Inorg. Chem. **1984**, *23*, 1079–1089 **1079**

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

Nuclear Magnetic Resonance Studies of Stereochemical Rearrangements in Pentagonal-Bipyramidal (η^5-Cyclopentadienyl)tris(*N*,*N*-dimethyldithiocarbamato)titanium(IV), -zirconium(IV), and -hafnium(IV)

ROBERT C. FAY,* JOHN R. WEIR, and ALAN H. BRUDER

Received September 22, 1983

(η^5-Cyclopentadienyl)tris(*N*,*N*-dimethyldithiocarbamato)titanium(IV), -zirconium(IV), and -hafnium(IV), CpM(Me$_2$dtc)$_3$ (M = Ti, Zr, Hf), are of interest as examples of seven-coordinate pentagonal-bipyramidal (PB) complexes in which metal-centered rearrangement is slow on the NMR time scale at room temperature. Variable-temperature ^{1}H NMR studies exhibit evidence of three kinetic processes: (i) exchange of dithiocarbamate methyl groups within the equatorial ligands (process Ie); (ii) exchange of methyl groups within the unique ligand (process Iu); (iii) exchange of the equatorial and unique ligands (process II). Rates and activation parameters have been determined by total line-shape analysis. Process Ie in CpTi(Me$_2$dtc)$_3$ (ΔG^*(70 °C) $\simeq$ 14 kcal/mol) is $\sim 10^2$–10^3 times faster than process Iu and $\sim 10^3$ times faster than process Ie in CpM(Me$_2$dtc)$_3$ (M = Zr, Hf) (ΔG^*(70 °C) $\simeq$ 19 kcal/mol). Rates of processes Ie and Iu in CpM(Me$_2$dtc)$_3$ (M = Zr, Hf) are the same within a factor of 2. The barrier ΔG^*(70 °C) for process II in CpTi(Me$_2$dtc)$_3$ is 18–19 kcal/mol. Values of ΔS^* are near zero, and the rates and activation parameters are relatively independent of the nature and polarity of the solvent. Processes Ie and Iu are believed to involve rotation about the C$\overset{\cdots}{-}$N bond in the dithiocarbamate ligands, perhaps preceded by rupture of an equatorial metal–sulfur bond. The faster rate of process Ie in CpTi(Me$_2$dtc)$_3$ appears to be related to the unusually long Ti–S bonds to the equatorial ligands in this compound. A double-facial twist mechanism involving a capped-trigonal-prismatic transition state of C_s symmetry is proposed for process II. The barrier to this polytopal rearrangement is discussed in terms of steric and electronic effects. Also included in this paper are characterization data for the CpM(Me$_2$dtc)$_3$ complexes and a permutational analysis for rearrangements of PB complexes of the type M(AA)$_3$X.

Introduction

Stereochemical nonrigidity is a ubiquitous feature of the chemistry of seven-coordinate complexes because the three common seven-coordinate polytopes, the pentagonal bipyramid (PB), capped octahedron (CO), and capped trigonal prism (CTP), are easily interconverted by relatively small atomic displacements.[1-4] Consequently, the recently reported (η^5-cyclopentadienyl)tris(*N*,*N*-disubstituted dithiocarbamato)metal complexes, CpM(R$_2$dtc)$_3$ and (MeCp)M(R$_2$dtc)$_3$ (M = Ti, Zr, Hf; Cp = η^5-C$_5$H$_5$; MeCp = η^5-CH$_3$C$_5$H$_4$),[5-14] are of considerable interest since metal-centered rearrangement in these compounds is slow on the NMR time scale at room temperature. In contrast, Ti(Me$_2$dtc)$_3$Cl is stereochemically nonrigid at −90 °C.[15]

We have previously reported the X-ray crystal structures and certain qualitative features of the ^{1}H NMR spectra of CpTi(Me$_2$dtc)$_3$[6] and CpZr(Me$_2$dtc)$_3$.[5] These compounds have PB structures in which the cyclopentadienyl ligand occupies an axial position. In this paper, we present a full account of our ^{1}H NMR line-shape studies of dithiocarbamate methyl group exchange in CpM(Me$_2$dtc)$_3$ (M = Ti, Zr, Hf). The NMR spectra exhibit evidence of three kinetic processes: (i) exchange of methyl groups within the equatorial ligands; (ii) exchange of methyl groups within the unique ligand; (iii) exchange of the equatorial and unique ligands. The kinetics and mechanisms of these processes are discussed in terms of structure and bonding.

Experimental Section

Preparation of Compounds. Anhydrous sodium *N*,*N*-dimethyldithiocarbamate, Na(Me$_2$dtc), was prepared as previously described.[15] *N*,*N*,*N'*,*N'*-Tetramethylthiuran disulfide was synthesized by oxidation of Na(Me$_2$dtc) with aqueous K$_3$[Fe(CN)$_6$][16] and was dried by heating in vacuo (80 °C (0.01 torr)) for 48 h; mp 154–157 °C (lit.[16] mp 151 °C). Bis(η^5-cyclopentadienyl)dichlorohafnium(IV), Cp$_2$HfCl$_2$, was prepared by reaction of hafnium(IV) chloride and thallium(I) cyclopentadienide in refluxing tetrahydrofuran;[17] mp 229–232 °C dec (lit.[17] mp 230 °C dec). Solvents were dried by refluxing for at least 24 h over calcium hydride (dichloromethane and hexane) or lithium aluminum hydride (tetrahydrofuran) and were distilled immediately prior to use. The CpM(Me$_2$dtc)$_3$ (M = Ti, Zr, Hf) complexes were prepared and subsequently handled under an atmosphere of dry dinitrogen or argon.

(η^5-Cyclopentadienyl)tris(*N*,*N*-dimethyldithiocarbamato)titanium(IV)–Dichloromethane, CpTi(Me$_2$dtc)$_3$·CH$_2$Cl$_2$. Under an argon atmosphere, Na(Me$_2$dtc) (3.24 g, 22.6 mmol) and *N*,*N*,*N'*,*N'*-tetramethylthiuram disulfide (1.35 g, 5.61 mmol) were added to a solution of Cp$_2$TiCl$_2$ (2.49 g, 10.0 mmol) in dry, degassed tetrahydrofuran (80 mL). The resulting dark red slurry was stirred at room temperature for 16 h. The color changed to dark green (after 15 min) and then to golden yellow. After 16 h, the reaction mixture consisted of a pale yellow solution and a golden yellow precipitate. The tetrahydrofuran was pumped off, and the residue was extracted with dichloromethane (80 mL). The extract was filtered, and to the dark brown filtrate was added hexane ($\sim$160 mL). On standing at room temperature, the solution deposited golden yellow crystals of CpTi(Me$_2$dtc)$_3$·CH$_2$Cl$_2$, yield 3.32 g (60%). Concentration of the solution to approxiately half its original volume and addition of more hexane (80 mL) afforded a second crop of crystals, 0.71 g (13%). Upon heating, the complex changes color from yellow to red-orange approximately 100 °C before melting with decomposition at 215–220

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°C. Anal. Calcd for $(C_5H_5)Ti(C_3H_6NS_2)_3 \cdot CH_2Cl_2$: C, 32.26; H, 4.51; Cl, 12.69; N, 7.52; Ti, 8.58. Found: C, 32.29; H, 4.62; Cl, 12.48; N, 7.28; Ti, 8.23. ^1H NMR (4.0 g/100 mL $CDCl_3$, 37 °C): δ 3.18 (br, 3 H, CH_3), 3.28 (15 H, CH_3), 5.30 (2 H, CH_2Cl_2), 6.02 (5 H, C_5H_5).

(η^5-Cyclopentadienyl)tris(*N*,*N*-dimethyldithiocarbamato)zirconium(IV)–Dichloromethane, $CpZr(Me_2dtc)_3 \cdot CH_2Cl_2$. This compound was prepared, as described earlier,[5] by reaction of Cp_2ZrCl_2 (1.86 g, 6.36 mmol) and $Na(Me_2dtc)$ (2.94 g, 20.5 mmol) in refluxing dichloromethane (100 mL). However, the prolonged reflux times (42 h) used previously[5] were shortened to 18 h. The crude product was contaminated with a brown impurity. Repeated recrystallization (3 times) from dichloromethane–hexane afforded colorless crystals of $CpZr(Me_2dtc)_3 \cdot CH_2Cl_2$. ^1H NMR (5.8 g/100 mL $CDCl_3$, 37 °C): δ 3.29 (3 H, CH_3), 3.30 (6 H, CH_3), 3.35 (3 H, CH_3), 3.36 (6 H, CH_3), 5.30 (2 H, CH_2Cl_2), 6.13 (5 H, C_5H_5).

(η^5-Cyclopentadienyl)tris(*N*,*N*-dimethyldithiocarbamato)hafnium(IV)–Dichloromethane, $CpHf(Me_2dtc)_3 \cdot CH_2Cl_2$. This compound was prepared by reaction for 18 h of Cp_2HfCl_2 (0.742 g, 1.95 mmol) and $Na(Me_2dtc)$ (1.20 g, 8.38 mmol) in refluxing dichloromethane (50 mL). The reaction mixture was filtered, and the dark brown filtrate was concentrated to ~25 mL. Addition of hexane (~50 mL) afforded 1.04 g of crude product as a light brown powder, 77% yield. Pure $CpHf(Me_2dtc)_3 \cdot CH_2Cl_2$ was obtained as a white powder after two recrystallizations from dichloromethane–hexane. Anal. Calcd for $(C_5H_5)Hf(C_3H_6NS_2)_3 \cdot CH_2Cl_2$: C, 26.14; H, 3.66; Cl, 10.29; Hf, 25.90; N, 6.10. Found: C, 26.16; H, 3.86; Cl, 10.16; Hf, 25.81; N, 6.03. This compound decomposes (turns light brown) without melting in the range 220–275 °C (lit.[1] mp 180 °C). ^1H NMR (7.5 g/100 mL $CDCl_3$, 37 °C): δ 3.26 (9 H, CH_3), 3.29 (3 H, CH_3), 3.36 (6 H, CH_3), 5.30 (2 H, CH_2Cl_2), 6.03 (5 H, C_5H_5).

Infrared Spectra. Infrared spectra were recorded in the region 4000–250 cm^{-1} with a Perkin-Elmer 521 grating spectrophotometer. The complexes were studied as mineral oil or hexachlorobutadiene mulls supported between cesium iodide plates. The estimated uncertainty in reported frequencies is ± 4 cm^{-1}.

Nuclear Magnetic Resonance Spectra. Proton chemical shifts (in ppm downfield from tetramethylsilane) were measured at ambient probe temperature (~37 °C) in $CDCl_3$ solution with a Varian A60-A spectrometer. Reported values are the averages of those obtained from four sweeps of each spectrum; the sweep width was calibrated with a standard sample of tetramethylsilane in chloroform.

Variable-temperature, continuous-wave ^1H NMR spectra of sealed, degassed solutions of the $CpM(Me_2dtc)_3$ complexes were recorded with a Bruker HX-90 spectrometer, which was locked on a solvent proton or deuterium resonance. Solvents were dried by refluxing for at least 24 h over calcium hydride (dichloromethane, dibromomethane, 1,1,2,2-tetrachloroethane, and toluene-d_8) or phosphorus(V) oxide (carbon disulfide). Diphenylmethane was dried over 10% sodium–90% lead (w/w) alloy (dri-Na, Fisher). Acetonitrile-d_3 (Aldrich) was used as received. In order to minimize possible thermal decomposition, solutions were freshly prepared and were stored at −78 °C until spectra were run. Ordinarily, at least five copies of the spectrum were recorded at each temperature in the coalescence region, and at least three copies in the high- and low-temperature limits. Probe temperatures, determined with a copper–constantan thermocouple immersed in dichloromethane or 1,1,2,2-tetrachloroethane, are estimated to be accurate to ±0.5 °C. The procedures used to eliminate or minimize the common sources of error in NMR line-broadening studies[18] are detailed in a previous paper.[19]

Rate constants for exchange of dithiocarbamate methyl groups among the inequivalent environments of the $CpM(Me_2dtc)_3$ complexes were determined by comparison of experimental spectra with theoretical spectra calculated with use of the total line-shape program PZDMFX.[20] Observed and calculated spectra were compared qualitatively, by overlaying one on the other, and quantitatively, by comparison of the following characteristic line-shape parameters: frequency separations ($\delta\nu$) and line widths at three-fourths ($w_{3/4}$), one-half ($w_{1/2}$), one-fourth ($w_{1/4}$), and in the case of $CpTi(Me_2dtc)_3$ one-eighth ($w_{1/8}$) maximum amplitude. T_2 values [$T_2 = (\pi w_{1/2})^{-1}$] at temperatures in the coalescence region were estimated by plotting log $w_{1/2}$ vs. $1/T$ over a wide temperature range and then extrapolating these plots from the slow-exchange region into the coalescence region. Values of T_2 were measured for the best resolved (lowest field) resonance, and it was assumed that all four methyl resonances have the same T_2 value at a given temperature. For $CpM(Me_2dtc)_3$ (M = Zr, Hf), T_2 proved to be temperature independent, while for $CpTi(Me_2dtc)_3$, which was studied at lower temperatures, T_2 exhibited a modest temperature dependence. The chemical shifts also showed a small temperature dependence. Chemical shifts in the coalescence region were determined by extrapolating linear plots of $\delta\nu$ vs. $1/T$ from the slow-exchange region into the coalescence region. The chemical shifts and T_2 values used in calculating the theoretical line shapes are given in the footnotes to Tables IV and S1.[21]

Results and Discussion

Synthesis and Characterization of Compounds. (η^5-Cyclopentadienyl)tris(*N*,*N*-dimethyldithiocarbamato)zirconium(IV) and -hafnium(IV), $CpM(Me_2dtc)_3$ (M = Zr, Hf), have been synthesized by reaction of Cp_2MCl_2 with a small excess of anhydrous $Na(Me_2dtc)_3$ in refluxing dichloromethane (eq 1).

$$Cp_2MCl_2 + 3Na(Me_2dtc)_3 \rightarrow CpM(Me_2dtc)_3 + 2NaCl + NaCp \quad (1)$$

Further reaction of the NaCp produced with the solvent is likely since NaCp is known to react with methyl iodide[22] and benzyl chloride[23] to yield substituted cyclopentadienes, RC_5H_5 (R = Me, CH_2Ph). Further reaction of the NaCp produced with the solvent is likely since NaCp is known to react with methyl iodide[22] and benzyl chloride[23] to yield substituted cyclopentadienes, RC_5H_5 (R = Me, CH_2Ph).

Attempts to prepare $CpTi(Me_2dtc)_3$ by the method employed for the zirconium and hafnium analogues resulted in green solutions that turned orange instantaneously upon exposure to the atmosphere. This behavior suggested formation of an oxygen-sensitive titanium(III) complex, possibly $CpTi(Me_2dtc)_2$.[24] Since $CpTiX_2$ (X = Cl, Br) complexes are oxidized to $CpTi(R_2dtc)X_2$ by thiuram disulfides,[25] 0.5 mol of tetramethylthiuram disulfide was added to the reaction mixture to oxidize the green titanium(III) complex. The stoichiometry indicated in reaction 2 afforded good yields of

$$Cp_2TiCl_2 + 2Na(Me_2dtc) + 0.5Me_2NC(S)S{-}SC(S)NMe_2 \rightarrow CpTi(Me_2dtc)_3 \quad (2)$$

$CpTi(Me_2dtc)_3$. The reaction was carried out in tetrahydrofuran at room temperature in order to minimize thermal decomposition of the product. Dichloromethane solutions of $CpTi(Me_2dtc)_3$ turn brown on standing at room temperature, and NMR measurements indicate ~10% decomposition within 48 h.

All three complexes crystallize from dichloromethane–hexane as dichloromethane solvates: $CpTi(Me_2dtc)_3 \cdot CH_2Cl_2$ as golden yellow crystals, $CpZr(Me_2dtc)_3 \cdot CH_2Cl_2$ as colorless crystals, and $CpHf(Me_2dtc)_3 \cdot CH_2Cl_2$ as a white powder. These compounds are soluble in chlorinated hydrocarbons, less soluble in aromatic hydrocarbons, acetonitrile, and carbon disulfide, and essentially insoluble in saturated hydrocarbons. The complexes are thermally stable in the solid state at room temperature, but they exhibit slow decomposition in solution at elevated temperatures. All three complexes behave as nonelectrolytes in dichloromethane; molar conductances of 10^{-3} M solutions at 25 °C are less than 0.05 Ω^{-1} cm^2 mol^{-1}.

Characteristic infrared frequencies for $CpM(Me_2dtc)_3$ (M = Ti, Zr, Hf) and $Na(Me_2dtc)$ are listed in Table I. The

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Table I. Characteristic Infrared Frequencies (cm^{-1}) for $CpM(Me_2dtc)_3\cdot CH_2Cl_2$ Complexes[a]

compd	$\nu(\mathrm{C}\underset{\cdot\cdot}{-}\mathrm{N})$	$\nu(\mathrm{C}\underset{\cdot\cdot}{-}\mathrm{S})$	ν(M–S)	other bands[b]
$CpTi(Me_2dtc)_3\cdot CH_2Cl_2$	1502 s, br	1002 m, 992 m	376 s, 340 s	1257 m, 1138 s, 1051 vw, 1019 m, 827 sh, 816 s, 739 s,[c] 702 w, 587 m, 558 w, 450 s, 423 vw, 357 vw
$CpZr(Me_2dtc)_3\cdot CH_2Cl_2$	1505 s, br	997 m, 986 m	355 m	1255 m, 1136 s, 1047 vw, 1014 m, 818 w, 806 s, 737 m,[c] 700 w, 582 m, 450 m, 427 vw, 402 w, 316 w
$CpHf(Me_2dtc)_3\cdot CH_2Cl_2$	1508 s, br	998 m, 987 m	347 m	1253 m, 1137 s, 1047 vw, 1016 m, 821 w, 810 s, 735 s,[c] 699 w, 582 m, 562 vw, 448 m, 424 w, 401 vw
$Na(Me_2dtc)$	1491 s, br[d]	976 vs, 961 vs		1247 s, 1130 s, 1042 m, 1021 vw, 577 s, 446 vs, 335 m, 301 w, 275 w

[a] Unless otherwise indicated, as Nujol mulls between CsI plates. [b] 2000–250-cm^{-1} region. [c] ν(C–Cl) of dichloromethane. [d] As a hexachlorobutadiene mull.

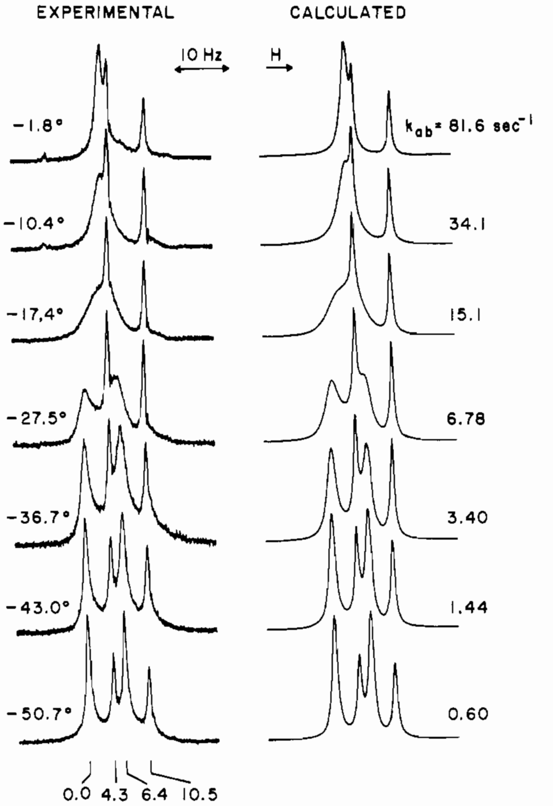


Figure 1. Observed and calculated ^1H NMR line shapes (low-temperature region) for the dithiocarbamate methyl resonances of $CpTi(Me_2dtc)_3$, 0.089 M in dichloromethane, at 90 MHz.

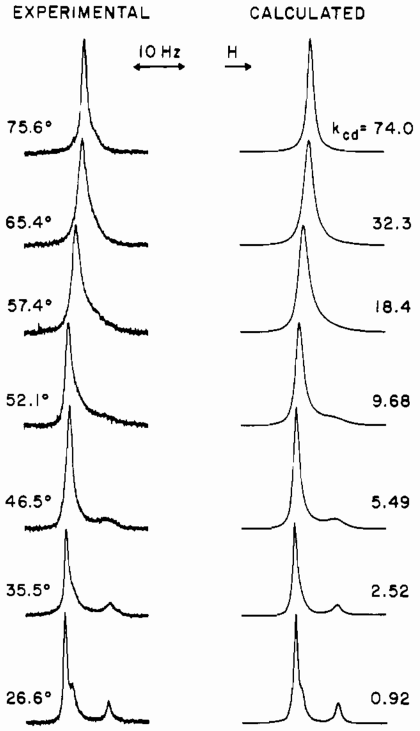
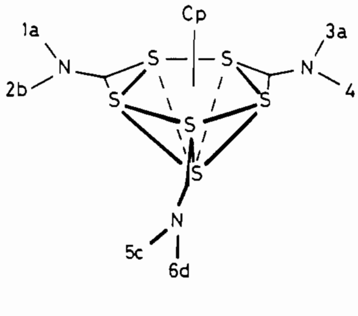


Figure 2. Observed and calculated ^1H NMR line shapes (high-temperature region) for the dithiocarbamate methyl resonances of $CpTi(Me_2dtc)_3$, 0.089 M in dichloromethane, at 90 MHz.

$CpM(Me_2dtc)_3$ complexes exhibit a broad $\nu(\mathrm{C}\underset{\cdot\cdot}{-}\mathrm{N})$ band at 1502–1508 cm^{-1}, a pair of closely spaced $\nu(\mathrm{C}\underset{\cdot\cdot}{-}\mathrm{S})$ bands at 986–1002 cm^{-1}, and bands due to the cyclopentadienyl ligands at ~810 and ~1015 cm^{-1}. The only significant difference in the spectra of the three complexes is in the ν(M–S) region where $CpTi(Me_2dtc)_3$ exhibits two strong, sharp bands at 340 and 376 cm^{-1} while $CpZr(Me_2dtc)_3$ and $CpHf(Me_2dtc)_3$ show only one band at 355 and 347 cm^{-1}, respectively.[26] This difference can be understood in terms of a difference in the metal–sulfur bond lengths. In $CpTi(Me_2dtc)_3$, the Ti–S bonds to the two equatorial ligands are longer (by ~0.07 Å), and presumably weaker, than the Ti–S bonds to the unique ligand,[6] whereas in $CpZr(Me_2dtc)_3$, the six Zr–S bond lengths are more nearly equal.[5] The presence, for all three complexes, of two $\nu(\mathrm{C}\underset{\cdot\cdot}{-}\mathrm{S})$ bands separated by ~10 cm^{-1} is of interest since observation of two $\nu(\mathrm{C}\underset{\cdot\cdot}{-}\mathrm{S})$ bands usually indicates the presence of both bidentate and monodentate dithiocarbamate ligands.[27,28] However, two $\nu(\mathrm{C}\underset{\cdot\cdot}{-}\mathrm{S})$ bands, separated by ~10 cm^{-1}, have been observed previously for $Ti(R_2dtc)_3Cl$ (R = Me, *i*-Bu),[15] demonstrating that small splittings of the $\nu(\mathrm{C}\underset{\cdot\cdot}{-}\mathrm{S})$ band are not inconsistent with the exclusive presence of bidentate dithiocarbamate ligands, especially in the case of complexes where the dithiocarbamate ligands are inequivalent.

Variable-Temperature ^1H NMR Spectra. The methyl regions of variable-temperature ^1H NMR spectra of $CpTi(Me_2dtc)_3$ are shown in Figures 1 and 2. In the slow-exchange limit, this complex exhibits a single cyclopentadienyl resonance and four dithiocarbamate methyl resonances of relative intensity 2:1:2:1 (Figure 1), consistent with the PB structure **1**



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found in the solid state.[6] The numbers in structure **1** label the dithiocarbamate methyl groups, and the letters label the inequivalent sites. Above -50 °C, the two resonances of

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(26) Our ν(Hf–S) frequency does not agree with the value of 380 cm^{-1} reported by Tuli et al.[11]

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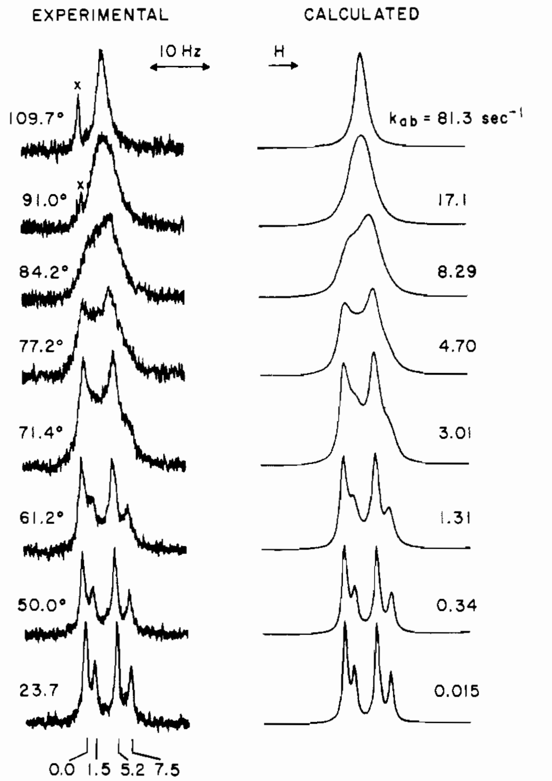


Figure 3. Observed and calculated ^1H NMR line shapes for the dithiocarbamate methyl resonances of $CpZr(Me_2dtc)_3$, 0.039 M in 1,1,2,2-tetrachloroethane, at 90 MHz. Resonances marked with × are due to thermal decomposition products.

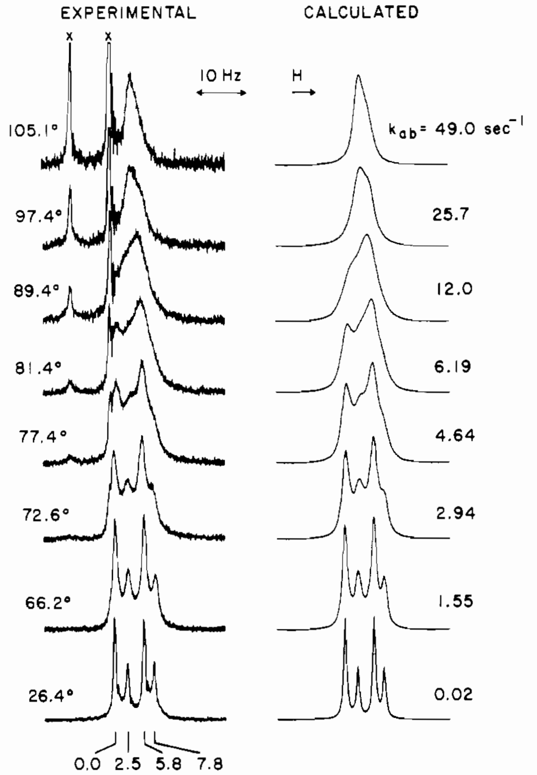


Figure 4. Observed and calculated ^1H NMR line shapes for the dithiocarbamate methyl resonances of $CpZr(Me_2dtc)_3$, 0.126 M in dibromomethane, at 90 MHz. Resonances marked with × are due to thermal decomposition products.

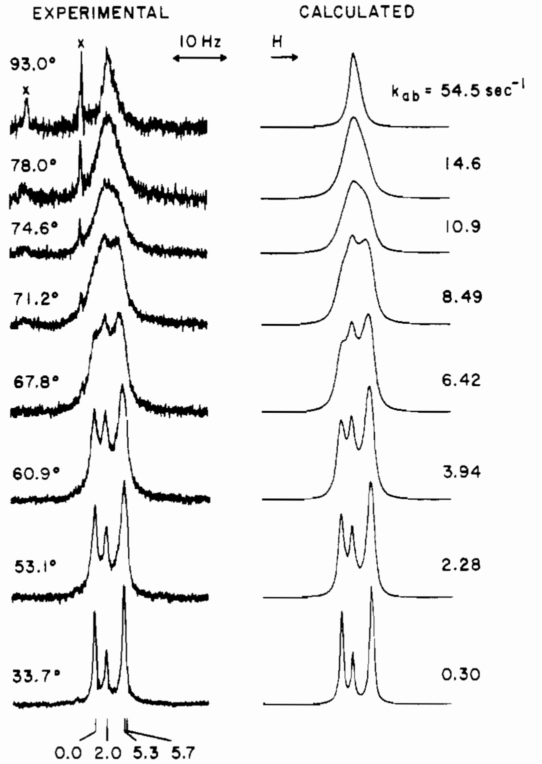


Figure 5. Observed and calculated ^1H NMR line shapes for the dithiocarbamate methyl resonances of $CpHf(Me_2dtc)_3$, 0.106 M in dibromomethane, at 90 MHz. Resonances marked with × are due to thermal decomposition products.

relative intensity 2 broaden and then coalesce into a single, broad line at −17 °C. The two resonances of relative intensity 1 remain sharp, giving a three-line pattern of methyl resonances (4:1:1), which persists until ~27 °C. Above 27 °C (Figure 2), the two lines of relative intensity 1 coalesce with each other and with the time-averaged line of relative intensity 4 to give a single time-averaged line above the coalescence temperature, T_c, of ~57 °C. The low-temperature kinetic process (T_c = −17 °C) is attributed to exchange of methyl groups between inequivalent sites a and b within the equatorial ligands (see structure **1**); this process is referred to hereafter as process Ie. The high-temperature coalescence process (T_c = 57 °C) can be interpreted in terms of a combination of (i) exchange of methyl groups between sites c and d within the unique ligand (process Iu) and (ii) exchange of the equatorial and unique ligands (process II).

The methyl region of ^1H NMR spectra of $CpZr(Me_2dtc)_3$ in 1,1,2,2-tetrachloroethane and dibromomethane is presented in Figures 3 and 4, respectively. The spectra in the slow-exchange region again point to PB structure **1**.[5] However, the low-temperature process (process Ie) observed in the titanium complex is very much slower in the zirconium compound. Consequently, the four methyl resonances of $CpZr(Me_2dtc)_3$ broaden simultaneously and coalesce into a single, time-averaged line at approximately 84–89 °C.

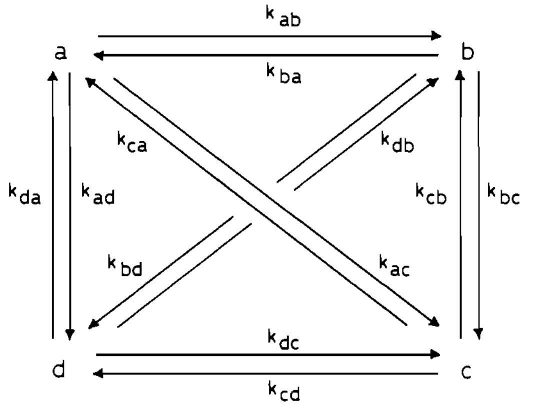
^1H NMR spectra of $CpHf(Me_2dtc)_3$ (Figure 5) are similar to spectra of the zirconium analogue except that for $CpHf(Me_2dtc)_3$ the two highest field resonances of the 2:1:2:1 pattern have nearly identical chemical shifts, giving three lines of relative intensity 2:1:3 in the slow-exchange limit. The chemical shifts of the two highest field resonances appear to be solvent dependent, and close examination of the spectrum in dichloromethane shows that the resonance line at highest field is asymmetric. Thus, although we do not have an X-ray crystal structure of $CpHf(Me_2dtc)_3$, we believe that this molecule has the same PB structure found in the solid state for the analogous titanium and zirconium compounds.[5,6]

On the basis of poorly resolved 60-MHz room-temperature ^1H NMR spectra, Garg and co-workers have suggested that $CpHf(Me_2dtc)_3$[11] and related $CpM(R_2dtc)_3$ and (MeCp)M-

$(R_2dtc)_3$ (M = Ti, Zr, Hf) complexes[11-14] have capped-octahedral (CO) or capped-trigonal-prismatic (CTP) structures. This seems unlikely in view of the steric congestion already present in the coordination group of the PB structure;[5,6] CTP and CO structures should be even more crowded than PB structures for seven-coordinate complexes that contain a relatively large "monodentate" ligand such as C_5H_5.[29]

As already mentioned, in $CpTi(Me_2dtc)_3$ process Ie is much faster than processes Iu and II. In $CpZr(Me_2dtc)_3$ and $CpHf(Me_2dtc)_3$, these three processes have more comparable rates. However, there is an interesting qualitative difference between the spectra of the zirconium and hafnium compounds. For $CpZr(Me_2dtc)_3$ (Figures 3 and 4), the two resonances of relative intensity 1 (due to sites c and d in structure **1**) broaden at slightly lower temperatures than the resonances of relative intensity 2 (due to sites a and b in **1**). The reverse broadening pattern is observed for $CpHf(Me_2dtc)_3$ (Figure 5); the resonances of relative intensity 2 broaden at slightly lower temperatures. This difference suggests that process Ie is the fastest for $CpHf(Me_2dtc)_3$, as for $CpTi(Me_2dtc)_3$, but process Iu is the fastest for $CpZr(Me_2dtc)_3$. These qualitative conclusions are borne out by a detailed analysis of the NMR line shapes (vide infra). For all three complexes, process II is required as well, else the spectra would exhibit two lines of relatively intensity 4:2 in the fast-exchange limit.

Kinetics of Methyl Group Exchange. Twelve rate constants are required to describe the exchange of methyl groups among four independent sites; these are given in eq 3. The forward and reverse rate constants are related by the relative populations of the sites; for PB structure **1**, $k_{ab} = k_{ba}$, $k_{cd} = k_{dc}$, $k_{ac} = {}^1/_2k_{ca}$, $k_{ad} = {}^1/_2k_{da}$, $k_{bc} = {}^1/_2k_{cb}$, and $k_{bd} = {}^1/_2k_{db}$. Thus, only six of the rate constants are independent. For PB structure **1**, k_{ab} is the rate constant for exchange of methyl groups within the equatorial ligands (process Ie), and k_{cd} is the rate constant for exchange of methyl groups within the unique ligand (process Iu). The rate constants k_{ac}, k_{ad}, k_{bc}, and k_{bd} refer to exchange of methyl groups between sites on the equatorial and unique ligands (process II). However, because the latter process involves exchange of bidentate ligands, exchange of methyl groups occurs in a pairwise fashion, affording the additional constraints $k_{ac} = k_{bd}$ and $k_{ad} = k_{bc}$. Thus, for the case at hand, of the 12 rate constants in eq 3, only four are independent, e.g. k_{ab}, k_{cd}, k_{ac}, and k_{ad}.



(3)

In order to further reduce the number of rate constants required to fit the NMR line shapes, we investigated the relationship between k_{ac} and k_{ad} by carrying out a permutational analysis[30-32] of the $CpM(Me_2dtc)_3$ system. The results (Tables II and III) apply generally to PB complexes $M(AA)_3X$ that contain an axial monodentate ligand and three symmetric bidentate ligands. Half (24) of the allowed 48 permutations are listed in Table II, grouped into NMR averaging sets (A_i). Operations that effect the same net site interchanges belong in the same averaging set. The permutations belonging to averaging sets A_2–A_6 effect exchange of dithiocarbamate methyl groups within one or more ligands but do not bring about ligand exchange (process Ie or Iu). The permutations belonging to averaging sets A_7–A_{12} involve exchange of one of the equatorial ligands and the unique ligand (exchange (eu)) (process II); the corresponding site interchanges involve (i) pairwise exchange of methyl groups between sites in one equatorial ligand the unique ligand (e.g. (ac), (bd)), (ii) cyclic permutation of methyl groups among all four sites in one equatorial ligand and the unique ligand (e.g. (adbc) and acbd)), or (iii) combination of the exchanges in i or ii with exchange of methyl groups in the remaining equatorial ligand (e.g. (ab), (ac), (bd)).

Table II. Permutational Analysis for Rearrangements of a Pentagonal-Bipyramidal $M(AA)_3X$ Complex

operation	ligand exchange	net site interchanges	averaging set
E	none	none	A_1
(12) (34)	none	(ab)	A_2
(56)	none	(cd)	A_3
(12)(34)	none	2(ab)	A_4
(12)(56) (34)(56)	none	(ab), (cd)	A_5
(12)(34)(56)	none	2(ab), (cd)	A_6
(15)(26) (35)(46)	(eu)	(ac), (bd)	A_7
(16)(25) (36)(45)	(eu)	(ad), (bc)	A_8
(1625) (3645)	(eu)	(adbc)[a]	A_9
(1526) (3546)	(eu)	(acbd)[a]	
(12)(35)(46) (15)(26)(34)	(eu)	(ab), (ac), (bd)	A_{10}
(12)(36)(45) (16)(25)(34)	(eu)	(ab), (ad), (bc)	A_{11}
(12)(3645) (34)(1625)	(eu)	(ab), (adbc)[a]	A_{12}
(12)(3546) (34)(1526)	(eu)	(ab), (acbd)[a]	

[a] The clockwise and counterclockwise cyclic site interchanges must be considered together because of microscopic reversibility.

Table III. Relative Rate Constants and Predicted Number (Relative Intensity) of Dithiocarbamate Methyl Resonances in the Fast-Exchange Limit for Rearrangements of a $CpM(Me_2dtc)_3$ Complex

averaging set[a]	k_{ab}	k_{cd}	k_{ac}[b]	k_{ad}[c]	Me resonances
A_1	0	0	0	0	4 (2:1:2:1)
A_2	$k/2$	0	0	0	3 (4:1:1)
A_3	0	k	0	0	3 (2:2:2)
A_4	k	0	0	0	3 (4:1:1)
A_5	$k/2$	k	0	0	2 (4:2)
A_6	k	k	0	0	2 (4:2)
A_7	0	0	$k/2$	0	2 (3:3)
A_8	0	0	0	$k/2$	2 (3:3)
A_9	0	0	$k/4$	$k/4$	1
A_{10}	$k/2$	0	$k/2$	0	1
A_{11}	$k/2$	0	0	$k/2$	1
A_{12}	$k/2$	0	$k/4$	$k/4$	1

[a] Averaging sets are defined in Table II. [b] $k_{ac} = k_{bd}$. [c] $k_{ad} = k_{bc}$.

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(29) Note also that in interpreting the ^1H NMR spectra of the $CpM(MePhdtc)_3$ and $(MeCp)M(MePhdtc)_3$ complexes Garg and co-workers[13] fail to take into account the possibility of isomerism arising from the asymmetry of the *N*-methyl-*N*-phenyldithiocarbamate ligand.

(30) Jesson, J. P.; Meakin, P. *Acc. Chem. Res.* **1973**, *6*, 269.

(31) Bickley, D. G.; Serpone, N. *Inorg. Chem.* **1976**, *15*, 948.

(32) Fay, R. C.; Lindmark, A. F. *J. Am. Chem. Soc.* **1983**, *105*, 2118.

The remaining 24 permutations, not listed in Table II, may be generated by multiplying the listed permutations by the reflection operation (13)(24). The unlisted permutations exchange the equivalent equatorial ligands (exchanges (ee) or (eue)). These permutations have the same effect on the NMR spectrum as the listed permutations.

Table III summarizes the relative values of the rate constants for each of the permutational mechanisms A_1–A_{12}. Also included in Table III, for each permutational mechanism, are the predicted number and relative intensity of dithiocarbamate methyl resonances in the fast-exchange limit for a rapidly rearranging CpM(Me$_2$dtc)$_3$ complex. It is evident that each of the possible permutational mechanisms for process II (A_7–A_{12}) predicts a unique relationship between k_{ac}, k_{ad}, and k_{ab}. In principle, one should be able to deduce the permutational mechanism from the relative values of these three rate constants. In the case of the CpM(Me$_2$dtc)$_3$ complexes, however, the permutational mechanism for process II could not be determined because processes Ie and/or Iu are much faster than process II. When k_{ab} and/or k_{cd} are very large compared with k_{ac} and k_{ad}, it is not possible to tell if (i) $k_{ac} = k_{ad} \neq 0$, (ii) $k_{ac} \neq k_{ad} = 0$, or (iii) $k_{ad} \neq k_{ac} = 0$. This was confirmed by calculations on CpZr(Me$_2$dtc)$_3$; permutational mechanisms A_{10}, A_{11}, and A_{12} gave equally good agreement between observed and calculated line shapes. We have decided to determine the rate constants for process II on the assumption of permutational mechanism A_{11} ($k_{ac} = 0$; $k_{ad} = k_{ab}$) because A_{11} corresponds to the physical mechanism (vide infra) that we consider to be most likely for the ligand-exchange process.

To summarize our discussion thus far, we have fit the NMR line shapes with three rate constants: k_{ab} (process Ie), k_{cd} (process Iu), and k_{ad} (process II). Because we are assuming permutational mechanism A_{11} for process II, process II makes a small contribution to the total value of k_{ab} (eq 4). The values of k_{ab} quoted in this paper refer to k_{ab} for process Ie, not k_{ab}(total). The following paragraphs describe the line-shape analysis for each of the CpM(Me$_2$dtc)$_3$ complexes.

$$k_{ab}(\text{total}) = k_{ab}(\text{process Ie}) + k_{ab}(\text{process II}) = k_{ab}(\text{process Ie}) + k_{ad} \quad (4)$$

A. CpTi(Me$_2$dtc)$_3$. Values of k_{ab} in the low-temperature region (Figure 1) were determined by comparison of observed methyl line shapes with theoretical line shapes calculated on the assumption that, in this temperature region, $k_{cd} = k_{ad} = 0$. The resulting values of k_{ab} were then extrapolated into the high-temperature region (Figure 2), and values of k_{cd} and k_{ad} were determined by calculating theoretical spectra as a function of k_{cd} for various fixed ratios of k_{ad}/k_{cd}; for dichloromethane solutions of CpTi(Me$_2$dtc)$_3$, the best-fit ratio of k_{ad}/k_{cd} proved to be 0.45. Note that this approximate procedure of assuming that k_{ad}/k_{cd} is temperature independent amounts to assuming that processes Iu and II have the same activation energy. Although there is no reason why these two processes must have the same activation energy, this simplifying assumption leads to satisfactory agreement between the observed and calculated spectra (Figure 2), and the paucity of structure in the line shapes in the high-temperature region precludes an independent determination of k_{cd} and k_{ad} at each temperature.

B. CpZr(Me$_2$dtc)$_3$. For this compound, processes Ie, Iu, and II occur simultaneously in the same temperature region. However, processes Ie and Iu are appreciably faster than process II. The observed line shapes (Figures 3 and 4) were fit satisfactorily on the assumption that all three processes have the same activation energy. Values of k_{ab} and k_{cd} were determined first by calculating theoretical spectra as a function of k_{ab} for a range of fixed ratios of k_{cd}/k_{ab}; the best-fit ratios of k_{cd}/k_{ab} were 1.78 and 1.28 for 1,1,2,2-tetrachloroethane and dibromomethane solutions, respectively. Values of k_{ad} were then determined by calculating theoretical spectra as a function k_{ad}/k_{ab} for the best-fit values of k_{ab} and k_{cd} already determined; the best-fit values of k_{ad}/k_{ab} were 0.054 and 0.044 for 1,1,2,2-tetrachloroethane and dibromomethane solutions, respectively. Because k_{ad} is so much smaller than k_{ab} and k_{cd}, reiteration of this procedure did not change the initially determined values of k_{ab} and k_{cd}.

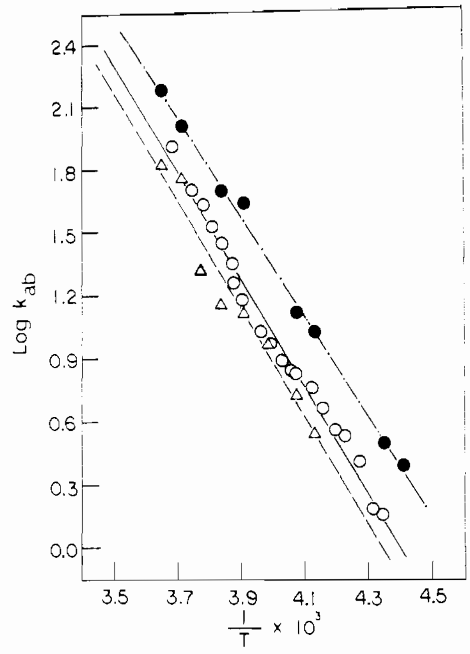

Figure 6. Arrhenius plots for process Ie in CpTi(Me$_2$dtc)$_3$: 0.089 M in dichloromethane (○); 0.076 M in acetonitrile-d_3–toluene-d_8 (●); 0.011 M in carbon disulfide–toluene-d_8 (△).

Assignment of the four resonance lines (Figures 3 and 4) is not required for determination of k_{ab} and k_{cd} but is required for determination of k_{ad}. We assumed that the lines could be assigned, in order of increasing field to sites a, c, b, and d, respectively. However, because k_{ad} is so much smaller than k_{ab} and k_{cd}, the alternative assignment (a, d, b, c in order of increasing field) resulted in little if any change in the calculated spectra.

C. CpHf(Me$_2$dtc)$_3$. The same approach employed for the zirconium compound afforded values of k_{ab} and a best-fit ratio of $k_{cd}/k_{ab} = 0.50$. However, the relative values of k_{ad} for CpHf(Me$_2$dtc)$_3$ are even smaller than for CpZr(Me$_2$dtc)$_3$. Values of k_{ad} for the hafnium compound could be determined by comparison of observed and calculated spectra only in the high-temperature region (88–93 °C); values of k_{ad} used to calculate the line shapes at lower temperature (Figure 5) were determined from the high-temperature values of k_{ad} by assuming the activation energy found for the zirconium compound.

Kinetic Results. Rate constants for CpTi(Me$_2$dtc)$_3$ in dichloromethane, CpZr(Me$_2$dtc)$_3$ in 1,1,2,2-tetrachloroethane and dibromomethane, and CpHf(Me$_2$dtc)$_3$ in dibromomethane are presented in Table IV. The titanium complex was studied in four additional solvents (0.89 mol of acetonitrile-d_3/0.11 mol of toluene-d_8, 0.89 mol of carbon disulfide/0.11 mol of toluene-d_8, 1,1,2,2-tetrachloroethane, and diphenylmethane); rate constants for these solutions are listed in Table S1.[21] Arrhenius and Eyring activation parameters were determined in the usual way from the least-squares straight lines of log k vs. $1/T$ plots (Figures 6–8) and log (k/T) vs. $1/T$ plots, respectively. The activation parameters are presented in Table V along with coalescence temperatures and values of k and $\Delta G^{\ddagger}$ at a common temperature in the coalescence region (70 °C).

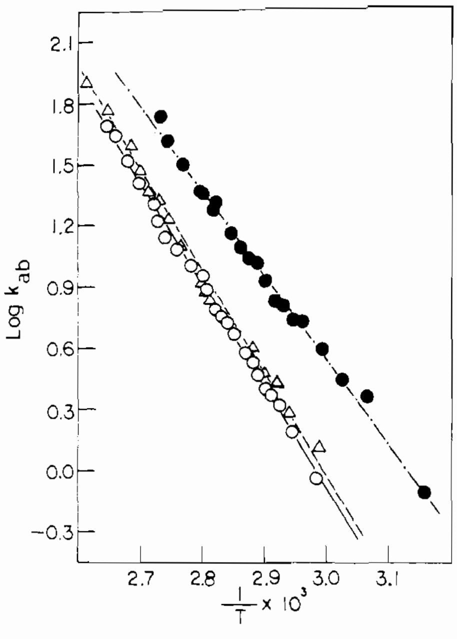

Figure 7. Arrhenius plots for process Ie: 0.039 M CpZr(Me$_2$dtc)$_3$ in 1,1,2,2-tetrachloroethane (△); 0.126 M CpZr(Me$_2$dtc)$_3$ in dibromomethane (○); 0.106 M CpHf(Me$_2$dtc)$_3$ in dibromomethane (●).

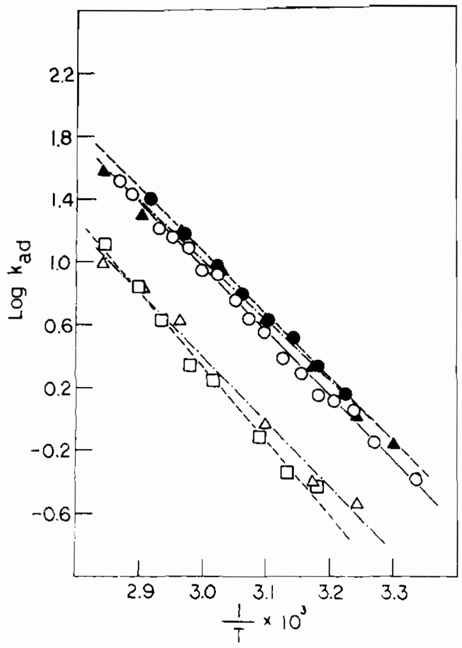

Figure 8. Arrhenius plots for process II in CpTi(Me$_2$dtc)$_3$: 0.089 M in dichloromethane (○); 0.076 M in acetonitrile-d_3–toluene-d_8 (▲); 0.011 M in carbon disulfide–toluene-d_8 (△); 0.065 M in 1,1,2,2-tetrachloroethane (●); 0.025 M in diphenylmethane (□).

For CpM(Me$_2$dtc)$_3$ (M = Zr, Hf), rate constants for processes Ie and Iu (Table IV) are the same within a factor of 2. However, for CpTi(Me$_2$dtc)$_3$ (Tables IV and S1[21]), process Ie is ~10^2–10^3 times faster than process Iu. At 70 °C (Table V), process Ie is ~10^3 times faster in the titanium complex than in the zirconium and hafnium compounds; the barrier $\Delta G^{\ddagger}$ (70 °C) for process Ie is ~14 kcal/mol for CpTi(Me$_2$dtc)$_3$ and ~19 kcal/mol for CpM(Me$_2$dtc)$_3$ (M = Zr, Hf). The faster rate of methyl group exchange within the equatorial ligands of CpTi(Me$_2$dtc)$_3$ appears to be related to weaker metal–sulfur bonds to the equatorial ligands in this compound. Because of crowding in the equatorial plane, the Ti–S bonds to the two equatorial ligands (2.609–2.666 Å, average 2.633 Å) are significantly longer than the Ti–S bonds to the unique ligand (2.565 and 2.570 Å).[6] In CpZr(Me$_2$dtc)$_3$,

Table IV. Rate Constants (s^{-1}) for Methyl Group Exchange in CpM(Me$_2$dtc)$_3$ Complexes

CpTi(Me$_2$dtc)$_3$ in CH$_2$Cl$_2$ ^{a}				CpZr(Me$_2$dtc)$_3$ in 1,1,2,2-C$_2$H$_2$Cl$_4$ ^{b}			
temp, °C	k_{ab}	k_{cd}	k_{ad}	temp, °C	k_{ab}	k_{cd}	k_{ad}
−43.0	1.44			61.2	1.31	2.33	0.071
−41.5	1.55			66.9	1.90	3.38	0.103
−39.2	2.62			69.0	2.64	4.70	0.143
−36.7	3.40			71.4	3.01	5.36	0.163
−34.8	3.69			73.8	3.92	6.98	0.212
−32.4	4.62			77.2	4.70	8.37	0.254
−30.7	5.81			81.1	5.99	10.7	0.324
−27.5	6.78			82.2	6.87	12.2	0.371
−26.8	6.97			83.3	7.52	13.4	0.406
−24.6	7.83			84.2	8.29	14.8	0.448
−22.6	9.42			86.4	10.1	18.0	0.546
−20.4	10.8			88.7	12.3	21.9	0.665
−17.4	15.1			91.0	17.1	30.4	0.924
−15.4	18.3			93.0	21.2	37.7	1.15
−15.0	23.2			95.2	23.5	41.8	1.27
−12.8	28.7			97.2	29.7	52.9	1.61
−10.4	34.1			99.3	39.9	71.0	2.16
−8.8	43.6			104.6	59.8	106	3.23
−6.2	51.2			109.7	81.3	145	4.39
−1.8	81.6						
26.6	498	0.92	0.41				
32.4	722	1.59	0.71				
35.5	869	2.52	1.13				
38.6	1050	2.92	1.31				
41.0	1210	3.19	1.43				
43.7	1410	4.30	1.93				
46.5	1650	5.49	2.46				
49.7	1980	7.94	3.56				
52.1	2260	9.68	4.34				
54.5	2570	12.5	5.62				
57.4	3020	18.4	8.26				
60.2	3510	19.5	8.74				
62.6	3970	27.2	12.2				
65.4	4590	32.3	14.5				
68.1	5210	36.6	16.4				
73.1	6650	60.7	27.2				
75.6	7550	74.0	33.1				

CpZr(Me$_2$dtc)$_3$ in CH$_2$Br$_2$ ^{c}				CpHf(Me$_2$dtc)$_3$ in CH$_2$Br$_2$ ^{d}			
temp, °C	k_{ab}	k_{cd}	k_{ad}	temp, °C	k_{ab}	k_{cd}	k_{ad}
61.9	0.92	1.18	0.040	43.6	0.78	0.39	0.007
66.2	1.55	1.98	0.068	53.1	2.28	1.14	0.020
68.5	2.07	2.65	0.091	57.4	2.77	1.38	0.026
70.0	2.30	2.94	0.101	60.9	3.94	1.97	0.042
71.3	2.53	3.24	0.111	64.3	5.29	2.64	0.060
72.6	2.94	3.76	0.129	66.2	5.40	2.70	0.062
73.7	3.37	4.31	0.148	67.8	6.42	3.21	0.083
75.1	3.73	4.77	0.164	69.4	6.56	3.28	0.085
77.4	4.64	5.94	0.204	71.2	8.49	4.24	0.115
78.9	5.24	6.71	0.230	72.8	10.4	5.20	0.150
80.3	5.71	7.31	0.250	74.6	10.9	5.45	0.159
81.4	6.19	7.92	0.271	76.3	12.4	6.20	0.182
82.9	7.71	9.87	0.338	78.0	14.6	7.30	0.216
84.0	8.85	11.3	0.388	81.0	20.4	10.2	0.286
87.1	10.3	13.2	0.452	81.6	18.9	9.45	0.268
89.4	12.0	15.4	0.526	83.9	22.6	11.3	0.367
91.9	13.8	17.7	0.606	84.8	22.8	11.4	0.371
93.6	16.9	21.6	0.742	88.0	31.0	15.5	0.532
94.4	20.4	26.1	0.896	91.4	41.5	20.8	0.655
97.4	25.7	32.9	1.13	93.0	54.5	27.2	0.808
100.2	32.8	42.0	1.44				
102.8	43.7	55.9	1.92				
105.1	49.0	62.7	2.15				

[a] 0.089 M. Variation in resonance frequencies (Hz at 90 MHz) from low temperaure (−43.0 °C) to high temperature (75.6 °C): $\nu_a = -10.89$ to -12.16; $\nu_c = -6.42$ to -7.09; $\nu_b = -4.28$ to -5.04; $\nu_d = 0.00$. Variation in T_2 (s^{-1}): 0.351 (−43.0 °C) to 0.587 (75.6 °C). [b] 0.039 M. $\nu_a = 0.00$; $\nu_c = 1.67$–1.85; $\nu_b = 5.39$–5.53; $\nu_d = 7.75$–8.00. $T_2 = 0.350$. [c] 0.126 M. $\nu_a = 0.00$; $\nu_c = 2.61$–2.71; $\nu_b = 5.82$–5.87; $\nu_d = 7.96$–8.15. $T_2 = 0.442$. [d] 0.106 M. $\nu_a = 0.00$; $\nu_c = 2.05$–2.14; $\nu_b = 5.34$–5.46; $\nu_d = 5.73$–6.15. $T_2 = 0.495$.

Table V. Kinetic Data for Methyl Group Exchange in CpM(Me_2dtc)$_3$ Complexes[a]

M	solvent	T_c,[b] °C	k(70 °C), s^{-1}	$\Delta G^{\ddagger}$(70 °C), kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	E_a, kcal/mol	log A
				Process Ie				
Ti	CH_2Cl_2	−17	6.1 × 10^3 [e]	14.2 ± 0.3	11.0 ± 0.7	−9.3 ± 2.8	11.5 ± 0.7	11.11 ± 0.61
Ti	CD_3CN-$C_6D_5CD_3$[c]	−22	8.6 × 10^3 [e]	14.0 ± 0.2	10.3 ± 0.6	−10.8 ± 2.5	10.8 ± 0.6	10.79 ± 0.55
Ti	CS_2-$C_6D_5CD_3$[d]	−17	4.8 × 10^3 [e]	14.4 ± 0.8	11.2 ± 2.5	−9.3 ± 9.8	11.7 ± 2.5	11.12 ± 2.15
Zr	1,1,2,2-$C_2H_2Cl_4$	84	2.6 ± 0.7	19.5 ± 0.2	21.7 ± 1.1	6.2 ± 3.1	22.4 ± 1.1	14.67 ± 0.69
Zr	CH_2Br_2	89	2.3 ± 0.3	19.6 ± 0.1	21.7 ± 0.6	6.0 ± 1.6	22.4 ± 0.6	14.62 ± 0.36
Hf	CH_2Br_2	74	8.0 ± 1.6	18.8 ± 0.1	18.1 ± 0.8	−2.0 ± 2.2	18.8 ± 0.8	12.85 ± 0.48
				Process II				
Ti	CH_2Cl_2	57	21 ± 4	18.1 ± 0.1	18.1 ± 0.6	−0.2 ± 0.6	18.7 ± 0.6	13.23 ± 0.43
Ti	CD_3CN-$C_6D_5CD_3$[c]	57	21 ± 7	18.1 ± 0.2	16.9 ± 1.2	−3.5 ± 3.8	17.5 ± 1.2	12.50 ± 0.82
Ti	CS_2-$C_6D_5CD_3$[d]	64	5.6 ± 4.6	19.0 ± 0.4	18.3 ± 3.3	−2.0 ± 10.1	19.0 ± 3.3	12.85 ± 2.21
Ti	1,1,2,2-$C_2H_2Cl_4$	53	26 ± 3	18.0 ± 0.1	17.6 ± 0.8	−1.0 ± 2.4	18.3 ± 0.8	13.05 ± 0.52
Ti	$CH_2(C_6H_5)_2$	67	5.6 ± 2.1	19.0 ± 0.2	21.0 ± 2.0	5.9 ± 6.1	21.7 ± 2.1	14.57 ± 1.35

[a] The uncertainties in the activation parameters are random errors estimated at the 95% confidence level. [b] Coalescence temperature. [c] 0.89 mol of CD_3CN/0.11 mol of toluene-d_8. [d] 0.89 mol of CS_2/0.11 mol of toluene-d_8. [e] Extrapolated values.

Table VI. Concentration Dependence of Rate Constants for Methyl Group Exchange in CpTi(Me_2dtc)$_3$

temp, °C	concn,[a] M	k_{ab}, s^{-1}	temp, °C	concn,[a] M	k_{ad},[b] s^{-1}
−27.5	0.010	5.4	41.0	0.010	2.1
	0.089	6.8		0.089	1.4
−17.4	0.010	13.1	57.4	0.010	8.3
	0.089	15.1		0.089	8.3
−6.2	0.010	57.0	65.4	0.010	15.6
	0.089	51.2		0.089	14.5

[a] In CH_2Cl_2. [b] $k_{cd} = 2.23k_{ad}$.

the lengths of the Zr–S bonds to the equatorial ligands (2.683–2.717 Å, average 2.701 Å) exceed the lengths of the bonds to the unique ligand (2.681 and 2.655 Å) by a much smaller amount.[5]

Process II is best studied in CpTi(Me_2dtc)$_3$; the barrier $\Delta G^{\ddagger}$ (70 °C) for the ligand-exchange process is 18–19 kcal/mol (Table V). Activation parameters for process II in CpM(Me_2dtc)$_3$ (M = Zr, Hf) could not be determined because process II is ~20–30 times (M = Zr) or ~40–90 times (M = Hf) slower than processes Ie and Iu and consequently the NMR line shapes are relatively insensitive to the value of k_{ad}.

Two additional observations on Table V are noted. First, the activation entropies $\Delta S^{\ddagger}$ are zero, within experimental uncertainty, for process II and not very far from zero for process Ie. Second, for processes Ie and II, the solvent-induced variation in the rate constants is less than a factor of 5, and the activation parameters are essentially independent of the nature and polarity of the solvent.

The concentration dependence of the rate constants was investigated for CpTi(Me_2dtc)$_3$. As expected, the rate constants (Table VI) are concentration independent, indicating that processes Ie, Iu, and II are first-order reactions.

The ^1H NMR spectrum at 70 °C of a CH_2Cl_2/CD_3CN (0.73:0.27 w/w) solution containing both CpTi(Me_2dtc)$_3$ (0.058 M) and Na(Me_2dtc) (0.096 M) exhibited separate methyl resonances for each compound. Similarly, the ^1H NMR spectrum at 75 °C of a CH_2Cl_2–tetrahydrofuran (1:1 w/w) solution of CpTi(Me_2dtc)$_3$ (0.006 M) and TlCp (0.04 M) showed separate, sharp cyclopentadienyl resonances for each compound. In each case, the line width of the CpTi(Me_2dtc)$_3$ resonance was essentially the same as in the absence of added Na(Me_2dtc) or TlCp. These results show that intermolecular exchange of dithiocarbamate and cyclopentadienyl ligands is slow on the NMR time scale at temperatures well above the coalescence temperature for methyl group exchange. Therefore, the mechanism of methyl group exchange (processes Ie, Iu, and II) cannot involve complete dissociation of dithiocarbamate or cyclopentadienyl ligands.

Mechanisms of Methyl Group Exchange. A. Process I. Possible mechanisms for exchange of methyl groups within the equatorial ligands (process Ie) are outlined in Figure 9. The most likely mechanism involves rotation about the C$\overset{\cdots}{-}$N partial double bond (mechanism a), perhaps preceded by rupture of an equatorial metal–sulfur bond to give an octahedral intermediate (mechanism b). One can, of course, envision a continuum of mechanisms intermediate between a and b that involve rotation about the C$\overset{\cdots}{-}$N bond accompanied by more or less M–S bond stretching. Rotation about the C$\overset{\cdots}{-}$N bond is a well established process in methyl N,N-dimethyldithiocarbamate,[33],[34] N,N,N',N'-tetramethylthiuran disulfide,[35] and $Cp_2ZrCl(Me_2dtc)$,[36] and values of $\Delta G^{\ddagger}$ (25 °C) for these compounds (14.7–16.2 kcal/mol)[33–36] are in the same range as the $\Delta G^{\ddagger}$ values for process Ie in the CpM(Me_2dtc)$_3$ complexes (Table V).

Mechanism c (Figure 9) involves rupture of an equatorial M–S bond to give an octahedral intermediate, followed by rotation of the dangling ligand about the M–S and/or C–S bonds and subsequent reattachment of the uncoordinated S atom. This mechanism cannot be ruled out, but it is not needed in view of the facile rotation about the C$\overset{\cdots}{-}$N bond in organic dithiocarbamates.[33–35] Mechanism c might possibly contribute to process Ie in the case of CpTi(Me_2dtc)$_3$, where process Ie is especially fast. Mechanism f (Figure 9) is similar to mechanism c, but it involves rupture of an M–S bond to the unique ligand. This mechanism is less likely than mechanism c because the M–S bonds to the unique ligand are shorter, and presumably stronger, than the bonds to the equatorial ligands.[5,6]

Mechanism d is a digonal twist of an entire planar dithiocarbamate ligand about its twofold axis. Pinnavaia et al.[37] have proposed this mechanism for the exchange of equatorial β-diketonate ring substituents in related CpZr(β-diketonate)$_3$ complexes. The transition state is an exceedingly crowded PB structure having the cyclopentadienyl ligand in an equatorial position. In view of the extreme crowding in the ground-state structures of CpM(Me_2dtc)$_3$ (M = Ti,[6] Zr[5]), we consider the digonal twist to be an unattractive mechanism, at least for CpM(Me_2dtc)$_3$ complexes.

In mechanism e (Figure 9), the unique ligand moves in its own plane giving a CTP transition state of C_{2v} symmetry. This polytopal rearrangement can be ruled out as the mechanism of process Ie because it predicts $k_{ab} = k_{cd}$ (permutational

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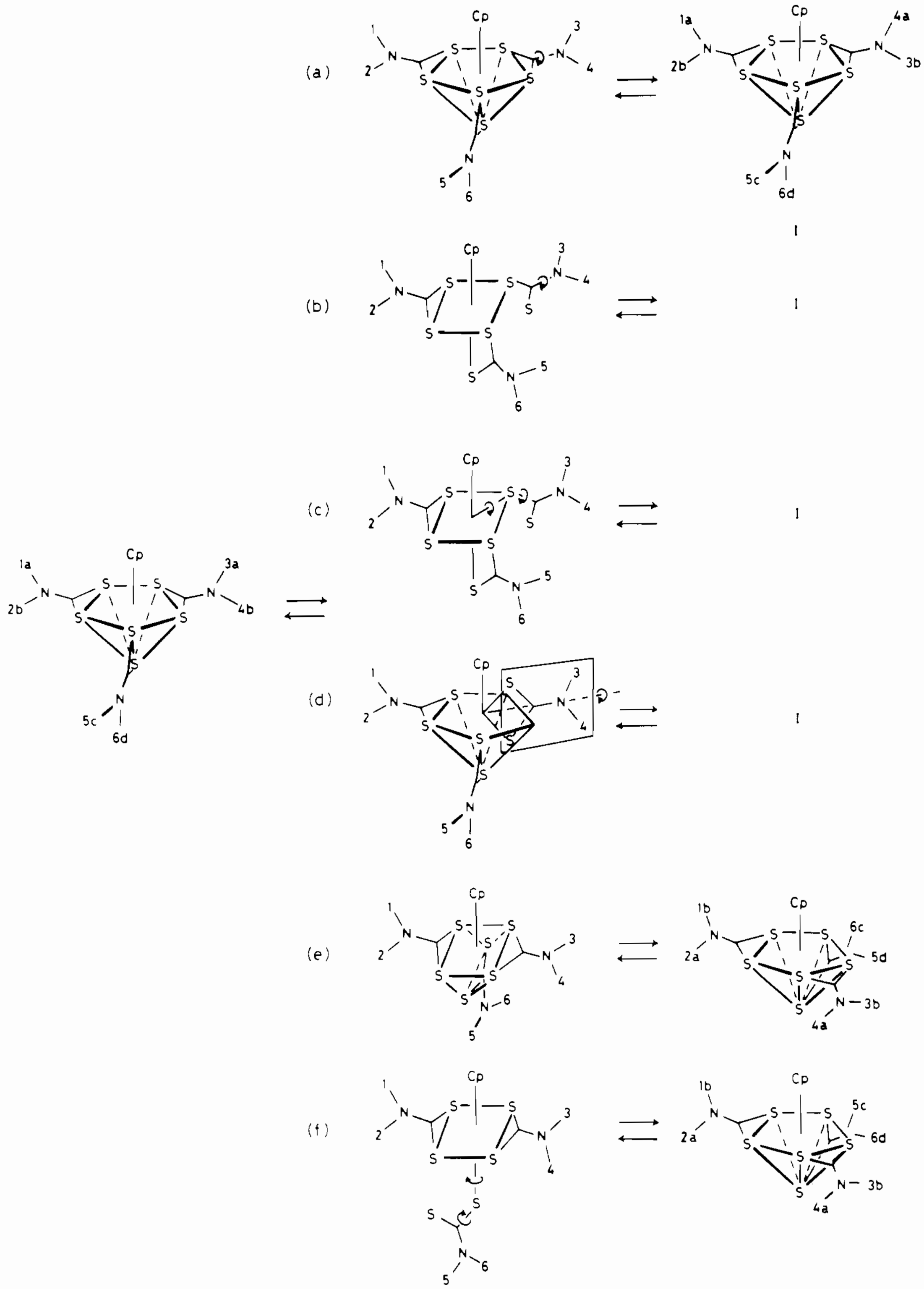


Figure 9. Possible mechanisms for process Ie in CpM(Me_2dtc)$_3$ complexes. All of these mechanisms exchange methyl groups 3 and 4 (and/or 1 and 2) between the inequivalent sites a and b of the equatorial ligands. Mechanisms a–d give the same permutational isomer (I).

mechanism A_6, Tables II and III), which is not in accord with experiment.

The most likely mechanisms for exchange of methyl groups within the unique ligand (process Iu) involve $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ rotation processes analogous to mechanisms a and b of Figure 9. Rotation about the $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ bond in the unique ligand may occur in the PB complex or in an octahedral intermediate formed by rupture of the equatorial M–S bond to the unique ligand.

The experimental evidence does not permit a clear-cut decision between mechanisms a and b. On the one hand, the fact that process Ie for CpTi(Me_2dtc)$_3$ is $\sim 10^2$–10^3 times faster than process Iu for CpTi(Me_2dtc)$_3$ and $\sim 10^3$ times faster than processes Ie and Iu for CpM(Me_2dtc)$_3$ (M = Zr, Hf) is readily understood in terms of facile rupture of the unusually long Ti–S bonds to the equatorial ligands (mechanism b). Moreover, extended Hückel calculations on $Cp_2ZrCl(S_2CH)$ indicate a very low barrier for rupture of the long Zr–S bond in $Cp_2ZrCl(Me_2dtc)$.[36] On the other hand, the absence of solvent effects for process Ie and values of ΔS^* near zero (Table V) are more consistent with a mechanism that does not involve M–S bond rupture (mechanism a). It may be that the barrier to $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ rotation in the equatorial

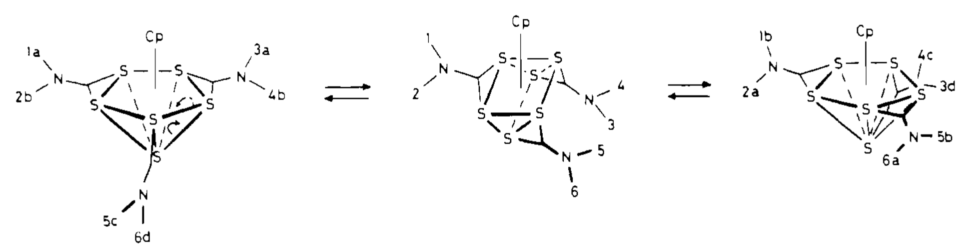
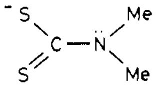
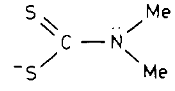


Figure 10. Double-facial twist mechanism for exchange of equatorial and unique ligands (process II). Numbers label dithiocarbamate methyl groups, and letters label the inequivalent environments.

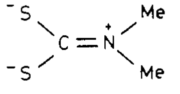
ligands of the fully chelated $CpTi(Me_2dtc)_3$ complex is lowered indirectly by the long Ti–S bonds to the equatorial ligands. Dithiocarbamate resonance structures **2a** and **b** should become



2a



2b



2c

relatively more important, and resonance structure **2c** relatively less important, as the M–S bond length increases. However, experimental evidence for a substantial weakening of the C–N bonds in the equatorial ligands of $CpTi(Me_2dtc)_3$ is lacking; the three C–N distances in $CpTi(Me_2dtc)_3$ are the same within 0.004 Å, and the mean C–N distance (1.345 (2) Å)[6] is only marginally longer than that in $CpZr(Me_2dtc)_3$ (1.334 (2) Å).[5]

B. Process II. We have considered two classes of mechanisms for the metal-centered process that exchanges the equatorial ligands and the unique ligand: (i) bond-rupture mechanisms and (ii) polytopal rearrangements. The bond-rupture mechanisms involve the opening of a metal–chelate ring to give a six-coordinate intermediate, such as the intermediates in mechanisms c and f of Figure 9, followed by rearrangement of the intermediate and subsequent reattachment of the dangling ligand. We prefer a polytopal rearrangement for the following reasons.

First, the absence of appreciable solvent effects and values of $\Delta S^{\ddagger}$ near zero for process II (Table V) are more compatible with a polytopal rearrangement than with a mechanism involving scission of a polar covalent bond. Second, the relative rearrangement rates of $CpTi(Me_2dtc)_3$ and the "isostructural" $Ti(Me_2dtc)_3Cl$ complex are inconsistent with a bond-rupture mechanism. The coalescence temperature for process II in $CpTi(Me_2dtc)_3$ is ~60 °C (Table V), while $Ti(Me_2dtc)_3Cl$ is still nonrigid on the NMR time scale at −90 °C,[15] despite the fact that the Ti–S bonds in $CpTi(Me_2dtc)_3$ (average 2.611 Å)[6] are 0.10 Å longer, and presumably weaker, than those in $Ti(Me_2dtc)_3Cl$ (2.512 Å).[38] If the maximum in the free energy profile is attained upon rupture of a Ti–S bond, then $CpTi(Me_2dtc)_3$ should rearrange more rapidly than $Ti(Me_2dtc)_3Cl$. This line of argument has been developed by Pinnavaia et al.[37] in support of a twist mechanism for $CpZr(\beta\text{-diketonate})_3$ complexes. Third, the most likely six-coordinate intermediates are octahedral (see Figure 9) and reattachment of the dangling ligand at the alternate equatorial coordination site does *not* suffice to exchange the unique and equatorial ligands. Ligand exchange can be effected if there is a trigonal twist in the octahedral intermediate prior to re-formation of the PB complex. However, a trigonal twist in the six-coordinate intermediate should have a higher barrier than a polytopal rearrangement in the seven-coordinate complex.

The most attractive polytopal rearrangement involves a concerted rotation of a pair of adjacent triangular faces of the PB (see Figure 10). The transition state is a CTP of C_s symmetry in which the Cp ligand occupies the capping site on one of the quadrilateral faces. The product PB is obtained after the triangular faces have been rotated by 120°. We refer to this mechanism as the double-facial twist. The clockwise twist shown in Figure 10 effects the methyl group permutation (145236); counterclockwise rotation of the symmetry-equivalent pair of adjacent triangular faces gives the equivalent permutation (163254). These permutations are products of the reflection operation (13)(24) and the operations of the A_{11} averaging set (Table II): [(13)(24)][(12)(36)(45)] = (145236); [(13)(24)][(16)(25)(34)] = (163254). The rate constants for this mechanism are given by $k_{ab} = k_{ad} = k_{bc}$, the relationship that was assumed for process II in the fitting of the NMR line shapes. For complexes that contain a large "monodentate" ligand like Cp, the CTP should be a more stable transition state than the more highly crowded capped octahedron and end-capped trigonal prism.

A CTP transition state has been suggested previously for rearrangements of the PB complexes $TaX(\eta^4\text{-naphthalene})(Me_2PC_2H_4PMe_2)_2$ (X = Cl, Me)[39] and $[MoH(C_2H_4)_2(cis\text{-}Ph_2PCH{=}CHPPh_2)_2]^+$.[40] These rearrangements effect pairwise exchange of the axial and equatorial P atoms and appear to take place by a mechanism involving a 90° rotation of an equatorial edge of the PB. The latter motion, quite different from the double-facial twist, cannot account for the rearrangements of $M(AA)_3X$ complexes in which the monodentate ligand occupies an axial coordination site.

We have also considered a polytopal rearrangement involving rotation of a single triangular face of the PB but judge this mechanism to be less likely than the double-facial twist because the irregular geometry of the single-facial twist transition state does not correspond to the geometry of any of the stable seven-coordination polyhedra.[4] In cases where k_{ac} and k_{ad} can be accurately determined, the single- and double-facial twist mechanisms can be distinguished experimentally. For the single-facial twist, $k_{ac} = k_{ad} = {}^1/_2 k_{ab}$; for the double-facial twist, $k_{ad} = k_{ab}$ and $k_{ac} = 0$.

Factors Affecting the Fluxionality of $M(AA)_3X$ Complexes. The rates of metal-centered rearrangement of pentagonal-bipyramidal $M(AA)_3X$ complexes depend on the size and electronic properties of the monodentate ligand that occupies the axial coordination site. The following complexes are nonrigid on the NMR time scale, even at very low temperatures: $Ti(R_2dtc)_3Cl$ (R = Me, Et, *i*-Bu),[15] $Ru(Et_2dtc)_3Cl$,[41,42] $Ru(R_2dtc)_3I\cdot I_2$ (R = Me, Et, Bzl),[42,43] and $Zr(acac)_3X$ (X = Cl, Br).[44] In contrast, the analogous $CpM(Me_2dtc)_3$,

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Table VII. Symmetry of Valence Orbitals in C_{5v} Pentagonal-Bipyramidal and C_s Capped-Trigonal-Prismatic $M(Me_2dtc)_3X$ (X = Cp, Cl) Complexes

valence orbitals	C_{5v}	C_s
metal orbitals	$3a_1 + 2e_1 + e_2$	$6a' + 3a''$
s	a_1	a'
p	$a_1 + e_1$	$2a' + a''$
d	$a_1 + e_1 + e_2$	$3a' + 2a''$
	$CpM(Me_2dtc)_3$	
ligand orbitals	$3a_1 + 2e_1 + e_2$	$5a' + 4a''$
π(Cp)	$a_1 + e_1$	$2a' + a''$
$\sigma(S_{eq})$[a]	$a_1 + e_1 + e_2$	$2a' + 2a''$
$\sigma(S_{ax}$ or $S_{xz})$[a]	a_1	$a' + a''$
	$M(Me_2dtc)_3Cl$	
ligand orbitals	$3a_1 + e_1 + e_2$	$4a' + 3a''$
σ(Cl)	a_1	a'
$\sigma(S_{eq})$	$a_1 + e_1 + e_2$	$2a' + 2a''$
$\sigma(S_{ax}$ or $S_{xz})$	a_1	$a' + a''$

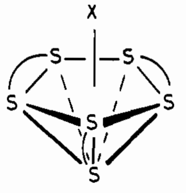
[a] S_{eq} and S_{ax} denote the equatorial and axial sulfur atoms. S_{xz} refers to the two sulfur atoms in **4** that lie in the *xz* plane.

$CpZr(\beta\text{-diketonate})_3$,[37,45,46] and $MoY(Me_2dtc)_3$ (Y = NO,[47,48] NS,[49] $N_2C_6H_4X$,[50] $NCPh_3$,[51] etc.) complexes are stereochemically rigid on the NMR time scale at readily accessible temperatures; indeed, most of these complexes are rigid at room temperature. The monothiocarbamate complex, $Ti(Me_2mtc)_3Cl$, exhibits an intermediate rate of rearrangement (T_c = −58 °C; $\Delta G^\ddagger(-58\ °C)$ = 10.8 kcal/mol).[52]

The greater rigidity of the cyclopentadienyl complexes in comparison with the analogous halo complexes is due, at least in part, to steric effects. The barrier to the double-facial twist mechanism should be higher in complexes that contain the more bulky Cp ligand. Moreover, the halo complexes may be able to rearrange via a CO transition state,[52] a path that is probably not available to the cyclopentadienyl complexes. The possibility of dissociation of a halide ion also needs to be considered. This appears to be the rearrangement mechanism for the $Ru(R_2dtc)_3X$ (X = Cl, I) complexes,[41,42] but it has been ruled out for $Ti(Me_2mtc)_3Cl$.[52]

The rigidity of the $MoY(Me_2dtc)_3$ complexes is especially interesting because the high rearrangement barrier in this case cannot be attributed to a steric effect. Davis et al.[48] have reported $\Delta G^\ddagger$ (87 °C) = 18.5 kcal/mol for $Mo(NO)(Me_2dtc)_3$; they could not rule out a polytopal rearrangement but favored a mechanism involving simultaneous Mo–S bond rupture and rotation about the $C\overset{\cdots}{-}N$ bond. Bishop et al.[50] have obtained $\Delta G^\ddagger(50\ °C)$ = 17.5–18.5 kcal/mol for the aryldiazenido complexes, $Mo(N_2C_6H_4X)(Me_2dtc)_3$ (X = *p*-OMe, *p*-Me, H, *p*-Cl, *m*-NO_2, *p*-NO_2); they preferred a polytopal rearrangement on the basis of relatively small substituent effects and values of $\Delta S^\ddagger$ near zero. No attempt was made in these studies to distinguish processes Ie, Iu, and II. Nevertheless, it is interesting to note that the $\Delta G^\ddagger$ values for the $MoY(Me_2dtc)_3$ complexes are very similar to those for process II in $CpTi(Me_2dtc)_3$ (Table V). It is tempting to suggest that the $MoY(Me_2dtc)_3$ complexes also rearrange by a double-facial twist mechanism.

The high barrier to rearrangement in the $MoY(Me_2dtc)_3$ complexes is presumably due to an electronic effect, which suggests that electronic effects may also contribute to the barrier in the $CpM(Me_2dtc)_3$ complexes. Indeed, Pinnavaia et al.[37] have proposed that the greater rigidity of $CpZr(\beta\text{-diketonate})_3$ complexes relative to the analogous $Zr(acac)_3Cl$ complex[44] is due to the fact that the Cp ligand interacts with three valence orbitals on the metal while the Cl atom most likely uses only one. To see how the bonding requirements of the Cp and Cl ligands might affect the barrier to a double-facial twist mechanism, we consider in Table VII the symmetry of the metal and ligand valence orbitals in $M(Me_2dtc)_3X$ (X = Cp, Cl) complexes having C_{5v} PB geometry **3** and C_s CTP geometry **4**. The metal s, p, and d valence orbitals transform as $3a_1 + e_1 + e_2$ in C_{5v} and as $6a' + 3a''$ in C_s. The $CpM(Me_2dtc)_3$ (M = Ti, Zr, Hf) complexes are 18-electron complexes, and the three occupied Cp π orbitals and six sulfur σ orbitals transform as $3a_1 + 2e_1 + e_2$ in C_{5v} but as $5a' + 4a''$ in C_s. Thus, there is a nice match between the symmetries of the metal and ligand orbitals in the PB ground state, but in the CTP transition state, the metal is short one orbital of a'' symmetry. In particular, the metal d_{xz} orbital, which can be used exclusively for bonding to the Cp ligand in **3**, must be shared between the Cp ligand and the two sulfur atoms lying in the *xz* plane in **4**. The corresponding weakening of the bonding in the CTP will increase the barrier to rearrangement via the double-facial twist mechanism. On the other hand, in the 14-electron $Ti(Me_2dtc)_3Cl$ complex, only seven metal orbitals are needed to interact with the ligand σ orbitals. The ligand orbitals transform as $3a_1 + e_1 + e_2$ in C_{5v} and as $4a' + 3a''$ in C_s, and there are sufficient metal valence orbitals of these symmetries in both PB and CTP geometries. This symmetry argument predicts that, other things being equal, the barrier to the double-facial twist should be higher for 18-electron d^0 complexes than for 14-electron d^0 complexes.



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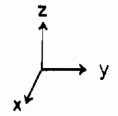

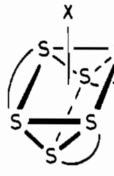

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A relatively high barrier for the $MoY(Me_2dtc)_3$ complexes is consistent with this picture since, in these compounds also, 18 valence electrons are involved in the bonding. In $Mo(NO)(Me_2dtc)_3$, for example, the occupied d_{xz} and d_{xy} orbitals of Mo(II) are stabilized by interaction with the π^* orbitals of NO^+.[53] The stabilization of the d_{xz} orbital will decrease on going from the PB to the CTP, thus increasing the rearrangement barrier for the double-facial twist mechanism.

Acknowledgment. The support of this research by National Science Foundation Grant GP-30691X is gratefully acknowledged. R.C.F. thanks Dr. M. L. H. Green for generous hospitality during a period of sabbatical leave.

Registry No. $CpTi(Me_2dtc)_3$, 67891-22-9; $CpZr(Me_2dtc)_3$, 61113-31-3; $CpHf(Me_2dtc)_3$, 74822-09-6; $Na(Me_2dtc)$, 128-04-1; Cp_2TiCl_2, 1271-19-8; Cp_2ZrCl_2, 1291-32-3; Cp_2HfCl_2, 12116-66-4; $Me_2NC(S)S{-}SC(S)NMe_2$, 137-26-8.

Supplementary Material Available: Table S1 giving rate constants for methyl group exchange in $CpTi(Me_2dtc)_3$ in various solvents (2 pages). Ordering information is given on any current masthead page.

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