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Synthesis and Molecular Rearrangements of (η^5-Pentamethylcyclopentadienyl)tris(*N*,*N*-dimethyldithiocarbamato)zirconium(IV)

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(η^5-Pentamethylcyclopentadienyl)tris(*N*,*N*-dimethyldithiocarbamato)zirconium(IV), $Cp^*Zr(Me_2dtc)_3$, has been prepared by reaction of $(Cp^*ZrCl_3)_x$ with anhydrous $Na(Me_2dtc)$ in dichloromethane and has been characterized by IR and ^1H NMR spectroscopy. The complex has a pentagonal-bipyramidal structure in which the Cp* ligand occupies an axial position. Variable-temperature ^1H NMR studies have afforded rate constants for three kinetic processes: (i) exchange of dithiocarbamate methyl groups between inequivalent sites within the equatorial ligands (process Ie), (ii) exchange of dithiocarbamate methyl groups within the unique ligand (process Iu), and (iii) exchange of the equatorial and unique ligands (process II). $Cp^*Zr(Me_2dtc)_3$ and the analogous $CpZr(Me_2dtc)_3$ complex have similar rates for processes Ie and Iu, but process II is appreciably slower in the more crowded Cp* derivative. These results are in accord with a ligand-centered C=N bond rotation mechanism for processes Ie and Iu and a metal-centered polytopal rearrangement for process II.

Introduction

Previous papers from this laboratory have described X-ray[1,2] and NMR[3] studies of (η^5-cyclopentadienyl)tris(*N*,*N*-dimethyldithiocarbamato) complexes, $CpM(Me_2dtc)_3$ (M = Ti, Zr, Hf; Cp = η^5-C_5H_5). These complexes have a seven-coordinate pentagonal-bipyramidal structure in which the η^5-cyclopentadienyl ligand occupies an axial position. Variable-temperature ^1H NMR spectra of the $CpM(Me_2dtc)_3$ complexes exhibit evidence of three kinetic processes: (i) exchange of methyl groups within the equatorial ligands, (ii) exchange of methyl groups within the unique ligand, and (iii) exchange of the equatorial and unique ligands. For the latter process, we have proposed a polytopal rearrangement mechanism proceeding through a capped-trigonal-prismatic transition state.[3] In order to test this suggestion further, we have prepared and studied variable-temperature ^1H NMR spectra of the more crowded η^5-pentamethylcyclopentadienyl analogue $Cp^*Zr(Me_2dtc)_3$.

Experimental Section

Reagents. Sodium *N*,*N*-dimethyldithiocarbamate dihydrate, $Na(Me_2dtc)\cdot 2H_2O$, (Alfa) was dried in vacuo over phosphorus pentoxide at 110 °C until the IR spectrum no longer showed a water band near 3500 cm^{-1}. $(Cp^*ZrCl_3)_x$ was prepared by reaction of $ZrCl_4$ and LiCp* in toluene at reflux[4] and was purified by sublimation at 180 °C (0.8 Torr) [lit.[4] 160 °C (10^{-4} Torr)]. Solvents were dried by refluxing for at least 24 h over calcium hydride and were distilled immediately prior to use. $Cp^*Zr(Me_2dtc)_3$ was prepared and subsequently handled under a dry nitrogen atmosphere.

(η^5-Pentamethylcyclopentadienyl)tris(*N*,*N*-dimethyldithiocarbamato)zirconium(IV), $Cp^*Zr(Me_2dtc)_3$. A mixture of $(Cp^*ZrCl_3)_x$ (2.00 g, 6.01 mmol) and $Na(Me_2dtc)$ (2.67 g, 18.6 mmol) in 50 mL of dichloromethane was stirred for 16 h at room temperature. The mixture was filtered, and the very pale green filtrate was pumped to dryness. The resulting white residue was dissolved in ~10 mL of dichloromethane, and hexane (30 mL) was added slowly. Cooling the solution to 5 °C for 12 h afforded colorless crystals of $Cp^*Zr(Me_2dtc)_3{\cdot}xCH_2Cl_2$. The dichloromethane was pumped off, yielding $Cp^*Zr(Me_2dtc)_3$ as a white powder (2.85 g, 81%); upon heating, the compound darkens above 230 °C, but does not melt below 260 °C. Anal. Calcd for $(C_{10}H_{15})Zr(C_3H_6NS_2)_3$: C, 38.87; H, 5.67; N, 7.16. Found: C, 38.74; H, 5.56; N, 7.16. ^1H NMR ($CDCl_3$): δ 3.34 (6 H, CH_3), 3.30 (3 H, CH_3), 3.29 (6 H, CH_3), 3.26 (3 H, CH_3), 1.91 (15 H, C_5Me_5). IR (Nujol mull) (cm^{-1}): ν(C=N) 1511 s; ν(C=S) 995 m, 988 m; ν(Zr—S) 347 m; other bands 1253 m, 1128 s, 584 w, 453 w, 237 w.

Physical Measurements. Infrared spectra were recorded in the 4000–400-cm^{-1} region with a Perkin-Elmer 337 grating spectrophotometer and in the 700–200-cm^{-1} region with an IBM FT/98 Fourier transform spectrometer. Proton chemical shifts were measured with a Bruker WM-300 300-MHz spectrometer. Variable-temperature ^1H NMR spectra of sealed, degassed chlorobenzene-d_5 solutions of $Cp^*Zr(Me_2dtc)_3$ were obtained at 400 MHz with a Varian XL-400 spectrometer.

Table I. Rate Constants (s^{-1}) for Dithiocarbamate Methyl Group Exchange in $Cp^*Zr(Me_2dtc)_3$[a]

temp, °C	k_{ab}	k_{cd}	k_{ad}
45.9		1.97	
50.9		3.09	
55.9		5.00	
60.9		7.76	
65.9		12.4	
71.0	3.23	18.5	
76.0	4.82	27.5	
81.1	7.57	37.4	
85.1	10.3	50.8	
89.1	15.0	68.1	
93.1	19.7	89.3	
97.2	26.5	118	
113.5	82.1	336	
117.6	106	431	
122.6	144	552	0.90
127.7	175	720	1.55
132.8	248	902	2.51

[a] 0.034 M in chlorobenzene-d_5. Variation in resonance frequencies (Hz at 400 MHz) and T_2 values (s) from 45.9 to 132.8 °C: $\nu_a = 0.00$, $T_2 = 0.349–0.293$; $\nu_b = 25.62–26.69$, $T_2 = 0.349–0.293$; $\nu_c = 26.34–17.96$, $T_2 = 0.368–0.372$; $\nu_d = 61.41–54.89$, $T_2 = 0.368–0.372$.

Rate constants for exchange of dithiocarbamate methyl groups among the inequivalent environments of $Cp^*Zr(Me_2dtc)_3$ were determined by comparison of experimental spectra with theoretical spectra calculated with use of the total line-shape program DNMR5.[5] Observed and calculated spectra were compared with respect to line widths at three-fourths ($w_{3/4}$), one-half ($w_{1/2}$), and one-fourth ($w_{1/4}$) maximum amplitude. Relaxation times, $T_2 = (\pi w_{1/2})^{-1}$, and chemical shifts in the absence of exchange were determined by plotting log $w_{1/2}$ vs $1/T$ and $\delta\nu$ vs $1/T$, respectively, and then linearly extrapolating these plots from the slow-exchange region into the coalescence region. T_2 values for the two best resolved resonances, the lowest field line (due to a methyl group in the equatorial ligand) and the highest field line (due to a methyl group in the unique ligand), are similar and exhibit relatively little temperature dependence. The other two dithiocarbamate methyl resonances overlap; it was assumed that both equatorial methyl groups have the same T_2 values and that both methyl groups in the unique ligand have the same T_2 values. The temperature dependence of the chemical shifts is substantial; the chemical shifts and T_2 values used in calculating the theoretical line shapes are given in the footnotes to Table I.

Results and Discussion

Synthesis and Characterization. $Cp^*Zr(Me_2dtc)_3$ was prepared in 81% yield by reaction in dichloromethane of $(Cp^*ZrCl_3)_x$ with

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(5) Quantum Chemistry Program Exchange, Indiana University.

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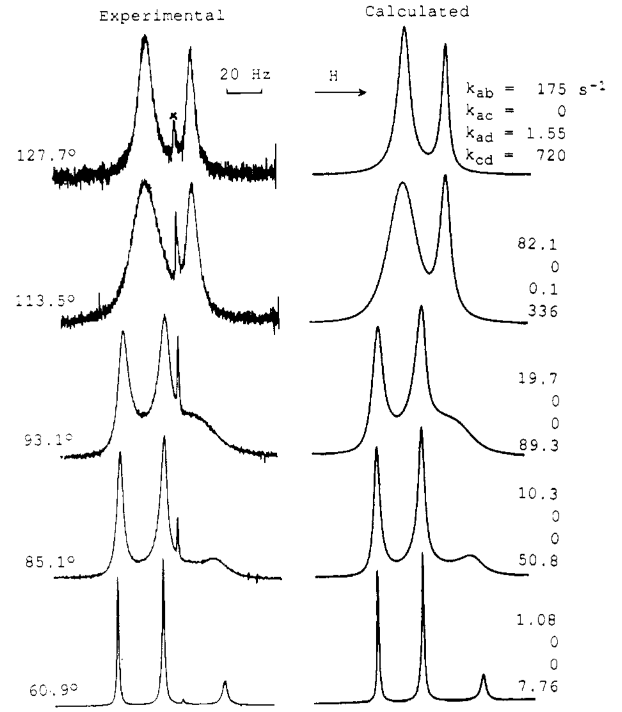
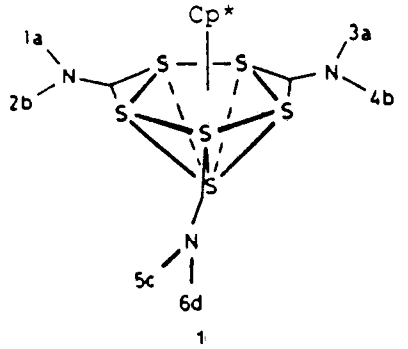


Figure 1. Observed and calculated ^{1}H NMR line shapes for the dithiocarbamate methyl resonances of Cp*Zr(Me$_2$dtc)$_3$, 0.034 M in chlorobenzene-d_5 at 400 MHz. The resonance marked with an × is due to an impurity.

3 equiv of anhydrous sodium *N*,*N*-dimethyldithiocarbamate. The compound was isolated from dichloromethane–hexane as colorless crystals of a dichloromethane solvate, Cp*Zr(Me$_2$dtc)$_3$·xCH$_2$Cl$_2$, and it changed to a white powder upon pumping off the solvent. Cp*Zr(Me$_2$dtc)$_3$ exhibits the usual, characteristic dithiocarbamate IR bands: $\nu(\mathrm{C{\cdots}N})$ 1511, $\nu(\mathrm{C{\cdots}S})$ 995 and 988, and ν(Zr—S) 347 cm^{-1}. The ^{1}H NMR spectrum of Cp*Zr(Me$_2$dtc)$_3$ in CDCl$_3$ solution at room temperature displays four dithiocarbamate methyl resonances of relative intensity 2:1:2:1, consistent with a pentagonal-bipyramidal structure **1** in which the pentamethylcyclopentadienly ligand occupies an axial position. The numbers in structure **1** label the dithiocarbamate methyl groups, and the letters label the inequivalent environments.



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Molecular Rearrangements. Variable-temperature ^{1}H NMR spectra of Cp*Zr(Me$_2$dtc)$_3$ in chlorobenzene-d_5 were studied at 400 MHz in the temperature region 5–138 °C. Observed and calculated spectra at selected temperatures are presented in Figure 1. At the lower temperatures (not shown), the dithiocarbamate methyl region exhibits four resonances of relative intensity 2:2:1:1. However, because of the temperature dependence of the chemical shifts in the absence of exchange, the two midfield resonances overlap at temperatures above 40 °C, giving an apparent three-line (2:3:1) spectrum. The two resonances of relative intensity 1:1 broaden first, above 45 °C, and coalescence into a time-averaged line at ~93 °C. The two resonances of relative intensity 2:2 broaden above 55 °C and merge into a time-averaged peak at ~107 °C. These two time-averaged resonances sharpen with increasing temperature and then begin to broaden at 138 °C, the limit of our measurements.

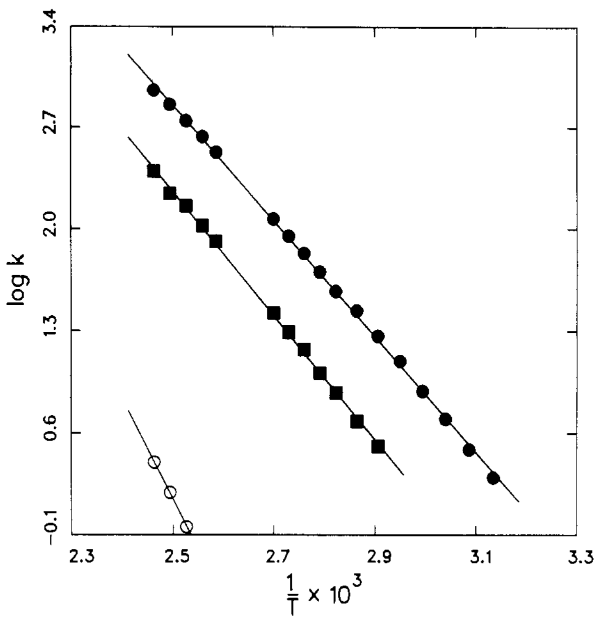

Figure 2. Arrhenius plots for exchange of dithiocarbamate methyl groups in Cp*Zr(Me$_2$dtc)$_3$, 0.034 M in chlorobenzene-d_5: ●, process Iu; ■, process Ie; ○, process II.

The variable-temperature spectra clearly exhibit evidence of two distinct kinetic processes: (i) exchange of methyl groups between inequivalent sites c and d (cf. structure **1**) within the unique dithiocarbamate ligand and (ii) exchange of methyl groups between sites a and b within the equatorial ligands. We refer to these processes as Iu and Ie, in accord with the nomenclature of ref 3. The broadening of the two time-averaged resonances at 138 °C and detailed line-shape analysis suggest the presence of a third, higher, temperature process (process II), which exchanges the unique and the equatorial ligands. In the case of CpZr(Me$_2$dtc)$_3$, process II is fast enough to give a single time-averaged resonance at ~85 °C (at 90 MHz).[3] Process II is slower in the pentamethylcyclopentadienyl derivative, and coalescence to a single methyl resonance does not occur within the temperature range of our measurements.

The kinetic and permutational analysis worked out for the pentagonal-bipyramidal CpM(Me$_2$dtc)$_3$ (M = Ti, Zr, Hf) complexes[3] applies to Cp*Zr(Me$_2$dtc)$_3$ as well. For exchange of methyl groups among the four sites of structure **1**, four independent rate constants are required, e.g. k_{ab}, k_{cd}, k_{ac}, and k_{ad}. At temperatures below 113 °C, spectra of Cp*Zr(Me$_2$dtc)$_3$ could be fit (cf. Figure 1) with just two independent rate constants, k_{ab} and k_{cd}, corresponding to processes Ie and Iu, respectively. Line-shape parameters for the lowest field resonance were employed for determination of k_{ab}, and line-shape parameters for the highest field resonance were used for determination of k_{cd}.

Above 113 °C, rate constants for process II (k_{ac} and/or k_{ad}) were included, and line-shape parameters for both time-averaged resonances were compared with those for the calculated spectrum until a best fit was obtained. Because k_{ab} is so much larger than k_{ac} and k_{ad}, it was not possible to tell if (i) $k_{ac} = k_{ad} \neq 0$, (ii) $k_{ac} \neq k_{ad} = 0$, or (iii) $k_{ad} \neq k_{ac} = 0$. The rate constants reported in Table I were obtained by assuming permutational mechanism A$_{11}$[3] ($k_{ad} \neq k_{ac} = 0$) because A$_{11}$ corresponds to the physical mechanism (vide infra) that we consider to be most likely for the ligand-exchange process.

Arrhenius and Eyring activation parameters were determined from the least-squares straight lines of log k vs $1/T$ plots (Figure 2) and log (k/T) vs $1/T$ plots, respectively. The activation parameters are presented in Table II along with coalescence temperatures and values of k and ΔG^* at a common temperature in the coalescence region. Because the coalescence temperature for process II is well above the temperature range studied, only a few

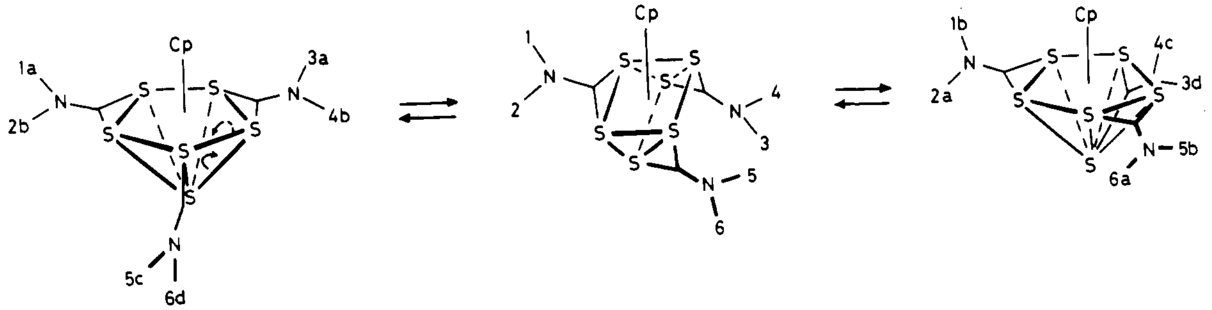

Figure 3. Double-facial twist mechanism for exchange of equatorial and unique ligands (process II). Numbers label dithiocarbamate methyl groups, and letters label the inequivalent environments.

Table II. Kinetic Data for Dithiocarbamate Methyl Group Exchange in $Cp^*Zr(Me_2dtc)_3$[a]

	process Ie	process Iu	process II
T_c,[b] °C	~107	~93	>137.8
$\Delta G^{\ddagger}(T_c)$, kcal/mol	19.5 ± 0.1	18.4 ± 0.1	
$\Delta H^{\ddagger}$, kcal/mol	18.8 ± 0.5	17.5 ± 0.3	31 ± 11
$\Delta S^{\ddagger}$, eu	−1.8 ± 1.3	−2.3 ± 0.7	20 ± 28
E_a, kcal/mol	19.5 ± 0.5	18.2 ± 0.3	32 ± 11
log A	12.9 ± 0.3	12.8 ± 0.2	18 ± 6
$\Delta G^{\ddagger}$(122.6 °C), kcal/mol	19.5 ± 0.1	18.4 ± 0.1	23.5 ± 0.2
k(122.6 °C), s^{-1}	144 ± 18	573 ± 68	0.94 ± 0.24

[a] In chlorobenzene-d_5 at 400 MHz. The uncertainties are random errors estimated at the 95% confidence level. [b] Coalescence temperature.

rate constants in the relatively slow exchange region could be determined for process II. Activation parameters for process II are estimates based on three data points and are subject to very large errors.

Rate constants for process Iu are slightly faster (by a factor of ~4) than those for process Ie, and rate constants for processes Iu and Ie are much faster (by a factor of ~10^2–10^3) than those for process II. For processes Iu and Ie, values of $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ are ~18–20 kcal/mol and values of $\Delta S^{\ddagger}$ are near zero. For process II, $\Delta G^{\ddagger}$(122.6 °C) is 23.5 ± 0.2 kcal/mol.

Possible mechanisms for processes Iu, Ie, and II have been discussed in detail in ref 3. Processes Iu and Ie probably involve rotation about the $\mathrm{C{=}N}$ partial double bond in the unique and equatorial dithiocarbamate ligands, respectively. Rotation about the $\mathrm{C{=}N}$ bond is a well-established process in methyl *N,N*-dimethyldithiocarbamate,[6,7] *N,N,N',N'*-tetramethylthiuram disulfide,[8] and $Cp_2ZrCl(Me_2dtc)$[9]; rotational barriers, $\Delta G^{\ddagger}$(25 °C), for these compounds are in the range 14.7–16.2 kcal/mol.[6-9] Although values of $\Delta G^{\ddagger}$(122.6 °C) for $Cp^*Zr(Me_2dtc)_3$ (Table II) are slightly higher (18.4 and 19.5 kcal/mol for processes Iu and Ie, respectively), they are nearly identical with values of $\Delta G^{\ddagger}$(70 °C) for $CpZr(Me_2dtc)_3$ (19.1 and 19.5 kcal/mol for processes Iu and Ie, respectively, in 1,1,2,2-tetrachloroethane solution[3]). Similar values of $\Delta G^{\ddagger}$ for the Cp and Cp* compounds would be expected if processes Iu and Ie are centered on the dithiocarbamate ligands. Also in support of a $\mathrm{C{=}N}$ rotation mechanism for processes Iu and Ie are the near-zero values of $\Delta S^{\ddagger}$.

Several lines of evidence suggest that process II in the $CpM(Me_2dtc)_3$ complexes involves a metal-centered polytopal rearrangement rather than a metal–sulfur bond rupture process; a double-facial twist mechanism (Figure 3) was proposed.[3] This mechanism involves a concerted rotation of two adjacent faces of the pentagonal bipyramid and proceeds through a capped-trigonal-prismatic transition state. A polytopal rearrangement should occur more slowly in the more crowded Cp* derivative than in the Cp analogue, whereas a Zr–S bond rupture process should be faster in the Cp* derivative. Comparison of the few rate constants that we were able to determine for process II in $Cp^*Zr(Me_2dtc)_3$ with extrapolated rate constants for $CpZr(Me_2dtc)_3$ indicates that process II is about 10 times slower in $Cp^*Zr(Me_2dtc)_3$. The slower rate of process II in the Cp* compound lends support to a polytopal rearrangement mechanism.

Registry No. IV, 110509-37-0; $(Cp^*ZrCl_3)_x$, 75181-07-6; $Na(Me_2dtc)_3$, 128-04-1.

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