$_2^+$. ^{1}H NMR (C$_6$D$_6$): δ 0.03 (s, 3 H, ZrCH$_3$), 1.15 (s, 2 H, CH$_2$), 1.95 (s, 6 H, NMe$_2$), 5.37 (s, 10 H, Cp$_2$).

Attempted Reaction of Cp$_2$Zr(Cl)CH$_2$NMe$_2$ (7) with CH$_3$OSO$_2$CF$_3$. Solutions of 7 in benzene were treated with excess CH$_3$OSO$_2$CF$_3$. No reaction was evident upon mixing. After 1–2 h a small amount of [(CH$_3$)$_4$N]OSO$_2$CF$_3$ precipitated, but this was less than 10% of the starting complex.

Attempted Reaction of Cp$_2$Zr(Cl)CH$_2$NMe$_2$ (7) with CO(g). A solution of 7 in THF was exposed to 1 atm of CO. The reaction mixture was monitored periodically by infrared spectroscopy, and no change in the appearance of the spectrum was noted. After 1–2 h the starting material could be recovered in good yield.

Attempted Reduction of Cp$_2$Zr(Cl)CH$_2$NMe$_2$ (7) with Sodium Amalgam. Solutions of 7 were stirred with an excess of sodium amalgam (approximately 2%) for up to 16 h. Samples were withdrawn periodically and examined by EPR spectroscopy. No evidence for formation of a paramagnetic species was found.

Bis(η^5-cyclopentadienyl)(α-(dimethylamino)benzyl)(trifluoroacetato)zirconium(IV) (10) was prepared by treating the methyl complex 6 with 1 equiv of CF$_3$CO$_2$H according to a procedure that has been reported elsewhere.[19]

Cp[η^5-C$_5$H$_4$(CMe$_2$Ph)]Zr(Cl)CH$_2$NMe$_2$ (11). To a THF solution (15 mL) of LiCH$_2$NMe$_2$ (2.44 mmol) at −78 °C was added a THF solution (10 mL) of 1.00 g (2.44 mmol) of Cp[η^5-C$_5$H$_4$(CMe$_2$Ph)]ZrCl$_2$.[17] The resulting solution was stirred for 2 h at −78 °C and then allowed to warm slowly to room temperature. The solvent was removed under aspirator vacuum, the residue extracted with benzene, and the extracts filtered through Celite. Concentration of the filtrate and treatment with hexane gave a white solid that was collected, washed with hexane, and dried under vacuum. Yield: 0.57 g or 54%. Mass spectrum (CI) (*m*/*e*): 432 (15.9%), parent + 1 (P + 1); 397 (79.0%), P + 1 − Cl; 374 (100%), P + 1 − CH$_2$NMe$_2$. ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 1.49 (q, 2 H, J_{AB} = 8 Hz, $\Delta\nu$ = 8 Hz, CH$_2$), 1.58 (s, 3 H, CMe), 1.68 (s, 3 H, CMe), 2.20 (br s, 6 H, NMe$_2$), 5.87, 5.55, 5.32 (m, 4 H, $^3J_{H-H}$ = 2.73 Hz, $^4J_{H-H}$ = 1.82 Hz by computer simulation, C$_5$H$_4$R), 5.60 (s, 5 H, Cp), 7.37 (m, 5 H, Ph). ^{1}H NMR (CDCl$_3$, 25 °C): δ 1.84 (q, 2 H, J_{AB} = 8 Hz, $\Delta\nu$ = 9 Hz, CH$_2$), 1.66 (s, 3 H, CMe), 1.71 (s, 3 H, CMe), 2.50 (br s, 3 H, NMe), 2.56 (br s, 3 H, NMe), 5.69, 5.89, 5.95 (m, 4 H, C$_5$H$_4$R), 5.79 (s, 5 H, Cp), 7.25 (m, 5 H, Ph).

Cp$_2$Zr(η^2-CHPhNMe$_2$)(μ-OC)Mo(CO)$_2$Cp (12). The methyl complex 6 (840 mg, 2.2 mmol) and Cp(CO)$_3$MoH (600 mg, 2.4 mmol) were mixed, and 10 mL of freshly distilled THF was added. As the compounds dissolved, gas was evolved and the color changed from dark brown to yellow. After the solution was stirred for 1 h at 25 °C the solvent was removed under vacuum. The resulting yellow oily residue was treated with 20 mL of toluene for $^1/_2$ h. Some insoluble material was removed by filtration, and the toluene was then removed under vacuum. The resulting solid was washed with 20 mL of hexane and then dried under vacuum to yield 1 g (70% yield) of tan 12. IR (Nujol): 1916 (s), 1816 (s), 1615 cm^{-1} (s, br). ^{1}H NMR (C$_6$D$_6$): δ 7.21 (m, 5 H, Ph), 5.67 (s, 5 H, Cp), 5.53 (s, 5 H, Cp), 5.41 (s, 5 H, Cp), 3.14 (s, 1 H, CH), 2.33 (s, 3 H, NMe), 2.4 (s, 3 H, NMe). Anal. Calcd for C$_{27}$H$_{27}$MoNO$_3$Zr: C, 53.98; H, 4.5; N, 2.33. Found: C, 53.76; H, 4.67; N, 2.19.

[Bis(η^5-cyclopentadienyl)(α-(dimethylamino)benzyl)(acetonitrile)zirconium(IV)] Tetraphenylborate (13). [*n*-Bu$_3$NH][BPh$_4$][20] was prepared by treating [*n*-Bu$_3$NH]Br (from *n*-Bu$_2$NH and *n*-BuBr in boiling toluene) with Na[BPh$_4$] in H$_2$O; it was recrystallized from hot ethyl acetate. A solution of 1.01 g (2 mmol) of [*n*-Bu$_3$NH][BPh$_4$] in 30 mL of THF was added over 30 min to a solution of the methyl complex 6 (740 mg, 2.0 mmol) in 30 mL of THF. The mixture was cooled to 0 °C and stirred for 12 h, during which time its yellow color changed to orange. The solution was concentrated to about 10 mL and treated with 20 mL of ether. A tan precipitate resulted, which, when dried under vacuum after the supernatant liquid was decanted, turned into a sticky orange solid. This was washed three times with 20 mL of ether and dried under vacuum again. In order to replace coordinated THF with MeCN, it was dissolved in 20 mL of MeCN, stirred for 15 min, stripped to dryness, and again dissolved in 20 mL of MeCN. Ether (10 mL) was added, and the resulting solution was left standing for 12 h. Orange crystals slowly separated, which were isolated by decanting the supernatant liquid and dried under a flow of N$_2$. A yield of 800 mg (56%) resulted. IR (KBr): 2301 (s), 2273 cm^{-1} (vs). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.42 (m, 8 H, BPh$_4^-$ ortho), 7.36 (m, 3 H, Ph), 7.20 (m, 2 H, Ph), 7.07 (t, *J* = 7.3 Hz, 8 H, BPh$_4^-$ meta), 6.92 (t, *J* = 7.3 Hz, 4 H, BPh$_4^-$ para), 6.03 (s, 5 H, Cp), 5.75 (s, 5 H, Cp), 3.69 (s, 1 H, CH), 2.76 (s, 3 H, NMe), 2.65 (s, 3 H, NMe), 1.69 (s, 3 H, MeCN). Anal. Calcd for C$_{45}$H$_{45}$BN$_2$Zr: C, 75.50; H, 6.29; N, 3.91; Zr, 12.75. Found: C, 75.26; H, 6.52; N, 3.77; Zr, 12.65.

Cp$_2$Zr(CH$_2$SCH$_3$)$_2$ (14). A solution containing 1.00 g (3.42 mmol) of Cp$_2$ZrCl$_2$ in 40 mL of THF was treated with 2 equiv of LiCH$_2$SMe[16] in hexane at room temperature. This caused the previously colorless solution to become yellow in color. After the solution was stirred for 3 h, the THF was evaporated, the yellow residue was extracted with benzene, and the extracts were filtered through Celite. Evaporation of the benzene and treatment of the residue with hexane (5 mL) and a few drops of ether gave an off-white solid that was collected, washed with a small amount of hexane, and dried under vacuum. Yield: 0.61 g or 52%. Mass spectrum (EI): no parent ion observed; *m*/*e* (100%), P − CH$_2$SCH$_3$. ^{1}H NMR (C$_6$D$_6$): δ 1.78 (s, 4 H, CH$_2$), 1.93 (s, 6 H, SCH$_3$), 5.45 (s, 10 H, Cp).

Variable-Temperature Proton NMR Spectra. The proton NMR spectra of 11 were recorded in chloroform-d_1 from −50 to +45 °C and in toluene-d_8 from −35 to +35 °C. Probe temperatures, estimated to be accurate to ±1.0 °C, were measured with a copper–constantan thermocouple. In the recording of spectra, care was taken (temperature equilibration, constant spin rate, maximum point density, etc.) to minimize the common sources of error in NMR line-broadening studies, as discussed by Gutowsky.[21a]

The spectra of 11 were analyzed with a line shape program written by the Barefield group at Georgia Tech that employed a classical formalism for the two-site exchange process. Calculated spectra were analyzed by visual comparison of the overlay with experimental spectra. The visual comparison was supplemented by comparison of some measured parameters, for example, peak separations, relative intensities, and peak widths. The transverse relaxation times, T_2, used to generate calculated spectra, were

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(19) Lubben, T. V.; Plössl, K.; Norton, J. R.; Miller, M. M.; Anderson, O. P. *Organometallics*, in press.

(20) (a) Hlatky, G. G.; Turner, H. W.; Eckmann, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728. (b) Jordan, R. F. Personal communication to J.R.N.

(21) (a) Allerhand, A.; Gutowsky, H. S.; Jonas, J.; Meinzer, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 3185. (b) Sandström, J. *Dynamic NMR Spectroscopy*; Academic: New York, 1982.

obtained from the line widths of the resonances involved in exchange at, or near, the low-temperature limit. The peak separation $\Delta\nu$ (for $CDCl_3$ and toluene-d_8 spectra) and the transverse relaxation times (for toluene-d_8 spectra) were found to be temperature dependent by analysis of the spectra in the absence of exchange. The exchange rate constant, k, was determined by the relation $k = \tau/2$, where τ was the lifetime determined from the spectral simulation. The uncertainties associated with the calculated activation parameters were obtained as described by Sandström.[21b]

In variable-temperature experiments with **5**, **6**, **10**, **12**, and **13**, the true probe temperature was determined at the beginning of each set of experiments from the peak separation of methanol or ethylene glycol.[22] The separation of the diastereotopic methyl groups $\Delta\nu$ proved temperature dependent for these compounds as it had for **11**, so their value of $\Delta\nu$ at the coalescence temperature was extrapolated from their spectra at or near the low-temperature limit. The rate constant k at the coalescence temperature was obtained from $k = \pi(\Delta\nu)/\sqrt{2}$.[21b]

Results and Discussion

Both organometallic reagents $PhCH(K)NMe_2$ and $LiCH_2NMe_2$ react with zirconocene or hafnocene chlorides in THF to give satisfactory yields of their (dimethylamino)alkyl derivatives. For example, treatment of Cp_2ZrCl_2 with 1 equivalent of $PhCH(K)NMe_2$ gives $Cp_2Zr(Cl)CH(Ph)NMe_2$ (**5**) in 48% yield (eq 2) and treatment of $Cp_2Zr(Me)Cl$ with 1 equivalent of $PhCH(K)NMe_2$ gives $Cp_2Zr(Me)CH(Ph)NMe_2$ (**6**) in 70% yield (eq 3).

$$Cp_2ZrCl_2 + K[PhCHNMe_2] \xrightarrow[-78\ ^\circ C]{THF} \underset{\mathbf{5}}{Cp_2Zr(Cl)CH(Ph)NMe_2} \quad (2)$$

$$Cp_2Zr(Me)Cl + K[PhCHNMe_2] \xrightarrow[-78\ ^\circ C]{THF} \underset{\mathbf{6}}{Cp_2Zr(Me)CH(Ph)NMe_2} \quad (3)$$

Treatment of Cp_2ZrCl_2 or Cp_2HfCl_2 with 1 equivalent of $LiCH_2NMe_2$ gives $Cp_2M(Cl)CH_2NMe_2$ (**7**, M = Zr; **8**, M = Hf) in 60% and 41% yield, respectively (eq 4). An excess of lithium reagent is not detrimental, for reasons that will be explained below.

$$Cp_2MCl_2 + LiCH_2NMe_2 \xrightarrow[-78\ ^\circ C]{THF} \underset{\substack{\mathbf{7}\ (M = Zn) \\ \mathbf{8}\ (M = Hf)}}{Cp_2M(Cl)CH_2NMe_2} \quad (4)$$

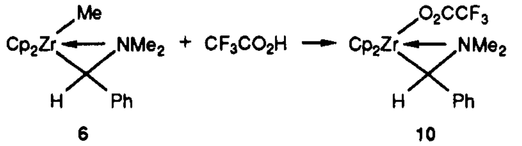
$LiCH_2NMe_2$ appears to be less useful in preparing (dimethylamino)methyl complexes from chloride complexes of the later transition elements. With $Ni(PPh_3)_2Cl_2$ and $Pt(PPh_3)_2Cl_2$ only zerovalent PPh_3 complexes were isolated, despite the fact that $(Ph_3P)Ni(Cl)(\eta^2\text{-}CH_2NMe_2)$ is known.[8a]

The (dimethylamino)alkyl complexes **5**–**8** are very sensitive to hydrolysis but are otherwise surprisingly unreactive. The ((dimethylamino)methyl)zirconium complex **7** does not react with excess $LiCH_2NMe_2$, whereas care must be taken to avoid disubstitution when alkylzirconocene complexes with α-phosphorus or α-sulfur substituents are prepared from lithium reagents.[1b,4] Phenyllithium does not react with **7** after 24 h at room temperature, but prolonged treatment of **7** with methyllithium does give a 36% yield of $Cp_2Zr(Me)CH_2NMe_2$ (**9**) (eq 5).

$$\underset{\mathbf{7}}{Cp_2Zr(Cl)CH_2NMe_2} + MeLi \xrightarrow[\text{room temp}]{Et_2O} \underset{\mathbf{9}}{Cp_2Zr(Me)CH_2NMe_2} \quad (5)$$

The ((dimethylamino)methyl)zirconium complex **7** is also unaffected by CO(g) (1 atm) after several hours at room temperature; most zircononcene alkyls,[23a] including those containing phosphinomethyl groups,[1e,23b,c] react readily with CO under these conditions. Similarly, **7** does not react with $CH_3OSO_2CF_3$ or CH_3I in benzene solution. In contrast, $CpFeCO_2(\eta^1\text{-}CH_2NMe_2)$ and $CpNi(PPh_3)(\eta^1\text{-}CH_2NMe_2)$ both react readily with methyl iodide in nonpolar solvents to produce the ammonium salts,[8a,b] and $Cp_2Zr(Cl)CH_2PPh_2$ reacts with methyl iodide (although the phosphonium salt apparently undergoes further reaction).[24] Unlike a variety of other $Cp_2Zr(Cl)R$ complexes, including $Cp_2Zr(Cl)CH_2PPh_2$,[1b,c,23a] **7** is apparently not reduced by sodium amalgam: no EPR signal was detectable after stirring a solution of **7** for 16 h with Na/Hg.

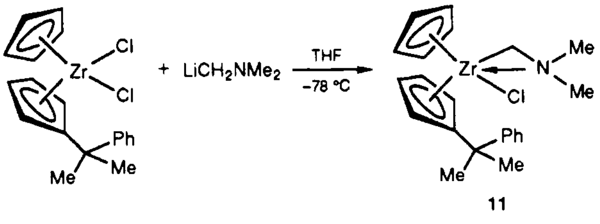
The low reactivity of **7** toward nucleophiles, electron donors, and electrophiles suggests that its α nitrogen is coordinated. While we were unable to grow crystals of **7** or of the methyl (dimethylamino)benzyl complex **6** suitable for X-ray analysis, we were able to obtain such crystals of the (dimethylamino)benzyl trifluoroacetate **10**, which was easily prepared by treating **6** with 1 equiv of CF_3CO_2H (eq 6). The resulting X-ray structure not only has confirmed that the nitrogen of **10** is coordinated but has established that the nitrogen occupies the "inside" coordination site, between the benzyl carbon and the $\eta^1\text{-}O_2CCF_3$ oxygen.[19]



6 **10** (6)

Variable-Temperature NMR Spectra and Their Implications for the Structure of These Compounds. The ^1H NMR spectrum of **10** shows that its (dimethylamino)benzyl nitrogen remains coordinated in solution. At room temperature in CD_2Cl_2 separate peaks at δ 2.83 and 2.75 are observed for the diastereotopic methyl groups of the (dimethylamino)benzyl ligand, but when a $C_2D_4Cl_2$ solution of **10** is heated to 84 °C, these peaks coalesce to a single peak (δ 2.80). Similar behavior is observed in the ^1H NMR spectra of the (dimethylamino)benzyl ligands of **5** and of **6**: the signals due to the diastereotopic methyl groups of **5** coalesce at 36 °C in C_6D_6, and the signals due to the diastereotopic methyl groups of **6** coalesce at 25 °C in CD_2Cl_2.

The methyls of a (dimethylamino)methyl ligand in a zirconocene complex can be made diastereotopic if the cyclopentadienyl rings are made inequivalent. Complex **11** was made in 54% yield (eq 7) by reaction of $LiCH_2NMe_2$ with $Cp[\eta^5\text{-}C_5H_4(CPhMe_2)]ZrCl_2$, the syn-



11 (7)

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[22] Van Geet, A. L. *Anal. Chem.* **1968**, *40*, 2227. Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679.

[23] (a) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Ellis Horwood: Chichester, England, 1986; Chapters 7, 8. (b) Choukroun, R.; Gervais, D. *J. Chem. Soc., Chem. Commun.* **1982**, 1300. (c) Young, S. J.; Hope, H.; Schore, N. E. *Organometallics* **1984**, *3*, 1585.

[24] Schore, N. E. Personal communication to E.K.B.

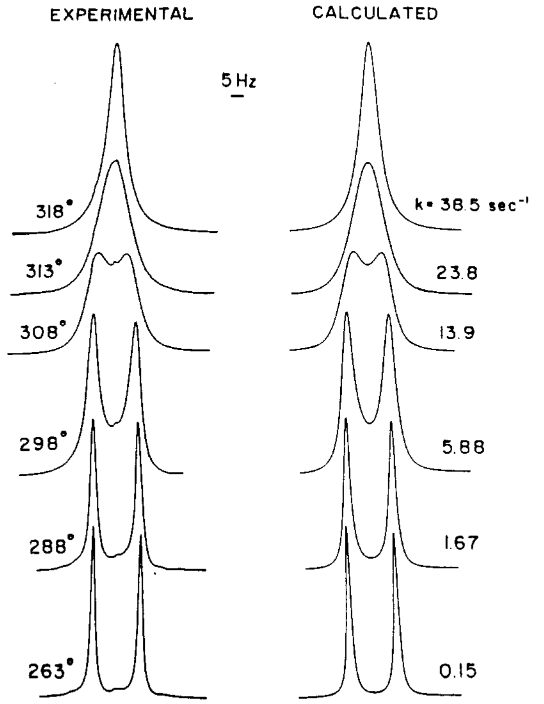


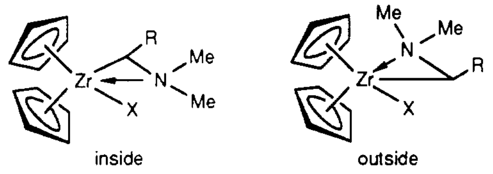
Figure 1. Temperature dependence of experimental and calculated line shapes for *N*-methyl resonances of Cp[η^5-C_5H_4-($CPhMe_2$)]Zr(Cl)(η^2-CH_2NMe_2) (11) in $CDCl_3$ solution at 300 MHz.

thesis of which had been outlined by Gautheron and coworkers.[17] In $CDCl_3$ at room temperature the ^1H NMR spectrum of 11 exhibited two broad singlets for the diastereotopic methyl groups on nitrogen, although in C_6D_6 solution at the same temperature only a single broad resonance was present. In both solvents an AB pattern was observed for the methylene protons of the CH_2NMe_2 ligand, and the diastereotopic methyl groups of the cyclopentadienyl substituent appeared as two singlets.

Examination of the temperature dependence of the spectra of 11 revealed two sharp resonances for the diastereotopic nitrogen methyls at low temperatures in both solvents; these collapsed to a single resonance as the temperature was increased. The $CDCl_3$ experimental results are shown in Figure 1, along with the spectral changes simulated using a two-site exchange model. Appropriate treatment of the resulting rate constants and the corresponding data from toluene solution yielded the activation parameters in Table I for the interconversion of the diastereotopic nitrogen methyls of 11. Over the same temperature range there were no changes in the parts of the ^1H NMR spectrum of 11 due to the CH_2 protons or to the methyl groups of the cyclopentadienyl substituent.

The exchange of the *N*-methyl groups in 11 requires that nitrogen–zirconium bond cleavage be followed by both inversion of configuration at nitrogen and CH_2–N bond rotation before the nitrogen–zirconium bond is re-formed. The free energies of activation for nitrogen inversion and C–N bond rotation in aliphatic amines can be estimated as 8 and 5 kcal/mol, respectively.[25] If we assume that these values are not greatly increased by the presence of a zirconium substituent and apply to the uncoordinated nitrogen in the η^1 isomer of **11**, they are not large enough to explain the *N*-methyl exchange $\Delta G^\ddagger$ values in Table I by themselves. The most likely explanation, illustrated in Figure 2, is that ΔG° for *cleaving the Zr–N bond* of **11** adds to $\Delta G^\ddagger$ for nitrogen inversion in the η^1 isomer ($\Delta G^\ddagger$ for C–N bond rotation in the η^1 isomer is much smaller) to give the overall $\Delta G^\ddagger$ for *N*-methyl exchange.[26] The Zr–N interaction energy in **11** can thus be estimated at 8 kcal/mol.

The observation of only one set of N–Me resonances for **5**, **6**, **10**, and **11** at low temperatures is consistent with either "inside" or "outside" nitrogen coordination but rules

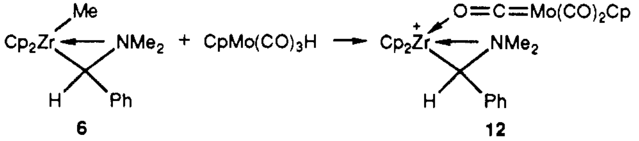


out the existence of both in solution. In view of (1) the "inside" coordination established for **10** in the solid state by X-ray crystallography, (2) our proposal that "outside" structures arise from the steric effects of substitution on the α carbon,[19] and (3) the argument that the (dimethylamino)methyl compounds **7–9** and **11**, being unsubstituted on the α carbon (R = H), should be even less likely to have an "outside" structure than the (dimethylamino)benzyl compound **10** (R = Ph), we believe that compounds **5–11** and their derivatives all have "inside" nitrogen coordination.

$\Delta G^\ddagger$ values for *N*-methyl exchange within **6** and **10** have been estimated from the observed coalescence temperatures for the *N*-methyl resonances of these compounds and placed in Table II along with the average value of $\Delta G^\ddagger$(25 °C) for **11** from Table I. It is probably safe to compare the $\Delta G^\ddagger$ values in Table II despite the fact that they have been measured at different temperatures; $\Delta S^\ddagger$ should be small for such intramolecular rearrangements, so these $\Delta G^\ddagger$ values should show little temperature dependence. The fact that there is no appreciable difference (the imprecision in our taking the numbers in Table II for $\Delta G^\ddagger$(298 K) is at least 0.5 kcal/mol) in the $\Delta G^\ddagger$ values for **6** and **11** suggests that the Zr–N interaction energy is about the same (8 kcal/mol) in both compounds.

The chemical shift separation $\Delta\nu$ for the diastereotopic *N*-methyl groups of **5** is so small that no reliable value for the rate constant or $\Delta G^\ddagger$ can be obtained from the coalescence temperature.[21b]

Other Derivatives of 6 That Retain the (Dimethylamino)benzyl Ligand. Other acids emulate the action of CF_3CO_2H in eq 6 and cleave the methyl ligand of **6** rather than the (dimethylamino)benzyl one. Use of the acidic[27] $CpMo(CO)_3H$ gave the heterobimetallic compound **12** (eq 8) in 70% yield. The (dimethylamino)benzyl



(8)

ligand in **6** may facilitate methane loss: the dissociated

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(25) Bushweller, C. H.; Fleischman, S. H.; Grady, G. L.; McGoff, P.; Rithner, C. D.; Whalon, M. R.; Brennan, J. G.; Marcantonio, R. P.; Domingue, R. P. *J. Am. Chem. Soc.* **1982**, *104*, 6224 and references cited. These values were determined by dynamic NMR at temperatures in the region of coalescence (ca. 125 K); however, since $\Delta S^\ddagger$ for these processes should be essentially zero, the $\Delta G^\ddagger$ values should still be correct at the temperatures of interest in the present study.

(26) The likelihood that $\Delta G^\ddagger$ for reversion of the η^1 isomer to the ground state is small makes it implausible that $\Delta G^\ddagger$ for breaking the Zr–N bond approaches the overall $\Delta G^\ddagger$ for *N*-methyl exchange.

(27) $CpMo(CO)_3H$ is known to have the kinetic acidity necessary to cleave a methyl ligand from Cp_2ZrMe_2: Edidin, R. T.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3945 and references therein.

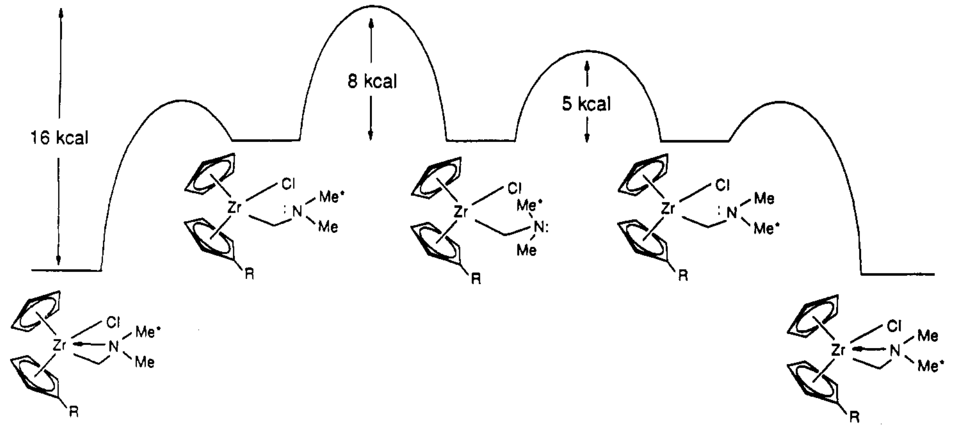


Figure 2. Qualitative energy vs reaction coordinate diagram for *N*-methyl group interchange in $Cp[\eta^5\text{-}C_5H_4(CPhMe_2)]Zr(Cl)(\eta^2\text{-}CH_2NMe_2)$ (11).

Table I. Activation Parameters for *N*-Methyl Group Exchange in $Cp[\eta^5\text{-}C_5H_4(CPhMe_2)]Zr(Cl)(\eta^2\text{-}CH_2NMe_2)$ (11)

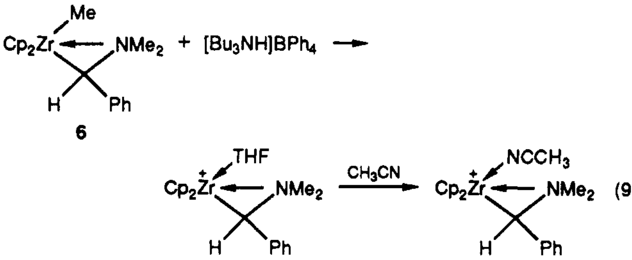
	solvent	
	$CDCl_3$[a]	toluene-d_8[b]
E_a, kcal/mol	17.7 ± 0.8	17.5 ± 0.6
ΔH^*, kcal/mol	17.1 ± 0.8	16.9 ± 0.6
ΔS^*, eu	2.3 ± 2.7	4.1 ± 2.1
ΔG^*(298 K), kcal/mol	16.4 ± 0.8	15.6 ± 0.6

[a] From least-squares analysis of nine data points obtained over the temperature range 263–318 K. [b] From least-squares analysis of six data points obtained over the temperature range 278–308 K.

nitrogen of an η^1-CH(Ph)NMe$_2$ ligand may be the initial site of protonation. One of us has suggested such a function for the acetyl oxygen in $Cp_2Zr(\eta^2\text{-}Ac)Me$ ($CpMo(CO)_3H$ eliminates methane much more rapidly from $Cp_2Zr(\eta^2\text{-}Ac)Me$ than from Cp_2ZrMe_2).[28]

The ^1H NMR signals due to the diastereotopic methyl groups in **12** showed negligible broadening (<4 Hz) even at 100 °C (toluene-d_8), so one can only say that the rate constant for *N*-methyl exchange in **12** is <12 s^{-1} and that ΔG^* is >20 kcal/mol at 100 °C (Table II).

Treatment of **6** with an acid whose conjugate base is not easily coordinated gives a cationic (dimethylamino)benzyl complex. Thus $[n\text{-}Bu_3NH][BPh_4]$, which is known to remove a methyl ligand from $Cp^*{}_2ZrMe_2$ and Cp_2ZrMe_2,[20] removed a methyl ligand from **6** in THF and presumably gave the THF solvate. Isolation of the cation, however, required the replacement of THF by acetonitrile, giving **13** in 56% yield (eq 9).



6

13

(9)

The ^1H NMR signals due to the diastereotopic methyl groups in **13** showed negligible broadening (<1 Hz) up to 70 °C in $C_2D_4Cl_2$, so one can only say that the rate constant for *N*-methyl exchange in **13** under those conditions is <3 s^{-1} and that ΔG^* for **13** is >19.4 kcal/mol in that solvent at 70 °C (Table II). The increase in ΔG^* in the order **6**, **11** < **10** ≤ **12**, **13** presumably reflects the increase in the strength of the Zr–N interaction as the other ligands become more electronegative and the positive charge on zirconium increases.

Table II. Coalescence Temperatures, Rate Constants, and Free Energies of Activation for the Interconversion of Diastereotopic Methyl Groups on Nitrogen

compd	solvent	coalescence temp, °C	rate constant, s^{-1}	ΔG^*, kcal/mol
5	C_6D_6	36	*a*	*a*
6	CD_2Cl_2	25	31.1	15.4
10	$C_2D_4Cl_2$	84	26.4	18.7
11	$CDCl_3$/toluene-d_8			16.0[b]
12	toluene-d_8	100	<12	>20.0
13	$C_2D_4Cl_2$	70	<3	>19.4

[a] As $\Delta\nu$ is very small (<5 Hz in C_6D_6), no reliable rate constant can be obtained. [b] The average 298 K value from the temperature-dependent rate study in Table I.

$Cp_2Zr(CH_2SMe)_2$ (14) has been prepared from Cp_2ZrCl_2 and 2 equiv of $LiCH_2SMe$. In toluene-d_8 there was no change in the appearance of its ^1H NMR spectrum between 298 and 248 K. Since an η^2 interaction of one of the thiomethyl ligands should result in a more complex spectrum, there is probably no Zr–S interaction over this temperature range.

The principal reason that α-sulfur substituents like the one in **14** and α-phosphorus substituents are less likely to coordinate to Zr(IV) than the α-nitrogen substituents in **5**–**13** is surely the greater interaction energy expected for a "hard" Lewis base like nitrogen than for a "soft" one like sulfur or phosphorus. However, the fact that η^2 interactions apparently exist in some $-CR_2SR'$ complexes that have substituents on carbon (e.g., $Cp_2Zr(Cl)CH(SiMe_3)SMe$[4]) raises the possibility that sulfur coordination can occur in order to reduce the steric interactions between these substituents and the cyclopentadienyl ligands.

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Registry No. **5**, 137918-95-7; **6**, 137365-76-5; **7**, 137918-96-8; **8**, 137918-98-0; **9**, 137918-98-0; **10**, 137365-77-6; **11**, 137918-99-1; **12**, 137964-53-5; **13**, 137919-01-8; **14**, 137919-02-9; $PhCH_2NMe_2$, 103-83-3; Cp_2ZrCl_2, 1291-32-3; $Cp_2ZrMeCl$, 1291-45-8; Cp_2HfCl_2, 12116-66-4; $Bu_3SnCH_2NMe_2$, 26285-62-1; $Cp[\eta^5\text{-}C_5H_4(CMe_2Ph)]ZrCl_2$, 66349-71-1; $Cp(CO)_3MoH$, 12176-06-6; $LiCH_2SMe$, 10415-47-1.

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[28] Marsella, J. A.; Huffman, J. C.; Caulton, K. G.; Longato, B.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 6360.