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Synthesis and Spectroscopy of Acetato and Dithiocarbamate Complexes of Bis(cyclopentadienyl)zirconium(IV)

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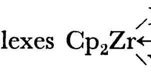
Several acetato and dithiocarbamate complexes of bis(cyclopentadienyl)zirconium(IV), $Cp_2Zr(X)OAc$ (X= Me, Cl, OAc), $Cp_2Zr(X)dmtc$ (X=Me, Cl; dmtc=S_2CNMe_2), and $Cp_2Zr(X)detc$ (X=Me, Cl; detc=S_2CNEt_2) have been prepared. Infrared, ^1H NMR and mass spectra of these complexes suggest the chelation of acetato (except for one acetato group in $Cp_2Zr(OAc)_2$) and dithiocarbamate groups, affording 18-electron configuration of the zirconium atom. The infrared spectrum of diacetate bis(cyclopentadienyl)zirconium(IV) shows that one acetato group acts as bidentate ligand and the other as unidentate. Remarkable benzene- and hexafluorobenzene-induced shifts were observed in the ^1H NMR signal of methyl group attached to the zirconium atom and the dithiocarbamate group.

The structure and reactivity of bis(cyclopentadienyl)zirconium(IV) complexes are of considerable interest in comparison with those of titanium analogs in view of the fact that the zirconium atom has larger ionic radius and smaller ionization potentials than the titanium atom.

Very few[1-3] 18-electron bis(cyclopentadienyl)zirconium complexes  $Cp_2Zr\overset{X}{\underset{Y}{\leftarrow}}L$, which are thought to be a reaction intermediate, have been reported. In these complexes the X, Y, and L groups take coplanar three coordinated configuration. Brainina *et al.*[4] reported the preparation of acetate chlorobis(cyclopentadienyl)zirconium(IV) but gave no spectral data. Wailes *et al.*[5] reported only ^1H NMR data of diacetate bis(cyclopentadienyl)zirconium(IV) in $CDCl_3$. Neither groups, however, made any suggestions for the structures.

This paper reports the preparation of several dithiocarbamate bis(cyclopentadienyl)zirconium(IV), with some spectroscopic discussion on their structures. No dithiocarbamate derivatives of bis(cyclopentadienyl)zirconium(IV) have been reported, except for monocyclopentadienylzirconium(IV) complex $CpZr(S_2CNMe_2)_3$.[6] The preparation of some acetate bis(cyclopentadienyl)zirconium(IV) is also reported.

Experimental

General. Preparation and recrystallization were carried out under argon or nitrogen atmosphere. Solvents were dried in the usual manner and distilled. Chlorobis(cyclopentadienyl)(methyl)zirconium(IV) and thallium(I) dimethyl and diethyldithiocarbamate were prepared by the procedures reported.[7,8] Thallium(I) acetate and thallium(I) dithiocarbamates were used as a fine powder stored over P_2O_5. Infrared and mass spectra were recorded on a Hitachi 225 spectrophotometer and a JEOL model JMS-07 spectrometer, respectively. ^1H NMR spectra were recorded on a JEOL model JNM-PS-100 spectrometer operating at 100 MHz and a Varian A60-D spectrometer operating at 60 MHz. Chemical shifts were measured relative to tetramethylsilane as an internal standard. Melting points were measured in sealed capillary tubes and are uncorrected.

Preparation. *Acetato Bis(cyclopentadienyl)(methyl)zirconium(IV)* **1**: Thallium(I) acetate (0.58 g, 2.2 mmol) was gradually added to a solution of chlorobis(cyclopentadienyl)(methyl)zirconium(IV) (0.54 g, 2 mmol) in 50 ml of dichloromethane and the mixture was stirred at room temperature for 4 h. The filtrate was evaporated *in vacuo*, and the yellow residue was recrystallized twice from benzene-hexane to give white crystals **1** (0.21 g, 35% yield). Am attempt to prepare **1** by the reaction of $(Cp_2ZrMe)_2O$[9] with Ac_2O was unsuccessful, although $Cp_2Zr(Cl)OAc$ was prepared[4] by the treatment of $(Cp_2ZrCl)_2O$ with Ac_2O.

Acetato Chlorobis(cyclopentadienyl)zirconium(IV) **2**: Dichlorobis(cyclopentadienyl)zirconium(IV) (0.58 g, 2 mmol) was treated with thallium(I) acetate (0.58 g, 2.2 mmol) to give **2** (0.40 g, 64% yield) after recrystallization twice from dichloromethane–hexane.

Diacetate Bis(cyclopentadienyl)zirconium(IV) **3**: Sodium acetate (0.36 g, 4.4 mmol) was added to a solution of dichloro bis(cyclopentadienyl)zirconium(IV) (0.58 g, 2 mmol) in 40 ml of benzene and the mixture was refluxed for 6 h with stirring. The yellow filtrate was evaporated *in vacuo*. The orange residue was recrystallized three times from benzene–hexane to give white crystals **3** (0.30 g, 45% yield).

Dimethyldithiocarbamate Bis(cyclopentadienyl)(methyl)zirconium(IV) **4**, *Dimethyldithiocarbamate Chlorobis(cyclopentadienyl)zirconium(IV)* **5**, *Diethyldithiocarbamate Bis(cyclopentadienyl)(methyl)zirconium(IV)* **6**, *and Diethyldithiocarbamate Chlorobis(cyclopentadienyl)zirconium(IV)* **7**: Complexes **4**—**7** were obtained as white crystals in 45(for **4**)—85%(for **7**) yield by the reaction of $Cp_2ZrMeCl$ or Cp_2ZrCl_2 with thallium(I)-dimethyl- or diethyldithiocarbamate in a similar way to

TABLE 1. ANALYTICAL DATA AND MELTING POINTS OF $Cp_2Zr(X)Y$

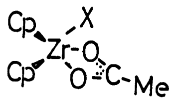
	Complexes	Mp(°C)	Found (Calcd) %		
			C	H	N
1	$Cp_2Zr(Me)OAc$	92—94	52.29 (52.84)	5.45 (5.35)	—
2	$Cp_2Zr(Cl)OAc$	137—138	45.06 (45.62)	4.04 (4.15)	—
3	$Cp_2Zr(OAc)_2$	100—101	49.65 (49.53)	4.62 (4.75)	—
4	$Cp_2Zr(Me)dmtc$[a]	156—158	46.93 (47.15)	5.35 (5.37)	4.01 (3.93)
5	$Cp_2Zr(Cl)dmtc$[a]	208 dec	41.22 (41.41)	4.22 (4.28)	3.65 (3.71)
6	$Cp_2Zr(Me)detc$[b]	131—132	50.80 (51.01)	5.96 (6.15)	3.23 (3.72)
7	$Cp_2Zr(Cl)detc$[b]	186 dec	44.05 (44.47)	4.95 (4.98)	3.43 (3.46)

a) dmtc=S_2CNMe_2. b) detc=S_2CNEt_2.

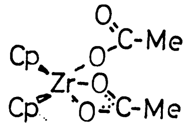
that for **1** and **2**.

Results and Discussion

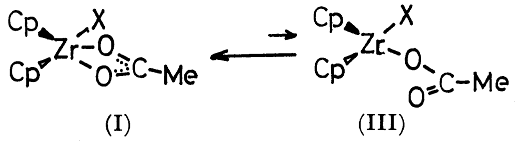
Acetato Derivatives (1—3). In the monoacetato complexes **1** and **2**, ν_{as}(OCO) and $\Delta(\nu_{as}-\nu_s)$ values (Table 2) suggest that the acetato group belongs to the category of the chelating structure[10] in the solid state. On the other hand, in the diacetate derivative **3** one acetato group acts as the bidentate ligand and the other as unidentate in the solid state. Bridging and ionic structures of the acetate groups are excluded on the basis of molecular weight measurements and negligible molar conductivities (Table 3). In mass spectra of these complexes no ion heavier than the parent ion or the (M–Me)+ ion was detected (Table 4). The results suggest the following structures I and II for complexes **1**—**3** in the solid state. The IR spectra of **1** and **2** in CH_2Cl_2, however, give additional weak bands at *ca.* 1640 and 1300 cm^{-1}. The results indicate that there is some portion of III in equilibrium with I in CH_2Cl_2.



1 (X=Me)
2 (X=Cl)
(I)

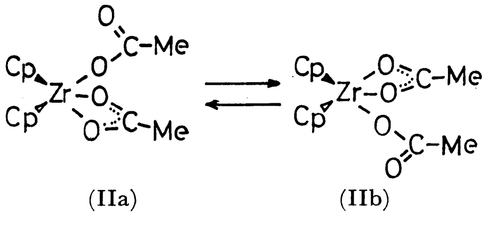


3
(II)



(I) (III)

The structure of **3** is of interest as compared with that of analogous titanium(IV) complex $Cp_2Ti(OAc)_2$.[11] In the latter both acetate groups are unidentate, although the bidentate acetate group was reported for Cp_2Ti^{III}-OAc.[12] The difference in structure of these diacetate complexes might be mainly due to the difference in their ionic radii (Ti(IV) 0.62—0.65 Å, Zr(IV) 0.79—0.87 Å). In the ^{1}H NMR spectrum of **3** methyl signals of the two acetate groups were observed as a singlet resonance even at −91 °C in CH_2Cl_2. The IR spectrum of **3** in CH_2Cl_2 shows little difference from that in the solid state. The IR and ^{1}H NMR data suggest that there is a rapid interconversion process IIa—IIb between two acetate groups in CH_2Cl_2.



(IIa) (IIb)

Table 2. IR data[a)] for the complexes (in cm^{-1})

Complexes	ν_{as}(OCO)	ν_s(OCO)[b)]	Δ[c)]	ν Zr–Me
1	1533	1467	66	440
2	1535	1465	70	—
3	1642 1540	1305 1480	337 60	—

Complexes	νC=N[d)]	νZr–S	νZr–Me
4	1512	358 355	425
5	1523	367	—
6	1495	360	423
7	1500	366	—

a) Nujol mulls. b) Hexachlorobutadiene mulls. c) $\Delta = \nu_{as}(OCO) - \nu_s(OCO)$. d) Reported νC=N values in unidentate dithiocarbamate compounds. Me_2NCS_2Me[13)] 1498; $(Me_2NCS_2)_2$[14] 1505; $Me_2NCS_2Na \cdot H_2O$[15)] 1480; Et_2NCS_2-Me[13)] 1489; $(Et_2NCS_2)_2$[16)] 1487; $Et_2NCS_2Na \cdot xH_2O$ 1475.

Table 3. Mol wt and molar conductivities of $Cp_2Zr(X)OAc$

Complexes	Mol wt[a)]	(Calcd)	Molar conductivity[b)] (× 10^{-3} M concn)
1	330	(295)	0.032 (1.03)
2	325	(316)	0.020 (1.02)
3	360	(340)	0.074 (0.59)

a) Determined cryoscopically in C_6H_6.
b) Ω^{-1} cm^2 mol^{-1} in CH_2Cl_2 at 25 °C.

Table 4. Mass spectral data[a)] for $Cp_2Zr(X)Y$

Complexes	Temp °C	*m/e* (intensity) assignment
1	100	279(100) $[M-Me]^+$, 43(10)$MeC^+{=}O$
2	150	314(13)M^+, 279(15) $[M-Cl]^+$, 249 (100) $[M-Cp]^+$, 43(19)$MeC^+{=}O$
3	100	273(100) $[M-Cp]^+$, 43(33)$MeC^+{=}O$
4	150	340(100) $[M-Me]^+$, 88(7)$Me_2NC^+{=}S$
5	200	375(6)M^+, 340(22) $[M-Cl]^+$, 310 (100) $[M-Cp]^+$, 88(15)$Me_2NC^+{=}S$
6	130	368(100) $[M-Me]^+$, 116(17)$Et_2NC^+{=}S$
7	150	403(5)M^+, 368(2) $[M-Cl]^+$, 338(100) $[M-Cp]^+$, 116(2)$Et_2NC^+{=}S$

a) Ionizing voltage: 30 eV.

Dithiocarbamate Derivatives (4—7). IR spectra: The νC=N frequency of complexes **4**—**7** together with that of methyl dialkyldithiocarbamate, tetraalkylthiuram disulfide, and sodium dialkyldithiocarbamate is summarized in Table 2. The IR spectra of complexes **4**—**7** in CH_2Cl_2 show little difference from those in the solid state. Complexes **4**—**7** exhibited the νC=N band at higher frequency than the corresponding unidentate dithiocarbamate compounds containing the same *N,N*-dialkyl group. The frequency of this band of **4**—**7** is nearly the same as that of $CpZr(S_2CNR_2)_3$,[6,17)] in which chelation of the dithiocarbamate groups has been demonstrated by X-ray crystal analysis.[6)] Thus the higher νC=N values suggest the chelation of dithiocarbamate groups in the complexes.

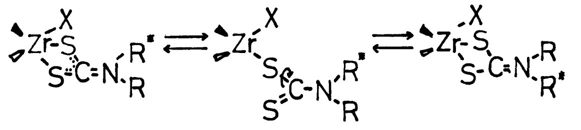
^{1}H NMR Spectra and the Structures: One sharp N–Me proton signal was observed at 23 °C in CH_2Cl_2 in complexes **4** and **5**, the latter showing two N–Me proton signals under 0 °C. One kind of sharp N–CH_2 and two

Table 5. ^{1}H NMR data[a] for complexes in CH_2Cl_2, C_6D_6, and C_6F_6 (Zr) = Cp_2Zr

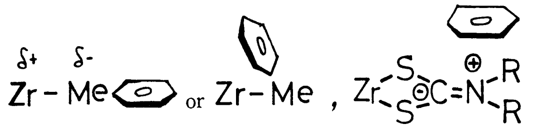
Complexes		Assignment	CH_2Cl_2[b]	C_6D_6[b]	C_6F_6[c]	Δ[d]	Δ^*[e]
1	(Zr)OAc Me	Cp	5.92	5.73	5.85	+0.19	−0.07
		C–Me	1.80	1.61	1.80	+0.19	+0.00
		Zr–Me	0.00	0.43	−0.35	−0.43	+0.35
2	(Zr)OAc Cl	Cp	6.20	5.86		+0.34	
		C–Me	1.96	1.61		+0.35	
3	(Zr)OAc OAc	Cp	6.23	5.98		+0.25	
		C–Me	2.00	1.82		+0.18	
4	(Zr)dmtc Me	Cp	5.79	5.73	5.65	+0.06	+0.14
		N–Me	3.25[f]	2.69	3.40	+0.53	−0.15
		Zr–Me	−0.06	0.47	−0.43	−0.53	+0.37
5	(Zr)dmtc Cl	Cp	6.09	5.96		+0.13	
		N–Me	3.30[g]	2.58		+0.72	
6	(Zr)detc Me	Cp	5.88	5.72	5.70	+0.16	+0.18
		N–CH_2	3.72(q)	3.38(q) 3.36(q)	3.92(q)	+0.35	−0.20
		C–Me	1.19(t)[h] 1.21(t)[h]	0.89(t) 0.86(t)	1.40(t)	+0.33	−0.20
		Zr–Me	−0.06	0.47	−0.43	−0.53	+0.37
7	(Zr)detc Cl	Cp	6.07	6.00		+0.07	
		N–CH_2	3.75(q)	3.37(q)		+0.38	
		C–Me	1.26(t)[h] 1.24(t)[h]	0.86(t)		−0.39	
	$(Zr)Me_2$[i]	Cp	6.08	5.80	6.05	+0.28	+0.03
		Zr–Me	−0.40	−0.14	−0.57	−0.26	−0.17
	(Zr)MeCl	Cp	6.22	5.73		+0.49	
		Zr–Me	0.28	0.32		−0.04	
	$(Zr)Cl_2$	Cp	6.68	5.83		+0.85	

a) δ value (ppm); (q) quartet; (t) triplet; other, sharp singlet except as noted. b) Recorded on a JEOL model JNM-PS-100 spectrometer at 23 °C operating at 100 MHz. c) Recorded on a Varian A-60-D spectrometer at 40 °C operating at 60 MHz. d) $\Delta = \delta(CH_2Cl_2) - \delta(C_6D_6)$. e) $\Delta^* = \delta(CH_2Cl_2) - \delta(C_6F_6)$. f) Singlet even at −97 °C. g) Coalesces to doublet at 0 °C. h) Coalesces to triplet at about 34 °C. i) Ref. 7.

sorts of sharp C–Me proton signals were observed at 23 °C in complexes **6** and **7**. The C–Me proton signals coalesced at 34 °C. On the other hand, very broad N-Me and N-CH_2 proton signals were observed in Me_2NCS_2Me and Et_2NCS_2Me at 23 °C in CH_2Cl_2, due to the high rotational barrier around the S_2C=N bond.[13] The chemical shifts of *N*-alkyl protons of complexes **4**—**7** are nearly the same as those of $CpZr(S_2CNR_2)_3$. The IR and ^{1}H NMR data suggest that these dithiocarbamate groups complexes **4**—**7** are chelating in the solid state and in CH_2Cl_2. The two *N*-alkyl protons might be magnetically equivalent by the following equilibration IVa—IVc over −97 °C in **4**, 0 °C in **5**, and 34 °C in **6** and **7**.


(IVa) (IVb) (IVc)

Chemical Shifts of Cp Proton, and Solvent-induced Shifts. Table 5 shows ^{1}H NMR data for complexes **1**—**7** in CH_2Cl_2, C_6D_6, and C_6F_6 together with those for Cp_2ZrMe_2, $Cp_2Zr(Me)Cl$, Cp_2ZrCl_2. In a series of $Cp_2Zr(X)$-OAc the order of high field shifts of Cp proton in CH_2Cl_2 is X=Me>Cl≥OAc (unidentate). Similarly in Cp_2Zr(X)Me the order is X=dmtc>detc>OAc(chelating)>Me>Cl, and in Cp_2Zr(X)Cl it is X=detc≥dmtc>OAc-(chelating)≥Me>Cl. Thus the overall order of high field shifts of the Cp proton in CH_2Cl_2 is as follows: dmtc≥detc>OAc(chelating)≥Me>Cl≥OAc(unidentate). The signals of Cp proton in bis(cyclopentadienyl)-zirconium(IV) complexes in $CDCl_3$ shift in general to high field in line with electron donating effect of ligands on the zirconium atom.[18] The order is in line with that of electron donating ability of ligands. Remarkably low field shifts for (Zr)–CH_3 proton signals and high field shifts for N–CH_3 proton signals in dithiocarbamate groups were observed in benzene (Tables 5). The specific benzene-induced solvent shifts are interpreted by the following benzene-solute stereospecific interaction. Benzene–dithiocarbamate interaction has been reported by Hatton and Richards[19–20] and Honda *et al.*[21–22] Hexafluorobenzene[23–24] induces low field shifts of protons at the electron-deficient site in a solute molecule and high field shifts of protons at the electron-rich site, the direction of these shifts being reversed in ben-



zene. In our zirconium complexes appreciable hexafluorobenzene induced shifts were also observed in (Zr)–CH_3, N–CH_3, and N–CH_2CH_3 proton signals.

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