

$\text{H}_3)_2\text{SO}_3$, $\text{Yb}-\text{O}(\text{sulfoxide}) = 2.24$ (3) Å. The short distances in **8**, relative to the $\text{Ln}-\text{O}(\text{P})$ distances in the 10-coordinate complexes, are expected due to the lower coordination number in **8**. Further, the difference in 9-coordinate radii between $\text{Gd}(\text{III})$ (1.247 Å) and $\text{Yb}(\text{III})$ (1.182 Å) accounts for much of the difference in $\text{Ln}-\text{O}(\text{S})$ bond distances between **8** and $\text{Yb}(\text{NO}_3)_3 \cdot [(\text{CH}_3)_2\text{SO}]_3$. The $\text{Gd}-\text{O}(\text{water})$ bond distance, 2.378 (5) Å, appears to be normal. The average $\text{Gd}-\text{O}(\text{nitrate})$ distance, 2.477 Å (range 2.397–2.542 Å), also is similar to those found in other gadolinium nitrate structures.

Conclusion

It has been shown in this study that several (sulfonylmethyl)phosphonates may be easily prepared and purified, and the synthesis developed is sufficiently general that it would be applicable to formation of numerous derivatives. Coordination chemistry of these ligands with the uranyl ion revealed that, unlike that in (carbamoylmethyl)phosphonates, only monodentate binding through the phosphoryl oxygen atom was realized. Synthesis and stabilization of (sulfinylmethyl)phosphonates proved to be more difficult. In fact, the close analogue with the CMP ligand family $(\text{RO})_2\text{P}(\text{O})\text{CH}_2\text{S}(\text{O})\text{NET}_2$ could not be isolated. The coordination chemistry of $(i\text{-C}_3\text{H}_7\text{O})_2\text{P}(\text{O})\text{CH}_2\text{S}(\text{O})(p\text{-CH}_3\text{C}_6\text{H}_4)$ with uranyl ion resulted in the formation of a complex **8** in which the ligand was bonded in a bidentate fashion. With the lanthanides La and

Gd bidentate bonding modes were also deduced, but unlike CMP-lanthanide complexes, only one ligand was found bonded to the lanthanide ion. Clearly, there are several features that distinguish these ligands from the CMP family. Unfortunately, the instability of the known derivatives toward disproportionation makes these ligands useless for practical liquid-liquid extraction. We are, however, presently engaged in attempts to reduce this decomposition tendency by variations in steric and electronic effects on the (sulfinylmethyl)phosphonate backbone.

Acknowledgment. R.T.P. wishes to recognize financial support for this work from Los Alamos National Laboratory (Contract SP-8614) and the Department of Energy, Office of Basic Energy Sciences (Contract 85ER-40079).

Registry No. 1, 120991-41-5; 2, 121029-36-5; 3, 120991-42-6; 4, 121011-75-4; 5, 120991-43-7; 6, 121011-76-5; 7, 121011-77-6; 8, 121011-78-7; 9, 120991-44-8; 10, 121011-79-8; $\text{ClCH}_2\text{S}(\text{C}_6\text{H}_{11})$, 68483-71-6; $(i\text{-C}_3\text{H}_7\text{O})_3\text{P}$, 116-17-6; $(i\text{-C}_3\text{H}_7\text{O})_2\text{P}(\text{O})\text{CH}_2\text{S}(\text{C}_6\text{H}_{11})$, 120991-45-9; $(i\text{-C}_3\text{H}_7\text{O})_2\text{P}(\text{O})\text{CH}_2\text{S}(p\text{-CH}_3\text{C}_6\text{H}_4)$, 120991-46-0; $\text{ClCH}_2\text{S}(p\text{-CH}_3\text{C}_6\text{H}_4)$, 34125-84-3; Ph_2PCl , 1079-66-9; lithium ((dimethylamino)sulfonyl)carbanion, 61669-75-8.

Supplementary Material Available: Tables SI–SVI, listing additional characterization data and complete X-ray data, anisotropic thermal parameters, and bond angles and distances (11 pages); tables of calculated and observed structure factors (29 pages). Ordering information is given on any current masthead page.

Contribution from Baker Laboratory, Department of Chemistry, Cornell University, Ithaca, New York 14853

Influence of π -Donation on *N*-Methyl Group Exchange in Zirconocene *N,N*-Dimethyldithiocarbamates and *N,N*-Dimethylthiocarbamates

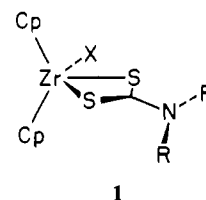
Douglas A. Femecc,^{1a} Michael E. Silver,^{1b} and Robert C. Fay*

Received January 11, 1989

The kinetics of *N*-methyl group exchange in zirconocene *N,N*-dimethyldithiocarbamates, $\text{Cp}_2\text{ZrX}(\text{Me}_2\text{dtc})$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{Me}, \text{CH}_2\text{SiMe}_3, \text{CH}_2\text{CMe}_2\text{Ph}, \text{CH}_2\text{Ph}, \text{OPh}, \text{Opy}$ (4-hydroxypyridinate), OXyl (2,6-dimethylphenoxide)), and *N,N*-dimethylthiocarbamates, $\text{Cp}_2\text{ZrX}(\text{Me}_2\text{mtc})$ ($\text{X} = \text{Cl}, \text{Opy}$), have been studied by variable-temperature ^1H NMR spectroscopy. For the $\text{Cp}_2\text{ZrX}(\text{Me}_2\text{dtc})$ complexes, rates and activation parameters are relatively independent of the nature of the monodentate ligand when $\text{X} = \text{halide}$ or alkyl ($k(25^\circ\text{C}) = 1\text{--}25 \text{ s}^{-1}$; $\Delta H^\ddagger = 14\text{--}17 \text{ kcal/mol}$), but there is a dramatic increase in rate as the π -donating ability of X varies in the order $\text{Cl} < \text{Opy} < \text{OPh}$; $k(25^\circ\text{C}) = 1.0 \times 10^4 \text{ s}^{-1}$ and $\Delta H^\ddagger = 9.8 \text{ kcal/mol}$ when $\text{X} = \text{OPh}$. No dramatic increase in exchange rate is observed for $\text{Cp}_2\text{ZrX}(\text{Me}_2\text{mtc})$ as X varies from Cl to Opy . Except for the aryloxy dithiocarbamate complexes, rates and activation parameters are similar to those for related organic dithiocarbamates and thiocarbamates, strongly suggesting a mechanism involving rotation about the $\text{C}=\text{N}$ bond. $\text{Cp}_2\text{ZrX}(\text{Me}_2\text{dtc})$ ($\text{X} = \text{OPh}, \text{Opy}$) is believed to exchange methyl groups by a Zr–S bond-rupture mechanism. This mechanism, which is promoted by the π -donor properties of the aryloxy ligands, is inaccessible in aryloxythiocarbamate complexes because it would give a higher energy, unobserved stereoisomer. Preparative methods for the $\text{Cp}_2\text{ZrX}(\text{Me}_2\text{dtc})$ and $\text{Cp}_2\text{ZrX}(\text{Me}_2\text{mtc})$ complexes and the $\text{Cp}_2\text{Zr}(\text{X})\text{Cl}$ intermediates are described.

Introduction

Chlorozirconocene dithiocarbamate complexes, $\text{Cp}_2\text{ZrCl}(\text{RR}'\text{dtc})$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{RR}'\text{dtc} = \text{S}_2\text{CNRR}'$),^{2–4} are interesting examples of fluxional, 18-electron, titanium group metallocenes. An X-ray study⁵ of the *N,N*-diethyl derivative, $\text{Cp}_2\text{ZrCl}(\text{Et}_2\text{dtc})$, has established the expected bent metallocene structure **1**, with the Zr atom, Cl atom, and the two S atoms of the planar, bidentate dithiocarbamate ligand in the quasi-mirror plane that bisects the $\text{Cp}-\text{Zr}-\text{Cp}$ angle. One interesting facet of this structure is con-



siderable crowding in the $\text{ZrClS}_2\text{C}_{10}$ coordination group as evidenced by very short nonbonded contacts and unusually long Zr–Cl and Zr–S bond lengths. The Zr–Cl distance is 2.556 (2) Å, 0.12 Å longer than that in Cp_2ZrCl_2 ,⁶ and the bond length to the lateral S atom is 2.723 (2) Å, 0.09 Å longer than the more normal bond to the interior S atom.

A ^1H NMR study⁵ of the *N,N*-dimethyl derivative, $\text{Cp}_2\text{ZrCl}(\text{Me}_2\text{dtc})$, has shown that the inequivalent *N*-methyl

- (1) (a) Present address: EG&G Idaho, Inc., 2151 N. Boulevard, Idaho Falls, ID 83415-2208. (b) Present address: Department of Chemistry, Hope College, Holland, MI 49423.
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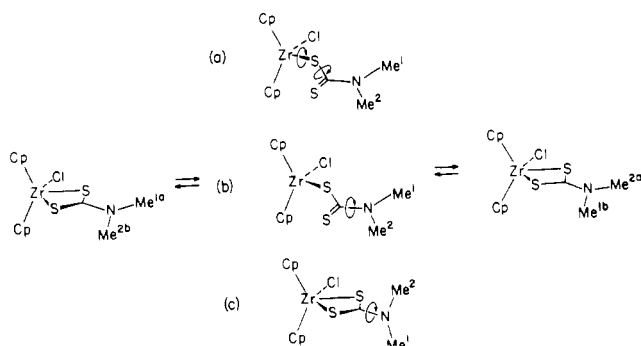


Figure 1. Possible mechanisms for methyl group exchange in $\text{Cp}_2\text{ZrCl}(\text{Me}_2\text{dtc})$. All three mechanisms exchange methyl groups 1 and 2 between inequivalent sites a and b. Microscopic reversibility requires that the intermediate in mechanism a must form by rupture of either Zr-S bond.

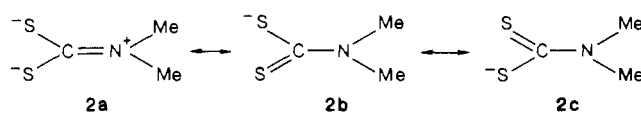
groups are exchanged by a process having a rate constant of 8.6 s^{-1} at 25°C . The mechanism of that process in $\text{Cp}_2\text{ZrCl}(\text{Me}_2\text{dtc})$ and related compounds is the focus of this paper.

On the basis of NMR experiments or extended Hückel calculations,⁵ we were able to rule out mechanisms involving ligand dissociation and polytopal rearrangement. The three mechanisms depicted in Figure 1 remain as viable possibilities. Mechanism a involves rupture of a Zr-S bond to give a four-coordinate intermediate, followed by rotation of the dangling ligand about the Zr-S and/or C-S bonds and subsequent reattachment of the uncoordinated S atom at the other sulfur coordination site. Mechanism b involves Zr-S bond rupture followed by rotation about the C=N partial double bond and subsequent reattachment of the uncoordinated S atom, while mechanism c features rotation about the C=N bond without Zr-S bond rupture. One can, of course, envision a continuum of mechanisms intermediate between b and c that involve rotation about the C=N bond accompanied by more or less Zr-S bond stretching.

Mechanisms a and b are attractive because the unusually long bond to the S atom in the lateral coordination site should be especially susceptible to bond rupture. Mechanisms b and c, involving rotation about the C=N bond, appear most likely because organic dithiocarbamates also exhibit *N*-methyl group exchange,⁷⁻¹⁰ with rates and activation parameters similar to those for $\text{Cp}_2\text{ZrCl}(\text{Me}_2\text{dtc})$. In the case of the organic dithiocarbamates, rotation about the C=N bond is the only plausible mechanism.

Extended Hückel calculations⁵ indicate that the barrier to Zr-S bond rupture should decrease with increasing π -donor character of the monodentate ligand, thus favoring bond rupture mechanism a or b for complexes that contain strong π -donor ligands. Mechanism a or b is also favored for complexes that contain sterically bulky monodentate ligands. Therefore, we decided to study the kinetics of methyl group exchange in complexes where the Cl atom of $\text{Cp}_2\text{ZrCl}(\text{Me}_2\text{dtc})$ is replaced by monodentate ligands having different electronic and steric properties.

The effect of the electronic properties of the monodentate ligand on the barrier to rotation about the C=N bond (mechanism b or c) may be anticipated on the basis of valence bond resonance structures **2a–2c**. Electronegative monodentate ligands should



make the Zr atom more positive, thus strengthening the Zr-S bonds and favoring the resonance structure (**2a**) that has a C=N double bond. Therefore, electronegative monodentate ligands may increase the barrier to rotation about the C=N bond. On the other

hand, strong π -donor monodentate ligands, such as alkoxides or aryloxides, should make the Zr atom less positive, thus weakening the Zr-S bonds and favoring the resonance structures (**2b** and **2c**) that have a C-N single bond. Consequently, strong π -donor monodentate ligands may decrease the barrier to rotation about the C=N bond. Sterically bulky monodentate ligands should similarly weaken the Zr-S bonds and lower the barrier to rotation about the C=N bond.

Reported in this paper are ^1H NMR kinetic studies of *N*-methyl group exchange in $\text{Cp}_2\text{ZrX}(\text{Me}_2\text{dtc})$, where $\text{X} = \text{halide, alkyl, or aryloxy}$. The corresponding *N,N*-dimethylthiocarbamate complexes, $\text{Cp}_2\text{ZrX}(\text{Me}_2\text{mtc})$ ($\text{X} = \text{Cl, 4-hydroxypyridinate}$), were also studied in an effort to further define the mechanism. Also described are preparative methods for the $\text{Cp}_2\text{ZrX}(\text{Me}_2\text{dtc})$ and $\text{Cp}_2\text{ZrX}(\text{Me}_2\text{mtc})$ complexes and the $\text{Cp}_2\text{Zr}(\text{X})\text{Cl}$ intermediates.

Experimental Section

Reagents and General Techniques. Cp_2ZrCl_2 ,¹¹ Cp_2ZrBr_2 ,¹² Cp_2ZrI_2 ,¹² and $[\text{Cp}_2\text{Zr}(\text{H})\text{Cl}]_x$ ¹³ were synthesized as described in the literature. $\text{Cp}_2\text{Zr}(\text{CH}_2\text{SiMe}_3)\text{Cl}$ was prepared¹⁴ by reaction of Cp_2ZrCl_2 and ((trimethylsilyl)methyl)magnesium chloride (Aldrich): mp $119\text{--}122^\circ\text{C}$ (lit.¹⁴ mp $118\text{--}121^\circ\text{C}$). ^1H NMR (CDCl_3): δ 0.05 (s, 9 H, CH_3), 0.96 (s, 2 H, CH_2), 6.28 (s, 10 H, C_5H_5). Benzylmagnesium chloride and (2-methyl-2-phenylpropyl)magnesium chloride were synthesized by reaction of the appropriate anhydrous alkyl chloride with a slight excess of magnesium metal in diethyl ether, and the solutions were used directly for synthesis of the corresponding $\text{Cp}_2\text{Zr}(\text{R})\text{Cl}$ compounds.

Lithium methoxide and lithium isopropoxide were prepared by reaction of lithium metal with a 20% excess of the appropriate alcohol (freshly distilled from calcium hydride) in a 3.5 M benzene solution. Trap-to-trap distillation to remove the solvent and excess alcohol left the lithium alkoxides as free-flowing, white powders. Phenol and 2,6-dimethylphenol (Aldrich) were purified by recrystallization from hexane. 4-Hydroxypyridine (Aldrich) was recrystallized from chloroform-methanol and dried in vacuo over phosphorus(V) oxide.

Sodium *N,N*-dimethyldithiocarbamate dihydrate, $\text{Na}(\text{Me}_2\text{dtc})\cdot 2\text{H}_2\text{O}$, (Aldrich) was dried in vacuo over phosphorus(V) oxide at 110°C until the IR spectrum no longer showed a water band near 3500 cm^{-1} . Anhydrous sodium *N,N*-dimethylthiocarbamate, $\text{Na}(\text{Me}_2\text{mtc})$,¹⁵ $\text{Cp}_2\text{ZrCl}(\text{Me}_2\text{dtc})$,⁵ and $\text{Cp}_2\text{ZrCl}(\text{Me}_2\text{mtc})$ ¹⁶ were prepared as described in the literature.

Benzene and hexane were dried and deoxygenated by refluxing each solvent for at least 24 h over potassium benzophenone ketyl; dichloromethane was dried by refluxing it over calcium hydride. Syntheses were carried out under anhydrous conditions in a dry argon atmosphere. Compounds were subsequently handled in a dry nitrogen atmosphere.

Bis(η^5 -cyclopentadienyl)bromo(*N,N*-dimethyldithiocarbamate)zirconium(IV), $\text{Cp}_2\text{ZrBr}(\text{Me}_2\text{dtc})$. A mixture of Cp_2ZrBr_2 (1.20 g, 3.15 mmol) and $\text{Na}(\text{Me}_2\text{dtc})$ (0.45 g, 3.1 mmol) was stirred for 24 h in dichloromethane ($\sim 100 \text{ mL}$) at reflux. The reaction mixture was filtered, and the solvent was removed from the filtrate by trap-to-trap distillation. The crude product (1.30 g, 98%) was dissolved in a minimum of dichloromethane, and hexane ($\sim 100 \text{ mL}$) was layered on top of the solution (hereafter dichloromethane under hexane). Slow diffusion of the hexane into the dichloromethane layer afforded clear, colorless crystals of $\text{Cp}_2\text{ZrBr}(\text{Me}_2\text{dtc})$, mp $270\text{--}272^\circ\text{C}$ dec. ^1H NMR (CDCl_3): δ 3.31 (s, 3 H, CH_3), 3.33 (s, 3 H, CH_3), 6.18 (s, 10 H, C_5H_5). IR (Nujol mull) (cm^{-1}): $\nu(\text{C=N})$, 1520 s; $\nu(\text{C=S})$, 994 m; $\nu(\text{Zr-S})$ 363 m, 338 m; other bands, 1399 s, 1255 m, 1145 m, 1020 m, 1011 m, 846 m, 795 s, 683 w, 573 w, 445 m. Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{BrNS}_2\text{Zr}$: C, 37.04; H, 3.83; Br, 18.96; N, 3.32; S, 15.21; Zr, 21.64. Found: C, 37.17; H, 3.84; Br, 18.82; N, 3.34; S, 15.38; Zr, 21.48.

Bis(η^5 -cyclopentadienyl)(*N,N*-dimethyldithiocarbamate)iodozirconium(IV), $\text{Cp}_2\text{ZrI}(\text{Me}_2\text{dtc})$. This compound was prepared by reaction for 12 h of Cp_2ZrI_2 (1.51 g, 3.18 mmol) and $\text{Na}(\text{Me}_2\text{dtc})$ (0.46 g, 3.2 mmol) in dichloromethane (100 mL) at room temperature. Crystallization from dichloromethane under hexane at -15°C afforded colorless crystals of $\text{Cp}_2\text{ZrI}(\text{Me}_2\text{dtc})$ (1.31 g, 88%). The crystals darken at 220°C , but do not melt below 265°C . ^1H NMR (CDCl_3): δ 3.27

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(s, 3 H, CH₃), 3.33 (s, 3 H, CH₃), 6.20 (s, 10 H, C₅H₅). IR (Nujol mull) (cm⁻¹): ν(C=N), 1524 m br; ν(C=S), 991 m; ν(Zr-S), 365 s, 341 s; ν(Zr-I), 187 m; other bands, 1440 w, 1387 s, 1250 w, 1144 m, 1066 w, 1022 m, 1016 m, 1009 m, 849 m, 804 vs, 608 w, 577 w, 446 m, 268 m, 206 w, 147 w, 114 m. Anal. Calcd for C₁₃H₁₆INS₂Zr: C, 33.33; H, 3.44; I, 27.09; N, 2.99. Found: C, 33.27; H, 3.48; I, 27.17; N, 2.99.

Bis(η⁵-cyclopentadienyl)(N,N-dimethyldithiocarbamato)methylzirconium(IV), Cp₂ZrMe(Me₂dtc). This compound was prepared by reaction for 8 h of 4.07 mL of 1.2 M methyl lithium in diethyl ether (4.9 mmol) (Alfa) with Cp₂ZrCl(Me₂dtc) (1.84 g, 4.88 mmol) in ~100 mL of benzene at room temperature. Two recrystallizations of the crude product (1.24 g, 71%) from dichloromethane under hexane afforded clear, colorless crystals of Cp₂ZrMe(Me₂dtc), mp 157–160 °C (lit.³ mp 156–158 °C). ¹H NMR (CDCl₃): δ 0.03 (s, 3 H, ZrCH₃), 3.29 (s, 6 H, NCH₃), 5.88 (s, 10 H, C₅H₅). IR (Nujol mull) (cm⁻¹): ν(C=N), 1517 s br; ν(C=S), 998; ν(Zr-C), 432 s; ν(Zr-S), 359 m, 334 s; other bands, 1390 s, 1255 s, 1147 m, 1122 w, 1060 w, 1009 m, 800 vs, 639 w, 587 m, 568 w, 454 w. Anal. Calcd for C₁₄H₁₉NS₂Zr: C, 47.15; H, 5.37; N, 3.93. Found: C, 46.96; H, 5.50; N, 3.98.

Bis(η⁵-cyclopentadienyl)(N,N-dimethyldithiocarbamato)(trimethylsilyl)methylzirconium(IV), Cp₂Zr(CH₂SiMe₃)(Me₂dtc). Na(Me₂dtc) (2.74 g, 19.1 mmol) was added to a solution of Cp₂Zr(CH₂SiMe₃)Cl (6.63 g, 19.3 mmol) in dichloromethane (75 mL), and the mixture was stirred for 8 h at room temperature. Sodium chloride was removed by filtration, and the filtrate was concentrated to 30 mL. Addition of hexane (70 mL) and chilling to -15 °C afforded light yellow crystals of Cp₂Zr(CH₂SiMe₃)(Me₂dtc) (3.82 g); an additional 1.49 g was obtained by further concentration of the solution and chilling: total yield 65%; mp 168–170.5 °C dec. ¹H NMR (CDCl₃): δ -0.09 (s, 2 H, CH₂), 0.11 (s, 9 H, SiCH₃), 3.30 (s, 6 H, NCH₃), 5.94 (s, 10 H, C₅H₅). IR (Nujol mull) (cm⁻¹): ν(C=N), 1501 m br; ν(C=S), 1001 w; ν(Zr-C), 416 m; ν(Zr-S), 353 m, 333 s; other bands, 1474 m, 1447 m, 1385 s, 1371 m, 1256 m, 1142 w, 1013 m, 935 m, 802 vs, 737 m, 719 m, 666 m, 580 w, 563 w, 448 m, 262 m. Anal. Calcd for C₁₇H₂₇NS₂SiZr: C, 47.61; H, 6.35; N, 3.27; Zr, 21.27. Found: C 47.08; H, 6.29; N, 3.21; Zr, 21.79.

Bis(η⁵-cyclopentadienyl)chloro(2-methyl-2-phenylpropyl)zirconium(IV), Cp₂Zr(CH₂CM₂Ph)Cl. A solution of (2-methyl-2-phenylpropyl)magnesium chloride (18 mmol) in diethyl ether (65 mL) was transferred via cannula into a solution of Cp₂ZrCl₂ (5.00 g, 17.1 mmol) in dichloromethane (65 mL). After the mixture had been stirred for 2 days, magnesium chloride was removed by filtration and was washed with 45 mL of dichloromethane. The combined filtrate and wash solution was concentrated to 30 mL. Addition of hexane (70 mL) precipitated a small amount of a white, chloroform-insoluble solid, which was removed by filtration. Concentration of the filtrate afforded a bright yellow, flocculent powder of Cp₂Zr(CH₂CM₂Ph)Cl (5.86 g 88%). The compound decomposes on heating at 200 °C to a white solid that does not melt below 260 °C. ¹H NMR (CDCl₃): δ 1.34 (s, 6 H, CH₃), 1.58 (s, 2 H CH₂), 6.06 (s, 10 H, C₅H₅), 7.15–7.5 (m, 5 H, C₆H₅). IR (Nujol mull) (cm⁻¹): ν(Zr-Cl), 338 vs br; other bands, 1495 w, 1466 s, 1447 s, 1375 m, 1281 w, 1188 w, 1045 w, 1013 m, 908 w, 841 m, 812 vs, 773 vs, 706 s, 633 w, 562 w, 525 m, 488 w, 419 w, 411 w, 382 m, 355 s, 305 m, 280 s, 262 m, 220 m. Anal. Calcd for C₂₀H₂₃ClZr: C, 61.58; H, 5.94; Zr, 23.39. Found: C, 60.63; H, 5.50; Zr, 23.27.

Bis(η⁵-cyclopentadienyl)(N,N-dimethyldithiocarbamato)(2-methyl-2-phenylpropyl)zirconium(IV), Cp₂Zr(CH₂CM₂Ph)(Me₂dtc). This compound was prepared in 64% yield from Cp₂Zr(CH₂CM₂Ph)Cl (5.86 g, 15.0 mmol) and Na(Me₂dtc) (2.15 g, 15.0 mmol) by the same procedure used for preparation of Cp₂Zr(CH₂SiMe₃)(Me₂dtc). The product was a yellow, polycrystalline solid; mp 137–139.5 °C. ¹H NMR (CDCl₃): δ 1.21 (s, 2 H, CH₂), 1.46 (s, 6 H, CCH₃), 3.29 (s, 6 H, NCH₃), 5.77 (s, 10 H, C₅H₅), 7.1–7.6 (m, 5 H, C₆H₅). IR (Nujol mull) (cm⁻¹): ν(C=N), 1514 m br; ν(C=S), 1000 m; ν(Zr-S), 353 m, 328 m; other bands, 1474 s, 1466 vs, 1445 s, 1385 s, 1285 w, 1254 m, 1190 w, 1144 m, 1063 w, 1022 m, 1009 s, 906 w, 843 w, 827 m, 804 vs, 797 vs, 768 s, 702 s, 584 w, 559 m, 449 m, 341 m. Anal. Calcd for C₂₃H₂₉NS₂Zr: C, 58.18; H, 6.16; N, 2.95. Found: C, 58.02; H, 6.51; N, 3.05.

Benzylbis(η⁵-cyclopentadienyl)chlorozirconium(IV), Cp₂Zr(CH₂Ph)Cl. This compound was prepared in 79% yield from benzylmagnesium chloride and Cp₂ZrCl₂ by a procedure similar to that employed for the synthesis of Cp₂Zr(CH₂CM₂Ph)Cl, except that a reaction time of only 1 h was necessary, to give orange crystals, mp 122–125 °C. ¹H NMR (C₆D₆): δ 2.27 (s, 2 H, CH₂), 5.64 (s, 10 H, C₅H₅), 6.9–7.35 (m, 5 H, C₆H₅). IR (Nujol mull) (cm⁻¹): ν(Zr-C), 407 m; ν(Zr-Cl), 347 s; other bands, 1589 w, 1483 m, 1466 s, 1447 m, 1398 w, 1377 m, 1366 w, 1209 m, 1175 w, 1028 w, 1016 m, 991 w, 810 vs, 748 s, 700 m, 530 w, 287 m, 220 w, 203 w. Anal. Calcd for C₁₇H₁₇ClZr: C, 58.68; H, 4.92. Found: C, 55.77; H, 5.20.

Benzylbis(η⁵-cyclopentadienyl)(N,N-dimethyldithiocarbamato)zirconium(IV), Cp₂Zr(CH₂Ph)(Me₂dtc). This compound was obtained as a

yellow powder in 82% yield from the reaction of Cp₂Zr(CH₂Ph)Cl (3.22 g, 9.25 mmol) and Na(Me₂dtc) (1.33 g, 9.29 mmol). The procedure was essentially the same as that used for preparation of Cp₂Zr-(CH₂SiMe₃)(Me₂dtc). Recrystallization from benzene under hexane at -15 °C afforded yellow-orange crystals; mp 161–163 °C. ¹H NMR (C₆D₅CD₃): δ 2.28 (s, 2 H, CH₂), 3.41 (s, 6 H, CH₃), 6.17 (s, 10 H, C₅H₅), 6.55–7.0 (m, 5 H, C₆H₅). IR (Nujol mull) (cm⁻¹): ν(C=N), 1518 s br; ν(C=S), 989 m; ν(Zr-C), 399 m; ν(Zr-S), 357 s, 330 s br; other bands, 1591 m, 1483 s, 1447 m, 1393 s, 1366 m, 1252 m, 1206 m, 1142 m, 1065 w, 1024 m, 1011 s, 826 s, 816 s, 802 vs, 750 s, 698 s, 627 w, 608 m, 581 w, 530 m, 447 m, 280 m, 257 w, 212 m, 199 s, 187 m, 158 w. Anal. Calcd for C₂₀H₂₃NS₂Zr: C, 55.51; H, 5.36; N, 3.24. Found: C, 53.64; H, 5.15; N, 3.26.

Bis(η⁵-cyclopentadienyl)chloromethoxyzirconium(IV), Cp₂Zr(OMe)Cl. **Method A.** Lithium methoxide (0.77 g, 20 mmol) was added to a solution of Cp₂ZrCl₂ (5.40 g, 18.5 mmol) in benzene (175 mL), and the mixture was stirred for 4 h. Lithium chloride was removed by filtration, and the solvent was removed by trap-to-trap distillation. The resulting light brown solid was stirred with hexane (50 mL) for 12 h. Filtration afforded white microcrystals of Cp₂Zr(OMe)Cl (4.15 g, 78%), mp 112–114 °C (lit.¹⁷ mp 111–114.5 °C). ¹H NMR (CDCl₃): δ 3.88 (s, 3 H, CH₃), 6.30 (s, 10 H, C₅H₅).

Method B. To a suspension of [Cp₂Zr(H)Cl]_x (3.00 g, 11.6 mequiv) in benzene (40 mL) was added dropwise a solution of methanol (0.47 mL, 11.7 mmol) in benzene (40 mL). Gas evolution was evident immediately. The mixture was stirred for 6 h, and then the solvent was removed from the clear, colorless solution by trap-to-trap distillation. The resulting white solid was stirred with hexane (60 mL) for 4 h. Filtration afforded a white powder of Cp₂Zr(OMe)Cl (3.24 g, 97%).

Attempted Synthesis of Bis(η⁵-cyclopentadienyl)(N,N-dimethyldithiocarbamato)methoxyzirconium(IV), Cp₂Zr(OMe)(Me₂dtc). Attempted preparation of this compound by reaction for 8 h of Cp₂Zr(OMe)Cl (4.80 g, 16.7 mmol) and Na(Me₂dtc) (2.50 g, 17.5 mmol) in benzene (100 mL) was unsuccessful. The product, a yellow crystalline solid (3.62 g), was identified by ¹H NMR as mainly CpZr(Me₂dtc)₃,¹⁸ mp >260 °C (lit.¹⁸ dec pt 270–275 °C). ¹H NMR (CDCl₃): δ 3.26 (s, 3 H, CH₃), 3.27 (s, 6 H, CH₃), 3.32 (s, 3 H, CH₃), 3.35 (s, 6 H, CH₃), 6.10 (s, 5 H, C₅H₅).

Bis(η⁵-cyclopentadienyl)chloroisopropoxyzirconium(IV), Cp₂Zr(OCHMe₂)Cl. Reaction of lithium isopropoxide and Cp₂ZrCl₂ (method A above) gave white microcrystals of Cp₂Zr(OCHMe₂)Cl in 63% yield; mp 80–82 °C (lit.¹⁷ mp 81–82.5 °C). ¹H NMR (CDCl₃): δ 1.10 (d, J = 6 Hz, 6 H, CH₃), 4.29 (septet, J = 6 Hz, 1 H, CH), 6.28 (s, 10 H, C₅H₅). This compound was also prepared, in 85% yield, by reaction of [Cp₂Zr(H)Cl]_x and isopropyl alcohol (method B above).

Attempted Synthesis of Bis(η⁵-cyclopentadienyl)(N,N-dimethyldithiocarbamato)isopropoxyzirconium(IV), Cp₂Zr(OCHMe₂)(Me₂dtc). Attempted preparation of this compound by reaction for 8 h of Cp₂Zr(OCHMe₂)Cl (5.03 g, 15.9 mmol) and Na(Me₂dtc) (2.40 g, 16.7 mmol) in benzene (100 mL) yielded an amber solid, identified as mainly CpZr(Me₂dtc)₃ (see above).

Bis(η⁵-cyclopentadienyl)chlorophenoxyzirconium(IV), Cp₂Zr(OPh)Cl. This compound was obtained in 85% yield as a sticky, off-white paste from the reaction of [Cp₂Zr(H)Cl]_x and phenol (method B above). Attempts to solidify the paste failed. Because the paste was difficult to handle, it was not submitted for elemental analysis. ¹H NMR (CDCl₃): δ 6.39 (s, 10 H, C₅H₅), 6.75–7.4 (m, 5 H, C₆H₅). IR (Nujol mull) (cm⁻¹): ν(Zr-O), 515 m; ν(Zr-Cl), 344 s br; other bands 1587 s, 1479 vs, 1441 w, 1275 s br, 1161 m, 1066 w, 1015 s, 876 s, 835 vs br, 756 s, 694 m, 625 m, 608 w, 442 m, 305 m, 282 m, 260 m, 166 m, 123 w.

Bis(η⁵-cyclopentadienyl)(N,N-dimethyldithiocarbamato)phenoxyzirconium(IV), Cp₂Zr(OPh)(Me₂dtc). Na(Me₂dtc) (1.30 g, 9.08 mmol) was added to a solution of Cp₂Zr(OPh)Cl (3.12 g, 8.92 mmol) in benzene (75 mL). The mixture was stirred for 18 h and then filtered to remove sodium chloride. Concentration of the filtrate to 30 mL and crystallization from benzene under hexane at -15 °C afforded yellow crystals of Cp₂Zr(OPh)(Me₂dtc) (3.16 g, 81%); mp 177–180 °C. ¹H NMR (CDCl₃): δ 3.39 (s, 6 H, CH₃), 6.20 (s, 10 H, C₅H₅), 6.55–7.2 (m, 5 H, C₆H₅). (The methyl region indicated the presence of a ~6% impurity of CpZr(Me₂dtc)₃; the amount of CpZr(Me₂dtc)₃ doubled in 6.5 h, and this compound was the sole detectable dithiocarbamate-containing species after 40 h.) IR (Nujol mull) (cm⁻¹): ν(C=N), 1520 w; ν(C=S), 993 w; ν(Zr-O), 513 m; ν(Zr-S), 359 m, 320 s br; other bands, 1584 m, 1460 vs, 1377 s, 1292 s, 1157 w, 1134 w, 1063 w, 1020 w, 870 m, 839 w, 808 m, 795 m, 760 m, 725 m, 696 w, 617 w, 600 m, 581 w, 447 m, 434 m, 255 w, 230 m, 199 m, 158 w. Anal. Calcd for C₁₉H₂₁NOS₂Zr: C, 52.49;

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H, 4.87; N, 3.22; Zr, 20.98. Found: C, 50.56; H, 4.78; N, 3.83; Zr, 20.43. These analyses are consistent with the presence of an 8% impurity of $\text{CpZr}(\text{Me}_2\text{dtc})_3$.

Bis(η^5 -cyclopentadienyl)chloro(4-hydroxypyridinato)zirconium(IV), $\text{Cp}_2\text{Zr}(\text{Opy})\text{Cl}$. This compound was prepared in 90% yield from $[\text{Cp}_2\text{Zr}(\text{H})\text{Cl}]_x$ and 4-hydroxypyridine (method B above). The reaction time was 1 day owing to the poor solubility of 4-hydroxypyridine in benzene. The product, a sticky amber paste, was not submitted for elemental analysis. $^1\text{H NMR}$ (CDCl_3): δ 6.37 (s, 10 H, C_5H_5), 6.48 (dd, 2 H, Opy), 8.34 (dd, 2 H, Opy). IR (Nujol mull) (cm^{-1}): $\nu(\text{Zr}-\text{O})$, 540 m; $\nu(\text{Zr}-\text{Cl})$, 343 s br; other bands, 1632 m, 1580 m, 1503 s, 1485 s, 1443 m, 1377 s, 1310 s, 1261 m, 1207 m, 1184 w, 1096 m br, 1016 s, 989 m, 885 m, 804 vs, 739 m, 675 w, 610 w, 463 w, 450 w.

Bis(η^5 -cyclopentadienyl)(*N,N*-dimethyldithiocarbamato)(4-hydroxypyridinato)zirconium(IV), $\text{Cp}_2\text{Zr}(\text{Opy})(\text{Me}_2\text{dtc})$. This compound was prepared by reaction of $\text{Na}(\text{Me}_2\text{dtc})$ (0.71 g, 4.96 mmol) and $\text{Cp}_2\text{Zr}(\text{Opy})\text{Cl}$ (1.73 g, 4.93 mmol) in benzene (100 mL). The procedure employed for synthesis of $\text{Cp}_2\text{Zr}(\text{OPh})(\text{Me}_2\text{dtc})$ afforded a beige powder of $\text{Cp}_2\text{Zr}(\text{Opy})(\text{Me}_2\text{dtc})$ (1.52 g, 71%), mp 160–165 °C. $^1\text{H NMR}$ (CDCl_3): δ 3.38 (s, 6 H, CH_3), 6.18 (s, 10 H, C_5H_5), 6.50 (dd, 2 H, Opy), 8.26 (dd, 2 H, Opy); the methyl region indicated the presence of a ~8% impurity of $\text{CpZr}(\text{Me}_2\text{dtc})_3$. IR (Nujol mull) (cm^{-1}): $\nu(\text{C}=\text{N})$, 1520 sh; $\nu(\text{C}=\text{S})$, 988 m; $\nu(\text{Zr}-\text{O})$, 540 m; $\nu(\text{Zr}-\text{S})$, 359 m, 330 s br; other bands, 1585 vs, 1501 vs, 1487 s, 1441 w, 1418 w, 1391 m, 1337 vs, 1317 m, 1252 m, 1207 m, 1146 m, 1015 m, 883 m, 804 vs, 732 m, 592 m, 449 w, 430 w, 224 m. Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_5\text{S}_2\text{Zr}$: C, 49.62; H, 4.63; N, 6.43; Zr, 20.94. Found: C, 50.04; H, 4.77; N, 5.53; Zr, 21.17.

Bis(η^5 -cyclopentadienyl)chloro(2,6-dimethylphenoxy)zirconium(IV), $\text{Cp}_2\text{Zr}(\text{OXyl})\text{Cl}$. This compound was prepared in 99% yield from $[\text{Cp}_2\text{Zr}(\text{H})\text{Cl}]_x$ and 2,6-dimethylphenol (method B above). The product was a white solid, mp 111–113 °C. $^1\text{H NMR}$ (CDCl_3): δ 2.15 (s, 6 H, CH_3), 6.34 (s, 10 H, C_5H_5), 6.6–7.0 (m, 3 H, Xyl ring H's). IR (Nujol mull) (cm^{-1}): $\nu(\text{Zr}-\text{O})$, 546 m; $\nu(\text{Zr}-\text{Cl})$, 341 s; other bands, 1589 w, 1466 vs, 1420 m, 1377 m, 1277 s, 1231 s, 1090 m, 1015 m, 891 m, 880 m, 800 s, 766 s, 731 w, 719 m, 565 w, 459 w, 432 w, 419 m, 399 m. Anal. Calcd for $\text{C}_{18}\text{H}_{19}\text{ClOZr}$: C, 57.19; H, 5.07; Zr, 24.13. Found: C, 54.77; H, 5.06; Zr, 24.65.

Bis(η^5 -cyclopentadienyl)(*N,N*-dimethyldithiocarbamato)(2,6-dimethylphenoxy)zirconium(IV), $\text{Cp}_2\text{Zr}(\text{OXyl})(\text{Me}_2\text{dtc})$. This compound was prepared by reaction of $\text{Na}(\text{Me}_2\text{dtc})$ (1.63 g, 11.4 mmol) and $\text{Cp}_2\text{Zr}(\text{OXyl})\text{Cl}$ (4.29 g, 11.4 mmol) in benzene (75 mL). The procedure employed for synthesis of $\text{Cp}_2\text{Zr}(\text{OPh})(\text{Me}_2\text{dtc})$ afforded light amber crystals of $\text{Cp}_2\text{Zr}(\text{OXyl})(\text{Me}_2\text{dtc})$ (4.75 g, 91%); mp 207–209 °C (softens at 170 °C). $^1\text{H NMR}$ (CDCl_3): δ 2.31 (s, 6 H, Xyl ring H's), 3.43 (s, 6 H, NCH_3), 6.19 (s, 10 H, C_5H_5), 6.55–7.0 (m, 3 H, Xyl ring H's); no resonances of $\text{CpZr}(\text{Me}_2\text{dtc})_3$ were observed. IR (Nujol mull) (cm^{-1}): $\nu(\text{C}=\text{N})$, 1510 m br; $\nu(\text{C}=\text{S})$, 999 m; $\nu(\text{Zr}-\text{O})$, 532 m; $\nu(\text{Zr}-\text{S})$, 359 m, 320 s br; other bands, 1587 w, 1472 s, 1452 s, 1420 w, 1387 s, 1275 s, 1252 m, 1236 s, 1140 m br, 1096 m, 1015 s, 864 m, 802 vs, 764 s, 741 m, 706 m, 583 w, 563 vw, 447 m, 430 w, 336 s, 231 w, 189 m, 133 m. Anal. Calcd for $\text{C}_{21}\text{H}_{25}\text{NOS}_2\text{Zr}$: C, 54.50; H, 5.45; N, 3.03. Found: C, 54.25; H, 5.46; N, 2.90.

Bis(η^5 -cyclopentadienyl)(*N,N*-dimethyldithiocarbamato)(4-hydroxypyridinato)zirconium(IV), $\text{Cp}_2\text{Zr}(\text{Opy})(\text{Me}_2\text{dtc})$. $\text{Na}(\text{Me}_2\text{dtc})$ (1.27 g, 9.99 mmol) was added to a solution of $\text{Cp}_2\text{Zr}(\text{Opy})\text{Cl}$ (3.50 g, 9.97 mmol) in benzene (150 mL), and the mixture was stirred for 16 h. Sodium chloride was removed by filtration, and the light yellow filtrate was concentrated to 50 mL. Addition of hexane precipitated a brown tar. The tar failed to crystallize from benzene–hexane, though it did solidify on standing. $^1\text{H NMR}$ (CDCl_3): δ 3.02 (s, 3 H, CH_3), 3.14 (s, 3 H, CH_3), 6.15 (s, 10 H, C_5H_5), 6.47 (dd, 2 H, Opy), 8.23 (dd, 2 H, Opy). IR (Nujol mull) (cm^{-1}): $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$, 1557 s br; $\nu(\text{Zr}-\text{O}(\text{mtc}))$, 554 m; $\nu(\text{Zr}-\text{Opy})$, 540 m; $\nu(\text{Zr}-\text{S})$, 324 s br; other bands, 1632 w, 1587 vs, 1503 vs, 1487 s, 1439 w, 1418 m, 1402 m, 1373 m, 1329 vs, 1252 w, 1207 m, 1136 m, 1013 m, 988 m, 880 m, 833 m, 808 vs, 801 vs, 735 m, 708 m, 592 m, 478 w, 432 w, 403 w, 230 m. Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_5\text{S}_2\text{Zr}$: C, 51.52; H, 4.80; N, 6.68; Zr, 21.74. Found: C, 51.55; H, 4.74; N, 6.17; Zr, 21.62.

Physical Measurements. Infrared spectra were recorded in the 4000–100- cm^{-1} region with an IBM IR/98-2A Fourier transform spectrometer or in the 4000–400- cm^{-1} region with a Perkin-Elmer 337 grating spectrophotometer. Proton chemical shifts were measured at ~37 °C with either a Varian CFT-20 80-MHz Fourier transform spectrometer, locked on the deuterium resonance of the solvent, or a Varian EM-390 90-MHz spectrometer, locked on tetramethylsilane.

Variable-temperature $^1\text{H NMR}$ spectra of sealed samples were obtained with a Bruker WM-300 300-MHz Fourier transform spectrometer, locked on the deuterium resonance of the solvent. Probe temperatures were determined with use of a copper–constantan thermocouple

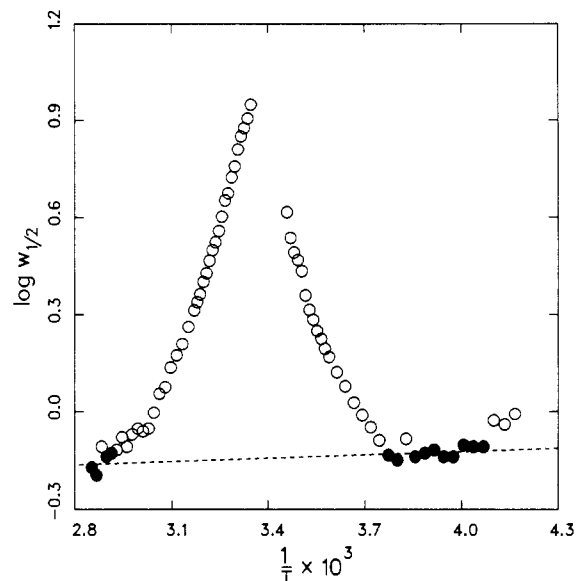


Figure 2. $\log w_{1/2}$ vs $1/T$ for the *N*-methyl resonances of $\text{Cp}_2\text{ZrCl}(\text{Me}_2\text{dtc})$, ~0.0006 M in $\text{C}_6\text{D}_5\text{CD}_3$. The least-squares straight line fit to the filled circles, shows the line width at half-maximum amplitude in the absence of exchange.

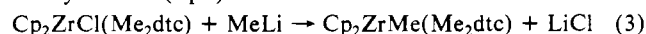
immersed in acetone or toluene and are estimated to be accurate to ± 0.5 °C. The concentration, solvent, and temperature range studied for each compound were as follows: $\text{Cp}_2\text{ZrCl}(\text{Me}_2\text{dtc})$, ~0.0006 M (solubility limited), $\text{C}_6\text{D}_5\text{CD}_3$, -33.1 to +77.3 °C; $\text{Cp}_2\text{ZrBr}(\text{Me}_2\text{dtc})$, 0.1 M, CD_2Cl_2 , 8.1–81.4 °C; $\text{Cp}_2\text{ZrI}(\text{Me}_2\text{dtc})$, ~0.002 M (solubility limited), $\text{C}_6\text{D}_5\text{CD}_3$, -14.2 to +79.3 °C; $\text{Cp}_2\text{Zr}(\text{CH}_2\text{Ph})(\text{Me}_2\text{dtc})$, 0.016 M, $\text{C}_6\text{D}_5\text{CD}_3$, -33.0 to +48.7 °C; $\text{Cp}_2\text{ZrMe}(\text{Me}_2\text{dtc})$, 0.1 M, CD_2Cl_2 , -92.4 to +28.2 °C; $\text{Cp}_2\text{Zr}(\text{CH}_2\text{SiMe}_3)(\text{Me}_2\text{dtc})$, 0.015 M, CD_2Cl_2 , -89.7 to +25.9 °C; $\text{Cp}_2\text{Zr}(\text{OPh})(\text{Me}_2\text{dtc})$, 0.011 M, CD_2Cl_2 , -94.4 to -3.2 °C; $\text{Cp}_2\text{Zr}(\text{Opy})(\text{Me}_2\text{dtc})$, 0.015 M, CD_2Cl_2 , -93.5 to +25.4 °C; $\text{Cp}_2\text{ZrCl}(\text{Me}_2\text{dtc})$, 0.016 M, $\text{C}_6\text{D}_5\text{CD}_3$, 25.4–116.9 °C; $\text{Cp}_2\text{Zr}(\text{Opy})(\text{Me}_2\text{dtc})$, 0.011 M, $\text{C}_6\text{D}_5\text{CD}_3$, 25.3–109.7 °C.

Rate constants for exchange of *N*-methyl groups were determined by quantitative comparison of experimental spectra with theoretical spectra¹⁹ iteratively calculated with use of a locally modified, interactive version of Saunders' NMR line-shape program.²⁰ To determine an average value of the rate constant at each temperature, observed and calculated spectra were compared with respect to line widths at three-fourths ($w_{3/4}$), half ($w_{1/2}$), and one-fourth ($w_{1/4}$) maximum amplitude, the frequency separation ($\delta\nu$) between the resonances, and the ratio of the maximum amplitude to the amplitude at the central minimum. Values of $w_{1/2}$ in the absence of exchange, $(w_{1/2})_0$, were determined by plotting $\log w_{1/2}$ vs $1/T$, and then linearly extrapolating these plots from the slow- or fast-exchange region into the coalescence region or, when possible, interpolating between the slow- and fast-exchange regions. Similarly, chemical shifts ($\delta\nu_0$) in the coalescence region were obtained by extrapolating linear plots of $\delta\nu$ vs $1/T$ from the slow-exchange region into the coalescence region. Sample $\log w_{1/2}$ vs. $1/T$ and $\delta\nu$ vs $1/T$ plots are shown in Figures 2 and 3. The values of $(w_{1/2})_0$ and $\delta\nu_0$ used in calculating theoretical line shapes are given in the footnotes to Table II.

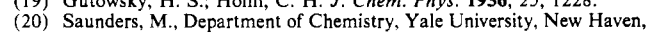
Results

Synthesis and Characterization of $\text{Cp}_2\text{ZrX}(\text{Me}_2\text{dtc})$ Complexes.

Halo- and alkylzirconocene *N,N*-dimethyldithiocarbamate complexes, $\text{Cp}_2\text{ZrX}(\text{Me}_2\text{dtc})$ ($\text{X} = \text{Br}, \text{I}$) and $\text{Cp}_2\text{ZrR}(\text{Me}_2\text{dtc})$ ($\text{R} = \text{CH}_2\text{SiMe}_3, \text{CH}_2\text{CMe}_2\text{Ph}, \text{CH}_2\text{Ph}$), have been synthesized in good yield by reaction of anhydrous $\text{Na}(\text{Me}_2\text{dtc})$ with the appropriate Cp_2ZrX_2 or $\text{Cp}_2\text{Zr}(\text{R})\text{Cl}$ complex in dichloromethane (eq 1 and 2). The methyl derivative was obtained by reaction



in benzene of the chloro complex with a diethyl ether solution of methyllithium (eq 3).



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(20) Saunders, M., Department of Chemistry, Yale University, New Haven, CT.

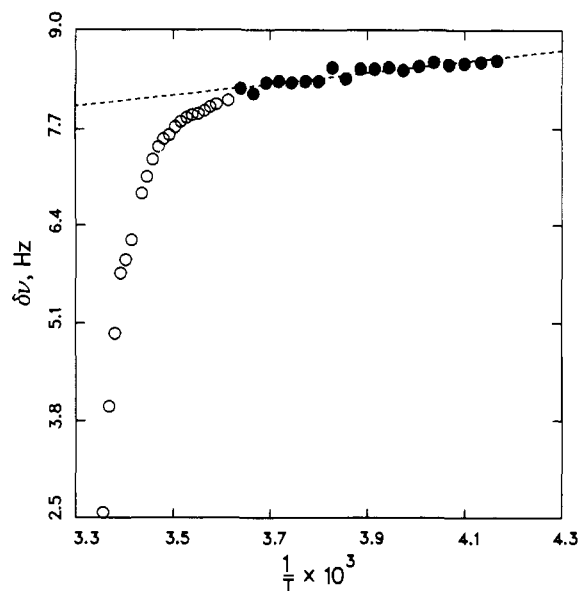
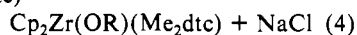


Figure 3. Frequency separation, $\delta\nu$, vs $1/T$ for the *N*-methyl resonances of Cp₂ZrCl(Me₂dtc), ~ 0.0006 M in C₆D₅CD₃. The least-squares straight line, fit to the filled circles, shows the temperature dependence of $\delta\nu$ in the absence of exchange.

Table I. Characteristic Infrared Bands of Cp₂ZrX(Me₂dtc) Complexes (cm⁻¹)

X	$\nu(\text{C}\rightarrow\text{N})$	$\nu(\text{C}\rightarrow\text{S})$	$\nu(\text{Zr}\text{--}\text{S})$	$\nu(\text{Zr}\text{--}\text{X})$
Cl	1525	997	364, 340	340
Br	1520	994	363, 338	
I	1524	991	365, 341	187
Me	1517	998	359, 334	432
CH ₂ SiMe ₃	1501	1001	353, 333	416
CH ₂ CMe ₂ Ph	1514	1000	353, 328	
CH ₂ Ph	1518	989	357, 330	399
OPh	1520	993	359, 320	513
Opy	1520	988	359, 330	540
OXyl	1510	999	359, 320	532

Attempted preparation of the alkoxy complexes Cp₂Zr(OR)(Me₂dtc) (OR = OMe, OCHMe₂) by reaction of the appropriate Cp₂Zr(OR)Cl with 1 equiv of Na(Me₂dtc) was unsuccessful. Alkoxide ligands appear to labilize one of the Cp ligands, and the isolated product was the stable, seven-coordinate CpZr(Me₂dtc)₃.¹⁸ However, the same synthetic method (eq 4) Cp₂Zr(OR)Cl + Na(Me₂dtc) →



did give the corresponding (aryloxy)zirconocenium dithiocarbamates, Cp₂Zr(OR)(Me₂dtc), where OR is phenoxide (OPh), 4-hydroxypyridinate (Opy), or xyloxy (OXyl). Cp₂Zr(OPh)(Me₂dtc) and Cp₂Zr(Opy)(Me₂dtc) are unstable in solution and decompose to give CpZr(Me₂dtc)₃, but the rate of decomposition is slow and does not preclude NMR line-shape studies. Interestingly, Cp₂Zr(OXyl)(Me₂dtc), which contains the more bulky 2,6-dimethylphenoxide ligand, showed no decomposition. Additional attempts to prepare the alkoxy complexes Cp₂Zr(OR)(Me₂dtc) (OR = OMe, OCHMe₂) by reaction of Cp₂ZrCl(Me₂dtc) with (i) the alcohol and pyridine or (ii) LiOR or NaOR, were also unsuccessful.

The Cp₂ZrX(Me₂dtc) (X = halide, alkyl, aryloxy) complexes were characterized by elemental analyses and by ¹H NMR and IR spectra. The infrared spectra exhibit a $\nu(\text{C}\rightarrow\text{N})$ band at 1500–1525 cm⁻¹ (Table I) and a single $\nu(\text{C}\rightarrow\text{S})$ band near 1000 cm⁻¹, characteristic of bidentate dithiocarbamate ligands.^{21,22} A relatively strong band near 360 cm⁻¹ is reasonably assigned^{18,23,24}

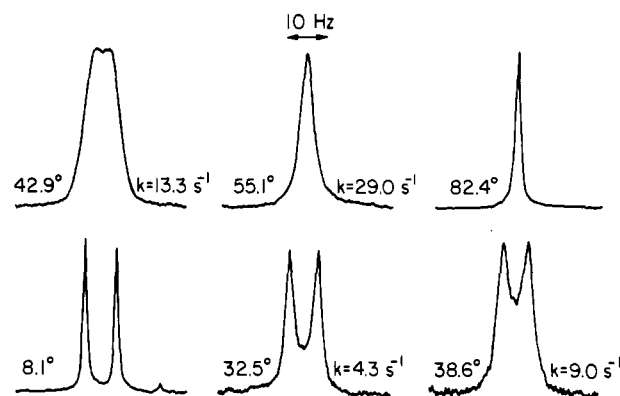
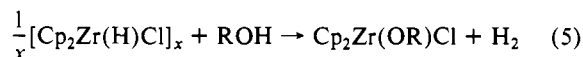


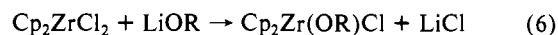
Figure 4. Methyl proton resonances of Cp₂ZrBr(Me₂dtc), 0.1 M in CD₂Cl₂ at 300 MHz.

to a $\nu(\text{Zr}\text{--}\text{S})$ mode, and a second strong band at 320–340 cm⁻¹ is tentatively assigned to the second $\nu(\text{Zr}\text{--}\text{S})$ mode; the related thiocarbamate complex Cp₂Zr(Opy)(Me₂mtc), exhibits only one $\nu(\text{Zr}\text{--}\text{S})$ band (at 324 cm⁻¹) and a $\nu(\text{Zr}\text{--}\text{O}(\text{mtc}))$ band (at 554 cm⁻¹). For most of the complexes, a unique, low-frequency band could be assigned to the $\nu(\text{Zr}\text{--}\text{X})$ (X = halide, alkyl, aryloxy) mode (see Table I).

Synthesis of Cp₂Zr(X)Cl Intermediates. The alkoxy- and (aryloxy)zirconocene chloride intermediates were prepared in excellent yields (85–99%) by reaction of [Cp₂Zr(H)Cl]_x with the appropriate alcohol in benzene (eq 5). This method capitalizes



on the hydridic nature of zirconocene hydrides²⁵ and produces hydrogen gas as the only byproduct, thus simplifying workup. A less satisfactory method for preparation of the alkoxy complexes, Cp₂Zr(OR)Cl (OR = OMe or OCHMe₂), is the reaction of Cp₂ZrCl₂ with 1 equiv of the lithium alkoxide (eq 6); this reaction



gives some of the disubstituted products, Cp₂Zr(OR)₂ (removed by extraction with hexane), resulting in lower yields (63–78%) of the desired monosubstituted compounds. Both preparative methods (eq 5 and 6) give better yields of Cp₂Zr(OR)Cl than those reported for treatment of Cp₂ZrCl₂ with the appropriate alcohol and triethylamine.¹⁷

The Cp₂Zr(R)Cl (R = CH₂SiMe₃, CH₂Ph, CH₂CMe₂Ph) complexes were prepared in good yield by reaction of a diethyl ether solution of the appropriate Grignard reagent with Cp₂ZrCl₂.¹⁴ Efforts to synthesize the butyl derivatives, Cp₂Zr(R)Cl (R = *n*-Bu, *sec*-Bu, *t*-Bu), by reaction of Cp₂ZrCl₂ with the corresponding butyllithium in tetrahydrofuran at –78 °C failed because of facile β -hydrogen elimination.²⁶

¹H NMR Studies of *N*-Methyl Group Exchange in Cp₂ZrX(Me₂dtc) and Cp₂ZrX(Me₂mtc) Complexes. In the slow-exchange limit, ¹H NMR spectra of the Cp₂ZrX(Me₂dtc) and Cp₂ZrX(Me₂mtc) complexes exhibit two equally intense *N*-methyl resonances, which coalesce to a single time-averaged resonance at higher temperatures. Representative spectra for Cp₂ZrBr(Me₂dtc) are presented in Figure 4. Rate constants for exchange of *N*-methyl groups were determined by total line-shape analysis as described in the Experimental Section. For Cp₂ZrX(Me₂dtc) (X = Cl, Br, I, CH₂Ph, OPh) and Cp₂ZrCl(Me₂mtc), frequency separations in the absence of exchange are large enough to allow accurate determination of rate constants over a considerable range of temperatures (Table II).

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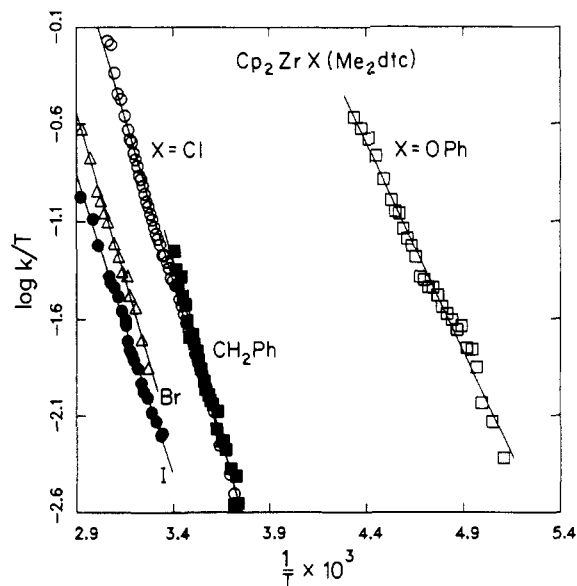


Figure 5. Eyring plot for *N*-methyl group exchange in $\text{Cp}_2\text{ZrX}(\text{Me}_2\text{dtc})$ complexes: X = Cl (open circles); Br (open triangles); I (filled circles); CH_2Ph (filled squares); OPh (open squares).

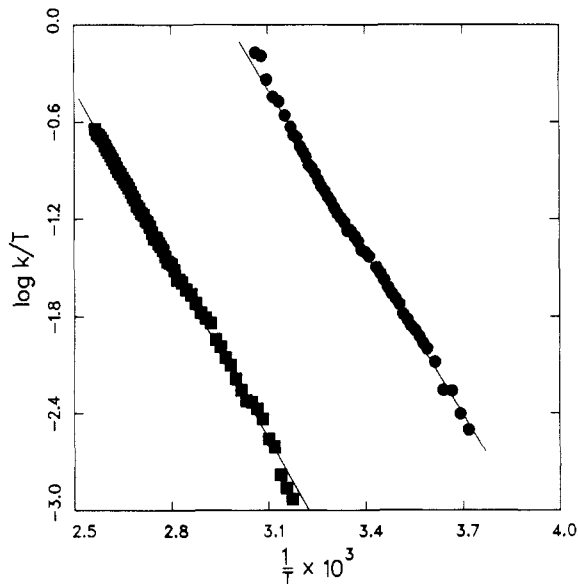


Figure 6. Eyring plot for *N*-methyl group exchange in $\text{Cp}_2\text{ZrCl}(\text{Me}_2\text{mtc})$ (filled squares) and $\text{Cp}_2\text{ZrCl}(\text{Me}_2\text{dtc})$ (filled circles).

Activation parameters, obtained from the least-squares straight lines of the $\log(k/T)$ vs $1/T$ plots in Figures 5 and 6, are presented in Table III. Also included in Table III are kinetic data for related organic dithiocarbamates and thiocarbamates, the methyl esters $\text{MeSC}(\text{S})\text{NMe}_2$ and $\text{MeOC}(\text{S})\text{NMe}_2$, and thiuram disulfide, $[\text{SC}(\text{S})\text{NMe}_2]_2$.^{7-10,27}

Two solvents (dichloromethane- d_2 and toluene- d_8) were used in our studies because the complexes exhibit a wide range of coalescence temperatures (Table III). Solvent effects appear to be unimportant; the rates of methyl group exchange for $\text{Cp}_2\text{ZrCl}(\text{Me}_2\text{dtc})$ in CD_2Cl_2 and $\text{C}_6\text{D}_5\text{CD}_3$ are the same within a factor of 2, and activation parameters are identical within experimental error.

Activation parameters could not be determined for $\text{Cp}_2\text{ZrX}(\text{Me}_2\text{dtc})$ (X = Me, CH_2SiMe_3 , $\text{CH}_2\text{CMe}_2\text{Ph}$, Opy) because frequency separations in the slow-exchange limit are too small (<2.5 Hz at 300 MHz) to allow accurate determination of the temperature dependence of the rate constants. Nevertheless, line-shape analysis for X = Me or Opy did give reliable estimates

Table II. Rate Constants for *N*-Methyl Group Exchange in $\text{Cp}_2\text{ZrX}(\text{Me}_2\text{dtc})$ and $\text{Cp}_2\text{ZrCl}(\text{Me}_2\text{mtc})$ Complexes

temp, °C	k , s ⁻¹	temp, °C	k , s ⁻¹	temp, °C	k , s ⁻¹	temp, °C	k , s ⁻¹
$\text{Cp}_2\text{ZrCl}(\text{Me}_2\text{dtc})^a$							
53.4	220	35.9	40.3	23.7	14.7	11.2	4.7
51.5	209	34.9	37.2	22.7	13.6	10.2	4.3
49.7	148	34.0	33.8	21.8	12.0	9.3	3.9
47.8	115	33.1	30.7	20.8	11.6	8.3	3.7
46.0	107	32.2	28.9	19.8	10.9	7.3	3.4
44.1	87.3	31.2	26.4	17.9	9.3	6.4	3.0
42.3	73.6	30.3	24.6	17.0	8.6	5.4	2.8
41.4	65.4	29.4	22.5	16.0	7.7	3.5	2.3
40.5	63.2	28.5	20.7	15.0	6.9	1.6	1.5
39.5	55.4	27.6	19.5	14.1	6.3	-0.4	1.5
38.6	51.3	26.6	18.2	13.1	5.9	-2.3	1.1
37.7	47.3	25.7	16.0	12.1	5.4	-4.2	0.8
36.8	42.2	24.8	16.0				
$\text{Cp}_2\text{ZrBr}(\text{Me}_2\text{dtc})^b$							
68.4	80.6	55.1	29.0	45.6	14.1	38.6	9.0
63.4	56.6	53.2	25.9	42.9	13.3	35.6	6.1
59.2	38.1	49.8	19.9	41.7	10.5	32.5	4.3
57.2	33.8	47.7	17.0				
$\text{Cp}_2\text{ZrI}(\text{Me}_2\text{dtc})^c$							
69.0	36.4	47.8	10.6	42.8	6.1	34.7	3.3
61.7	27.4	45.9	8.9	41.7	5.5	32.7	3.0
58.8	20.0	45.8	8.8	40.7	5.2	30.7	2.5
52.7	13.6	43.9	7.9	39.7	4.8	28.6	2.2
51.8	12.6	43.8	7.5	37.7	4.3	26.6	1.9
49.8	11.8	43.7	7.4	35.7	3.6	25.9	1.9
$\text{Cp}_2\text{Zr}(\text{CH}_2\text{Ph})(\text{Me}_2\text{dtc})^d$							
20.2	16.5	13.7	5.8	6.9	3.0	0.1	1.6
19.5	13.2	12.4	6.0	5.6	2.8	-0.8	1.4
18.5	10.9	11.7	5.3	5.0	2.6	-2.8	1.1
17.3	12.1	10.4	4.9	4.0	2.5	-4.2	0.7
16.6	9.5	9.8	4.3	2.6	1.9	-4.7	1.0
15.3	8.6	8.8	3.9	2.1	2.3	-5.7	0.7
14.6	7.1	7.5	3.3	0.7	1.6		
$\text{Cp}_2\text{Zr}(\text{OPh})(\text{Me}_2\text{dtc})^e$							
-42.5	62.8	-54.4	19.1	-61.3	7.7	-68.7	4.7
-44.5	54.5	-55.4	15.8	-62.3	7.7	-69.8	3.6
-46.5	47.7	-56.4	14.1	-63.4	7.0	-70.9	3.5
-48.4	38.6	-57.4	12.8	-64.4	6.1	-71.9	2.8
-50.4	29.0	-58.3	11.2	-65.5	5.5	-73.0	1.8
-52.4	22.5	-59.3	8.8	-66.6	5.1	-75.1	1.5
-53.4	19.6	-60.3	8.5	-67.7	4.5	-77.3	0.9
$\text{Cp}_2\text{ZrCl}(\text{Me}_2\text{mtc})^f$							
116.9	88.7	102.5	38.9	88.1	15.6	67.4	3.9
116.0	82.3	101.6	36.8	87.2	14.7	65.6	3.5
115.1	80.8	100.7	34.7	86.3	13.4	63.8	3.0
114.2	77.7	99.8	32.3	85.4	12.4	62.0	2.6
113.3	74.5	98.9	30.9	84.5	12.1	60.2	2.2
112.4	69.0	98.0	28.3	83.6	11.9	58.4	1.8
111.5	65.1	97.1	27.2	82.7	10.9	56.6	1.6
110.6	62.2	96.2	25.3	81.8	9.5	54.8	1.5
109.7	59.3	95.3	24.8	80.9	9.5	53.0	1.4
108.8	56.1	94.4	22.9	80.0	9.1	51.2	1.2
107.9	53.2	93.5	22.2	78.2	8.2	49.3	0.9
107.0	49.9	92.6	20.8	76.4	7.6	47.5	0.8
106.1	47.0	91.7	19.0	74.6	6.7	45.6	0.5
105.2	45.4	90.8	17.5	72.8	5.8	43.8	0.4
104.3	42.9	89.9	17.6	71.0	5.3	42.0	0.4
103.4	40.6	89.0	16.3	69.2	4.9		

^a ~0.0006 M in $\text{C}_6\text{D}_5\text{CD}_3$; variation in the line width in the absence of exchange, $(w_{1/2})_0$, from low temperature (-4.2 °C) to high temperature (53.4 °C) is 0.74-0.70 Hz; variation in the frequency separation in the absence of exchange, $\delta\nu_0$, from -4.2 to +53.4 °C is 8.31-7.83 Hz. ^b 0.1 M in CD_2Cl_2 ; $(w_{1/2})_0 = 1.00$ Hz; $\delta\nu_0 = 7.39-6.73$ Hz. ^c ~0.002 M in $\text{C}_6\text{D}_5\text{CD}_3$; $(w_{1/2})_0 = 0.51-0.48$ Hz; $\delta\nu_0 = 5.99-5.71$ Hz. ^d 0.016 M in $\text{C}_6\text{D}_5\text{CD}_3$; $(w_{1/2})_0 = 0.97-0.64$ Hz; $\delta\nu_0 = 3.23-1.95$ Hz. ^e 0.011 M in CD_2Cl_2 ; $(w_{1/2})_0 = 1.74-0.91$ Hz; $\delta\nu_0 = 4.78-3.85$ Hz. ^f 0.016 M in $\text{C}_6\text{D}_5\text{CD}_3$; $(w_{1/2})_0 = 0.48-0.40$ Hz; $\delta\nu_0 = 43.67-39.63$ Hz.

of rate constants at the coalescence temperatures; $k = 1.2$ s⁻¹ at -12 °C for $\text{Cp}_2\text{ZrMe}(\text{Me}_2\text{dtc})$ and $k = 3.3$ s⁻¹ at -43 °C for

Table III. Kinetic Data for *N*-Methyl Group Exchange in Cp₂ZrX(Me₂dtc), Cp₂ZrX(Me₂mtc), and Related Compounds^a

compd	T _c , ^b °C	k(25 °C), s ⁻¹	ΔG [‡] (25 °C), kcal/mol	ΔH [‡] , kcal/mol	ΔS [‡] , eu
Cp ₂ ZrCl(Me ₂ dtc) ^c	16	8.6 ± 1.2	16.2 ± 0.1	15.9 ± 2.0	-1.0 ± 6.8
Cp ₂ ZrCl(Me ₂ dtc) ^d	25	16.8 ± 3.1	15.8 ± 0.1	15.3 ± 0.3	-1.5 ± 1.0
Cp ₂ ZrBr(Me ₂ dtc) ^c	43	2.5 ± 0.4	16.9 ± 0.1	15.5 ± 0.8	-4.8 ± 2.4
Cp ₂ ZrI(Me ₂ dtc) ^d	51	1.6 ± 0.2	17.2 ± 0.1	14.2 ± 0.6	-10.0 ± 1.8
Cp ₂ Zr(CH ₂ Ph)(Me ₂ dtc) ^d	10	22.3 ± 5.0	15.6 ± 0.1	16.9 ± 0.8	4.3 ± 2.9
Cp ₂ ZrMe(Me ₂ dtc) ^c	-12	1.2 (-12 °C)	15.1 (-12 °C)		
Cp ₂ Zr(Opy)(Me ₂ dtc) ^c	-43	3.3 (-43 °C)	12.8 (-43 °C)		
Cp ₂ Zr(OPh)(Me ₂ dtc) ^c	-62	(1.0 ± 0.3) × 10 ⁴	12.0 ± 0.2	9.8 ± 0.5	-7.3 ± 2.2
MeSC(S)NMe ₂ ^e	2	(107)	14.7 ± 0.2	(9.7 ± 0.6)	(-17 ± 2)
MeSC(S)NMe ₂ ^f		(104)	14.7	12.5 ± 0.6	-7.4 ± 2.3
[SC(S)NMe ₂] ₂ ^g		(39)	15.3 ± 0.1	15.0 ± 0.4	-0.9 ± 2.0
[SC(S)NMe ₂] ₂ ^h		(16)	15.8	17.8	7 ± 4
Cp ₂ ZrCl(Me ₂ mtc) ^d	117	0.10 ± 0.02	18.8 ± 0.1	16.4 ± 0.2	-8.1 ± 0.6
Cp ₂ Zr(Opy)(Me ₂ mtc) ^d	>110	<100 (100 °C)	>19.1 (110 °C)		
MeOC(S)NMe ₂ ⁱ	75	(1.8)	17.1	13.6 ± 0.5	-11.7 ± 1.4
MeOC(S)NMe ₂ ^j		(0.66)	17.7	(13.9 ± 0.3)	-13 ± 2

^aThe uncertainties in rate constants and activation parameters determined in this work are random errors estimated at the 95% confidence level. Values calculated from reported activation parameters are enclosed in parentheses. ^bCoalescence temperature. For Cp₂ZrX(Me₂dtc) (X = CH₂SiMe₃ or CH₂CMe₂Ph), T_c ≈ -30 °C. ^cIn CD₂Cl₂. ^dData for Cp₂ZrCl(Me₂dtc) are from ref 5. ^eIn C₆D₅CD₃. ^fIn *n*-C₆H₁₄. ^gIn *n*-C₆H₁₄. ^hIn CDCl₃. ⁱIn CD₂Cl₂. ^jIn cyclohexane. ^kIn CDCl₃.²⁷

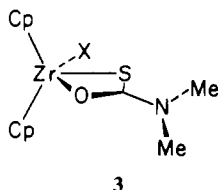
Cp₂Zr(Opy)(Me₂dtc). Rate constants were not determined for Cp₂ZrX(Me₂dtc) (X = CH₂SiMe₃ or CH₂CMe₂Ph), but coalescence temperatures of about -30 °C indicate that rate constants for these compounds are slightly higher than for the complexes where X = Me or CH₂Ph.

Kinetic Results for Cp₂ZrX(Me₂dtc) (X = Halide, Alkyl). Rate constants and activation parameters for *N*-methyl group exchange in the Cp₂ZrX(Me₂dtc) (X = halide, alkyl) complexes (Table III) are similar to corresponding values for the organic dithiocarbamates and are relatively independent of the nature of the halide or alkyl group. At -12 °C, the coalescence temperature for Cp₂ZrMe(Me₂dtc), rate constants (s⁻¹) for Cp₂ZrX(Me₂dtc) are as follows: 1.2 (X = Me); 0.34 (X = CH₂Ph); 0.40 (X = Cl); 0.052 (X = Br); 0.046 (X = I). The decrease in rate constants as the halide varies from Cl to Br to I is only a factor of 10, and the trend is determined by the activation entropies.

Kinetic Results for Cp₂ZrX(Me₂dtc) (X = Aryloxy). There is a dramatic increase in the rate of *N*-methyl group exchange, by a factor of 10³-10⁴, when X = Cl or CH₂Ph is replaced by a good π-donor ligand such as phenoxide. The corresponding decrease in ΔH[‡] is about 6-7 kcal/mol (Table III). When X is 4-hydroxypyridinate, a weaker π-donor than phenoxide, an intermediate rate of exchange is observed. At -43 °C, the coalescence temperature for Cp₂Zr(Opy)(Me₂dtc), rate constants (s⁻¹) are as follows: 0.007 (X = Cl); 3.3 (X = Opy); 61 (X = OPh).

For Cp₂Zr(OXyl)(Me₂dtc) in CD₂Cl₂ or CD₂Cl₂/C₆D₅CD₃ (1:1 v/v), a single *N*-methyl resonance was observed down to -94 °C, the limit of our measurements; ω_{1/2} = 2.5 Hz at -94 °C. Either the coalescence temperature is less than -94 °C, or the methyl resonances are accidentally degenerate. Since xyloxy should be a better π-donor than phenoxide, a coalescence temperature below that for Cp₂Zr(OPh)(Me₂dtc) (-62 °C) might be expected.

Kinetic Results for Cp₂ZrX(Me₂mtc) (X = Cl, Opy). ¹H NMR spectra (-90 to +109.7 °C) of the thiocarbamate complex Cp₂ZrCl(Me₂mtc) indicate the presence of only one isomer in solution, presumably isomer 3 having oxygen in the lateral co-



ordination site. This isomer was found in the crystal structure of Cp₂ZrCl(Me₂mtc),¹⁶ and extended Hückel calculations indicate that the isomer with reverse oxygen and sulfur site occupancies is of higher energy.²⁸

Comparison of kinetic results for Cp₂ZrCl(Me₂mtc) and Cp₂ZrCl(Me₂dtc) (Table III) indicates that the coalescence temperature is about 90 °C higher and the rate of methyl group exchange at 25 °C is about 100 times lower for Cp₂ZrCl(Me₂mtc) than for Cp₂ZrCl(Me₂dtc). The methyl esters behave similarly; MeOC(S)NMe₂ exhibits a higher coalescence temperature and a lower rate than MeSC(S)NMe₂.

Cp₂Zr(Opy)(Me₂mtc) displays a linear dependence of δν on 1/T from 25.3 °C (δν = 59 Hz) to 109.7 °C (δν = 46 Hz), the limit of our measurements. At 109.7 °C, there is little evidence of line broadening, indicating that the coalescence temperature, T_c, is higher than 109.7 °C. A rate constant of 100 s⁻¹ at the coalescence temperature was estimated from the relation k(T_c) = πδν₀/√2;¹⁹ this is an upper limit on the value of the rate constant at 109.7 °C. Thus, in contrast to the behavior of the dithiocarbamate complexes Cp₂ZrX(Me₂dtc) (X = Cl, Opy, OPh) (Table III), no dramatic decrease in coalescence temperature or increase in rate constant is observed on going from Cp₂ZrCl(Me₂mtc) (T_c = 117 °C; k = 59 s⁻¹ at 109.7 °C) to Cp₂Zr(Opy)(Me₂mtc) (T_c > 109.7 °C; k < 100 s⁻¹ at 109.7 °C).

Discussion

Mechanism of *N*-Methyl Group Exchange. The similarity of the rates and activation parameters for Cp₂ZrX(Me₂dtc) (X = halide or alkyl) and organic dithiocarbamates (Table III) suggests that exchange of *N*-methyl groups in the zirconocene complexes occurs by a mechanism involving rotation about the C- π N bond (mechanism b or c in Figure 1). Slightly lower rates for the Cp₂ZrX(Me₂dtc) complexes can be rationalized in terms of attachment of the dithiocarbamate ligand to an electropositive metal atom, which increases the double-bond character of the C- π N bond. The activation enthalpy is lower for the iodo complex than for the chloro and bromo analogues, consistent with the lower electronegativity and larger size of the iodide ligand, and ΔH[‡] is higher for the benzyl complex, consistent with a reduction in π-donating ability on going from a halide ligand to a CH₂Ph group. However, the differences in ΔH[‡] for the Cp₂ZrX(Me₂dtc) (X = halide or alkyl) complexes are small, and the nature of the halide or alkyl group appears to have relatively little effect on the barrier to rotation about the C- π N bond.

The parallel behavior of the chlorozirconocene complexes Cp₂ZrCl(Me₂mtc) and Cp₂ZrCl(Me₂dtc) and the corresponding methyl esters (higher T_c's and lower rates for the thiocarbamates, see Table III) further supports the notion that the mechanism of methyl group exchange in the chlorozirconocenium complexes

(28) Extended Hückel calculations indicate that the optimized stereoisomer having sulfur in the lateral coordination site is less stable by 6 kcal/mol than the optimized isomer having oxygen in the lateral site.

involves rotation about the C \rightarrow N bond.

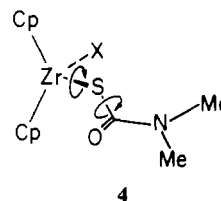
The dramatic increase in the exchange rates for the aryloxy dithiocarbamate complexes Cp₂Zr(OPh)(Me₂dtc) and Cp₂Zr(Opy)(Me₂dtc) is attributed to the π -donor properties of the aryloxy ligands; the rates increase as the π -donor character of the aryloxy increases in the order Opy < OPh. π -Donation from oxygen to the oxophilic Zr atom weakens the Zr-S bonds and lowers the barrier to N-methyl group exchange. If a C \rightarrow N rotation mechanism persists in the aryloxy complexes, C \rightarrow N rotation must be facilitated by preliminary rupture of a Zr-S bond (mechanism b in Figure 1) or by appreciable weakening of the zirconium-chelate interaction (mechanism c).

Alternatively, the anomalously high exchange rates for the aryloxy dithiocarbamate complexes may indicate that these complexes exchange methyl groups by a different mechanism, namely rupture of a Zr-S bond followed by rotation of the dangling ligand about the Zr-S and/or C-S bonds and subsequent reattachment of the uncoordinated S atom at the other sulfur coordination site (mechanism a in Figure 1). Zr-S bond rupture would be promoted by the π -donor properties of the aryloxy ligands, and a mechanism not involving rotation about the C \rightarrow N bond would help to explain how methyl group exchange in the aryloxy dithiocarbamates can be appreciably faster than that in organic dithiocarbamates.

Finally, we ask why the π -donor properties of aryloxy ligands greatly accelerate the rate of methyl group exchange in the dithiocarbamate complexes Cp₂ZrX(Me₂dtc) (X = OPh or Opy) but not in the analogous thiocarbamate Cp₂Zr(Opy)(Me₂mtc). If all of the complexes rearrange by mechanism b or c, we would attribute the lack of rate acceleration in Cp₂Zr(Opy)(Me₂mtc) to strong Zr-O bonding in the lateral coordination site. Since the Zr-O bond should be appreciably stronger than the corresponding Zr-S bond in the dithiocarbamates, the π -donating properties of aryloxy ligands may not be sufficient to break the Zr-O bond (mechanism b) or weaken the zirconium-chelate interaction (mechanism c).

Mechanism b or c, however, does not account for the fact that the rates of methyl group exchange in the aryloxy dithiocarbamate complexes are faster than those in organic dithiocarbamates. Therefore, we prefer a unique mechanism, mechanism a not involving rotation about the C \rightarrow N bond, for the aryloxy dithio-

carbamates. This mechanism, shown in 4, is not accessible for



aryloxy thiocarbamate complexes because rotation about the Zr-S and/or C-S bonds followed by reattachment of the uncoordinated O atom at the other coordination site, the interior site, would give the higher energy, unobserved stereoisomer that has sulfur in the lateral coordination site.²⁹ Consequently, even if the Zr-O bond does break in the monothiocarbamate complexes, methyl group exchange must involve rotation about the C \rightarrow N bond.

Conclusions. The Cp₂ZrX(Me₂dtc) (X = halide or alkyl) complexes and the Cp₂ZrX(Me₂mtc) (X = Cl or Opy) complexes have rates of N-methyl group exchange similar to those for related organic dithiocarbamates and thiocarbamates. A mechanism involving rotation about the C \rightarrow N bond is indicated, mechanism b or c in Figure 1. The aryloxy dithiocarbamate complexes, Cp₂ZrX(Me₂dtc) (X = OPh or Opy), have much higher rates of methyl group exchange, which suggests a different mechanism for these complexes, mechanism a in Figure 1 involving rupture of a Zr-S bond. This mechanism, which is promoted by the π -donor properties of the aryloxy ligands, is inaccessible in aryloxy thiocarbamate complexes because it would give a higher energy, unobserved stereoisomer.

Acknowledgment. Support for the Cornell Nuclear Magnetic Resonance Facility from the National Science Foundation Instrumentation Program (Grants CHE-79-04825 and PCM-80-18643) and the National Institutes of Health (Grant DHHS 08S0RR02002A) is gratefully acknowledged. The FT-IR spectrometer was obtained with support from the National Science Foundation (Grant CHE-83-04659).

(29) Rupture of the Zr-S bond followed by rotation of the dangling ligand and reattachment of the uncoordinated S atom at the other (lateral) coordination site would also give the unobserved stereoisomer.

Contribution from the Department of Chemistry,
University of Georgia, Athens, Georgia 30602

Metal Cluster Topology. 10. Polyhedral Gallium Cluster Anions in Intermetallic Phases of Gallium and Alkali Metals¹

R. B. King

Received February 16, 1989

Graph-theory-derived methods are used to study the chemical bonding topology in gallium-rich intermetallic phases of gallium and the alkali metals that contain globally delocalized Ga_n deltahedra (n = 8, 11, 12). Electron-precise chemical bonding models are presented for the following phases, assuming complete ionization of the alkali metals: (1) MGa₃ = M₃(Ga₈)(Ga) (M = K, Rb) containing Ga₈ bisdiphenoids ("D_{2d} dodecahedra"); (2) MGa₇ = M₂(Ga₁₂)(Ga₂) (M = Rb, Cs) containing Ga₁₂ icosahedra; (3) K₃Ga₁₃ = K₆(Ga₁₁)(Ga₁₂)(Ga)₃ containing both Ga₁₁ and Ga₁₂ deltahedra; (4) Na₂₂Ga₃₉ = Na₂₂(Ga₁₂)₂(Ga₁₅) containing two different types of Ga₁₂ icosahedra with novel Ga₁₅ polyhedra in the interstices. The Ga₁₅ polyhedra in Na₂₂Ga₃₉ have all but 1 degree 3 vertices indicative of edge-localized bonding as well as a pair of 3-coordinate gallium atoms connected by an abnormally short edge (2.43 Å) suggestive of a Ga=Ga double bond. Application of the same method to lithium/gallium phases such as Li₃Ga₁₄ indicates the presence of fewer electrons than the predicted closed-shell electronic configuration in accord with the tendency of lithium atoms to form partially covalent multicenter bonds.

Introduction

The importance and stability of the deltahedral borane anions B_nH_n²⁻ (6 ≤ n ≤ 12)^{2,3} in boron hydride chemistry raises the

question as to whether analogous species might be observed in the chemistry of the heavier congeners of boron, namely aluminum, gallium, indium, and thallium. However, so far no deltahedral metal hydride anions M_nH_n²⁻ (M = Al, Ga, In, Tl) have been

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