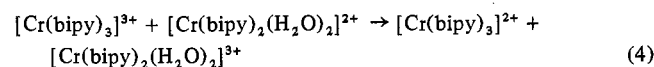


by Tucker and coworkers were influenced by slow oxidation of the reduced materials, it does indicate that slow oxidation together with continual reduction can produce similar results.

Various methods of oxidation of the reduced bis complex produced startlingly different results. Four different methods of oxidation are described in the Experimental Section. It has already been shown that rapid, oxygen gas oxidation (method 1) produced 0.5 equiv of $[\text{Cr}(\text{bipy})_3]^{3+}$ when no free bipyridine was present in the original solution and produced 1 full equiv of $[\text{Cr}(\text{bipy})_3]^{3+}$ when 1 equiv of free bipyridine was present in the original solution.

Slower methods of oxidation (method 2) did not result in formation of a tris complex. Spectral and polarographic properties characteristic of the tris complex were noticeably absent. Polarograms of the oxidized solutions (Figures 5C, 6B, 6C) were similar to but not identical with a polarogram of the starting complex, $[\text{Cr}(\text{bipy})_2\text{Cl}_2]^+$. We believe the product resulting from the slow oxidation methods was diaquobis(2,2'-bipyridine)chromium(III). The polarogram of our oxidation product was identical with the polarogram of this complex.^{10,21} That this should be the case can be seen by examining reactions 1-3 described above and reaction 4



described in a previous electrochemical study^{10,12} of $[\text{Cr}(\text{bipy})_3]^{3+}$. According to reactions 1-3, reduction of the bis complex, $[\text{Cr}(\text{bipy})_2\text{Cl}_2]^+$, ultimately produces some tris complex, $[\text{Cr}(\text{bipy})_3]^{2+}$, which is in rapid equilibrium with a re-

(21) D. M. Soignet, Ph.D. Dissertation, Louisiana State University in New Orleans, 1971.

duced bis complex, $[\text{Cr}(\text{bipy})_2(\text{H}_2\text{O})_2]^{2+}$. When oxidized slowly, any $[\text{Cr}(\text{bipy})_3]^{3+}$ produced reacts with unoxidized $[\text{Cr}(\text{bipy})_2(\text{H}_2\text{O})_2]^{2+}$ according to reaction 4. The tris chromium(II) complex is regenerated and the final oxidation product is the diaquobis complex. There is, of course, the possibility of direct oxidation of the bis complex but this is not important since it is present only in very small amounts since the combined equilibrium constant for reactions 2 and 3 strongly favors the tris complex.^{10,12} It can now be seen that $[\text{Cr}(\text{bipy})_3]^{3+}$ will be the final oxidation product only when the oxidation is performed in such a way that little or no reduced solution is allowed to mix with the already oxidized solution. Oxidation method 1 meets this requirement.

Electrochemical oxidation at -0.35 V (method 3) in the absence of oxygen produced only $[\text{Cr}(\text{bipy})_2(\text{H}_2\text{O})_2]^{3+}$ (Figures 5B, 6D) in the same manner as described for the slow oxygen and air oxidations.

Further successive one-electron reductions were performed at -1.08 and -1.13 V. Polarograms of the solutions resulting after each of these reductions are shown in Figure 1. The second one-electron reduction at -1.08 V produced a black suspension. Very little electroactive material was dissolved as evidenced by the small polarographic response (Figure 1C). Additional reduction at -1.13 V was, as expected, accomplished only very slowly and proceeded only to 0.6 electron per molecule. Again, the product was a black suspension. The black suspension is probably the tris(2,2'-bipyridine)chromium(0) complex described by Herzog and Schon.⁵ Rapid oxidation (method 1) produced almost quantitatively the tris complex $[\text{Cr}(\text{bipy})_3]^{3+}$.

Registry No. Dichlorobis(2,2'-bipyridine)chromium(III) chloride dihydrate, 26154-79-0; $[\text{Cr}(\text{bipy})_3]^{2+}$, 15276-15-0.

Contribution from the Laboratoire de Chimie de Coordination, Paris 5^e, France

Low-Frequency Infrared and Raman Spectra of π -Cyclopentadienyl Compounds of Titanium, Zirconium, and Hafnium

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The infrared and Raman spectra in the region $600\text{--}50\text{ cm}^{-1}$ are reported for the series of compounds CpTiX_3 and Cp_2MX_2 ($\text{M} = \text{Ti, Zr, Hf}$; $\text{X} = \text{Hal, Me}$; $\text{Cp} = \text{C}_5\text{H}_5$ ring). A comparative study of these spectra allows assignments to be made for the metal-ring and metal-ligand stretching modes.

Introduction

Although the wedge-shaped transition metal bis(cyclopentadienyl) complexes and the "open-sandwich" mono(cyclopentadienyls) are compounds of continuing interest, their vibrational properties have not yet been investigated with the same thoroughness as those of the ferrocene-type sandwich compounds. Thus, the metallocene dihalides Cp_2MX_2 ($\text{M} = \text{Ti, Zr, Hf}$; $\text{X} = \text{F, Cl, Br, I}$)¹ and the mono(cyclopentadienyl) trihalides CpTiX_3 ($\text{X} = \text{Cl, Br, I}$)²⁻⁴ have all been prepared,

but no definite assignments of the metal-ring vibrations have as yet been made, partly as a result of the paucity of Raman data. The study of these compounds is particularly interesting in view of their importance in polymerization catalysis and nitrogen fixation.

The recent preparation of Cp_2MMe_2 ($\text{M} = \text{Zr, Hf}$; $\text{Me} = \text{CH}_3$)⁵⁻⁷ has allowed us to study a series of compounds other than the halides, and this, together with new low-frequency

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Raman and infrared data, has permitted the assignment of many of the fundamental metal-ligand and ring tilt vibrations in the compounds CpTiX_3 ($X = \text{CH}_3, \text{Cl}, \text{Br}$) and Cp_2MX_2 ($M = \text{Ti}, \text{Zr}, \text{Hf}; X = \text{Me}, \text{F}, \text{Cl}, \text{Br}, \text{I}$). Our results are not altogether in agreement with recent assignments based only on infrared studies of the halides.⁸

Experimental Section

Materials. Cp_2MCl_2 compounds, purchased from Alfa Inorganics, were purified by sublimation or crystallization.

Cp_2MBr_2 compounds were prepared and purified by the method of Lappert and coworkers.¹

Cp_2MI_2 compounds were prepared by a novel procedure; HI gas was bubbled through solutions in benzene of the Cp_2MPh_2 ($M = \text{Ti}; \text{Ph} = \text{C}_6\text{H}_5$) or Cp_2MMe_2 ($M = \text{Zr}, \text{Hf}$) compounds, prepared from the respective dichlorides and phenyl- or methyl lithium. Evaporation of the solvent and subsequent sublimation gave compounds whose infrared and nmr spectra were identical with those given in literature for the diiodides.⁹

Cp_2TiF_2 was prepared as previously described¹⁰ from aqueous solutions of Cp_2TiCl_2 and NaF, and purified by sublimation.

$\text{Cp}_2\text{Ti}(\text{Me})_2$ was prepared and purified according to published procedures.¹¹ Nmr peaks were found at τ (ppm) 4.34 (Cp) and 10.05 (Me).

$\text{Cp}_2\text{M}(\text{Me})_2$ ($M = \text{Zr}, \text{Hf}$) compounds were prepared by the action of methyl lithium on the corresponding dichlorides suspended in anhydrous ethyl ether under nitrogen at -20° and were isolated as white crystalline compounds by solvent evaporation and sublimation at 80° (0.1 Torr). They were identified by their nmr spectra (peaks were found at τ (ppm) 3.29 and 4.00 (Cp) and τ 10.39 and 10.50 (Me), respectively).

CpTiCl_3 , purchased from Alfa Inorganics, was purified by passing HCl gas through a solution in diethyl ether prior to crystallization and sublimation.

CpTiBr_3 was obtained by a novel procedure by which Br_2 was added to an ethereal solution of CpTiMe_3 prepared *in situ* (see below) and isolated by solvent evaporation and subsequent sublimation at 120° (0.1 Torr).

$\text{CpTi}(\text{Me})_3$ was made by the method of Giannini and Cesca.¹² Nmr peaks for the product (in THF) were found at τ 3.75 (Cp) and 9.70 (Me), in agreement with the proposed composition.

Spectra. Infrared spectra in the region $600\text{--}300\text{ cm}^{-1}$ were scanned on a PE 225 grating spectrometer and samples prepared as Nujol mulls between CsBr plates with a CsBr reference, unless otherwise stated. Infrared spectra in the region $400\text{--}80\text{ cm}^{-1}$ were measured on a Beckman RIIC FS 720 interferometer as polyethylene disks. Raman spectra were run on a Coderg PHI spectrometer with a He-Ne laser source, between 50 and 800 cm^{-1} , either as solids or as solutions in THF or benzene, except where otherwise mentioned. Nmr spectra were run on a Varian A-60 spectrometer using TMS as the internal standard.

Results and Interpretation

Two recent papers have reported^{4,8} infrared spectra of titanium cyclopentadienyl alkoxides and cyclopentadienyl- and pentamethylcyclopentadienyltitanium trihalides, but no Raman results are given to corroborate assignments. Lappert and his coworkers¹ have presented the infrared spectra for all twelve group IVb bis(cyclopentadienyl) dihalides and also some Raman results but have made few assignments.

Our infrared spectra are substantially in agreement with those of the above authors for the compounds studied by them.

Problems arise in the interpretation of the spectra of the dihalides because the metal-ring and the metal-halogen stretching frequencies lie in the same region and because there is the possibility of interaction among the three A_1 modes $\nu(\text{M-Cp})$, $\nu(\text{M-Hal})$, and $\kappa(\text{M-Cp})$.¹³

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(12) H. Giannini and S. Cesca, *Tetrahedron. Lett.*, **14**, 19 (1960).

These difficulties are enhanced by the absence up to now of polarization data^{13a} and by the fact that practical difficulties arise due to the color or insolubility of certain halides and to their occasional decomposition or fluorescence in the laser beam.

In order to provide further information about the metal-ligand vibrations of the halides, it was decided in the present work to study the spectra of CpTiMe_3 and Cp_2MMe_2 ($M = \text{Ti}, \text{Zr}, \text{Hf}$) in the hope that the $\nu(\text{M-Me})$ vibrations would be readily identifiable and that they would not mix substantially with the skeletal modes.

It was found that the methyl compounds did not present the practical difficulties mentioned above and did indeed allow valuable information about the skeletal modes to be obtained.

I. CpTiX_3 Compounds. The results for these compounds are given in Table I. The analogous Zr and Hf compounds were not examined because of the difficulty of preparation; the trichlorides have been reported by Reid¹⁴ and we hope to examine these later.

The assignments have been made on the assumption that all these compounds have the "piano-stool" structure found for CpTiBr_3 ¹⁵ and $\text{CpMn}(\text{CO})_3$.¹⁶ For the assignment of the skeletal modes, an effective symmetry of C_{3v} was assumed (see for example ref 17).

The expected skeletal vibrations are thus $3 A_1 + 3 E$. In addition, these compounds should exhibit a ring tilt mode of E symmetry. Thus all seven expected bands should be Raman and infrared active.

CpTiMe_3 . As a result of the low thermal stability of this compound, only Raman data have thus far been obtained.

Raman and infrared studies on MeTiCl_3 ¹⁸⁻²⁰ and more recently on Me_2Ti ²¹ show the Ti-Me symmetric stretching frequency at 550 and 489 cm^{-1} , respectively. Also in $\text{CpMn}(\text{CO})_3$, a molecule of structure analogous to CpTiMe_3 , $\nu(\text{M-Cp}) A_1$ occurs as a very strong band in the Raman spectrum at 350 cm^{-1} .¹⁷

Thus $\nu(\text{Ti-Me}) A_1$ and $\nu(\text{Ti-Cp}) A_1$ in CpTiMe_3 may be expected around 500 and 350 cm^{-1} , respectively. The Raman spectrum exhibits two polarized bands at 517 and 357 cm^{-1} of strong intensity, which were attributed to these two modes without ambiguity. Moreover, no important mixing seems to occur between the two A_1 modes, which allows the important $\nu(\text{Ti-Cp}) A_1$ mode to be identified and its position in the other compounds to be predicted with a fair measure of certainty.

CpTiCl_3 . The recent vapor-phase Raman studies by Clark and coworkers²² show that $\nu(\text{Ti-Cl}) A_1$ in TiCl_4 is at 389

(13) We suggest that the ring tilt modes be designated $\kappa(\text{M-Cp})$ (from $\kappa\lambda\mu\omega = \text{incline}$) and use this designation throughout the paper.

(13a) Note Added in Proof. Assignments for metal-ring and metal-halogen vibrations in Cp_2MHal_2 compounds on the basis of infrared and Raman data were made in a paper by E. Maslowsky and K. Nakomoto [*Appl. Spectrosc.*, **18**, 25 (1971)] of which we became belatedly aware. Most of the assignments proposed here are in agreement with those made by these authors.

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Table I. Infrared and Raman Spectra of CpTiX_3 Compounds

Infrared	Raman	Assignments
CpTiCl_3^a		
454 s	460 w, dp	$\nu(\text{Ti-Cl})$ E
444 s	448 w, p	$\nu(\text{Ti-Cl})$ A_1
424 vs	432 w, dp	$\kappa(\text{Ti-Cp})$ E
383 w		na ^c
331 s	327 vs, p	$\nu(\text{Ti-Cp})$ A_1
	288 m, dp	na
167 w	166 m, dp	$\delta(\text{Cl-Ti-Cl})$ E
158 w		na
130 w	130 m, dp	$\delta(\text{Cp-Ti-Cl})$ E
125 m		na
68 w		na
CpTiBr_3^b		
422 m	424 m, p	$\nu[(\text{Ti-Br}) + (\text{Ti-Cp})]$ A_1
398 w	409 w, d	$\kappa(\text{Ti-Cp})$ E
355 s	363 w, dp	$\nu(\text{Ti-Br})$ E
286 w		na
259 m	270 m, dp	
238 w	240 vs, p	$\nu[(\text{Ti-Br}) + (\text{Ti-Cp})]$ A_1
138		
81		
78		
CpTiMe_3^a		
	517 s, p	$\nu(\text{Ti-Me})$ A_1
	357 s, p	$\nu(\text{Ti-Cp})$ A_1
	210 m, dp	na

^a Solutions in THF. ^b Solutions in benzene. ^c Not assigned.

cm^{-1} . La Lau¹⁹ reported $\nu(\text{Ti-Cl})$ A_1 in MeTiCl_3 at 391 cm^{-1} . The Raman spectrum of CpTiCl_3 shows only two polarized bands, that at 327 cm^{-1} being very strong and that at 448 cm^{-1} being weak. On the basis of the above, it is reasonable to assign the first to $\nu(\text{Ti-Cp})$ A_1 and the second to $\nu(\text{Ti-Cl})$ A_1 . The reversal of these assignments would place $\nu(\text{Ti-Cp})$ A_1 at 448 cm^{-1} , that is 91 cm^{-1} higher than in CpTiMe_3 . Such a considerable shift to higher frequencies in the trichloride would be difficult to justify, although it is hazardous to predict in these compounds the influence of the inductive effect of the ligand bound to the metal on the M-Cp stretching frequencies. This reversal would lead also to inconsistent results in the assignments made for the dihalides Cp_2MX_2 (*vide infra*).

The bands at 424 cm^{-1} in the infrared spectrum and at 432 cm^{-1} in the Raman spectrum correspond to similar bands in the region 400-430 cm^{-1} in the mono- and the bis(cyclopentadienyl)titanium compounds examined and are thus assigned to the asymmetric ring tilt, since this mode is almost independent of the nature of the other ligands present; also this frequency is close to 372 cm^{-1} assigned by Parker²³ to the same mode in $\text{CpMn}(\text{CO})_3$. The remaining assignments are tentative.

CpTiBr_3 . This compound was found to be unstable in THF solution in the laser beam, as were the other Br compounds. The Raman spectrum in benzene was satisfactory.

Clark²² gave $\nu(\text{Ti-Br})$ A_1 in TiBr_4 at 231.5 cm^{-1} . If the ratio $\nu(\text{Ti-Br})/\nu(\text{Ti-Cl})$ is taken as 0.75²⁴⁻²⁷ for related compounds, then $\nu(\text{Ti-Br})$ A_1 in CpTiBr_3 is predicted at $444 \times 0.75 = 333$ cm^{-1} , very close to the frequency found for $\nu(\text{Ti-Cl})$ A_1 in the trichloro and trimethyl compounds. Thus, considerable mixing of $\nu(\text{Ti-Cp})$ A_1 and $\nu(\text{Ti-Br})$ A_1 modes may be expected, particularly if there are $d_{\pi}-p_{\pi}$ metal-bromine interactions.²⁸ Again, only the Raman spectrum provides the necessary evidence, two polarized bands at $330 \pm 90 = 420$ and 240 cm^{-1} which are thus assigned to the two A_1 modes. The band at 240 cm^{-1} is of very high intensity. The band at 409 cm^{-1} is assigned to $\kappa(\text{Ti-Cp})$ E, by analogy with the bands in the other titanium compounds. The 363- cm^{-1} band is assigned to $\nu(\text{Ti-Br})$ E, since there is probably little interaction between this and other modes and since the equivalent T_2 vibration in TiBr_4 is at 393 cm^{-1} . The other assignments are again tentative.

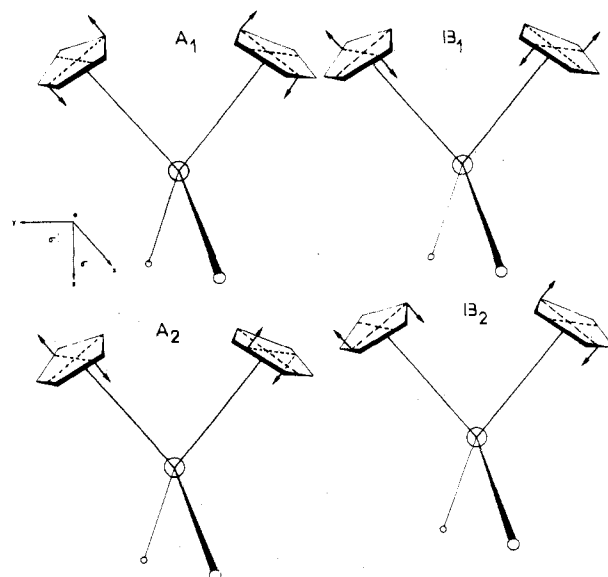


Figure 1. Ring tilt modes in Cp_2MX_2 compounds.

$\text{Cp})$ A_1 in the trichloro and trimethyl compounds. Thus, considerable mixing of $\nu(\text{Ti-Cp})$ A_1 and $\nu(\text{Ti-Br})$ A_1 modes may be expected, particularly if there are $d_{\pi}-p_{\pi}$ metal-bromine interactions.²⁸ Again, only the Raman spectrum provides the necessary evidence, two polarized bands at $330 \pm 90 = 420$ and 240 cm^{-1} which are thus assigned to the two A_1 modes. The band at 240 cm^{-1} is of very high intensity. The band at 409 cm^{-1} is assigned to $\kappa(\text{Ti-Cp})$ E, by analogy with the bands in the other titanium compounds. The 363- cm^{-1} band is assigned to $\nu(\text{Ti-Br})$ E, since there is probably little interaction between this and other modes and since the equivalent T_2 vibration in TiBr_4 is at 393 cm^{-1} . The other assignments are again tentative.

II. Cp_2MX_2 Compounds. The results for these compounds are given in Table II. The compounds are taken to have the C_{2v} structure found for Cp_2TiCl_2 ,²⁹ Cp_2ZrCl_2 , and Cp_2ZrF_2 .³⁰ The expected skeletal vibrations are thus $4 A_1 + A_2 + 2 B_1 + 2 B_2$. Two A_1 bands $\nu(\text{M-X})$ and $\nu(\text{M-Cp})$ are expected to occur between 200 and 500 cm^{-1} , and the other two, at lower frequencies. In addition, there is one ring tilt vibration of each symmetry species (Figure 1). All modes are³¹ Raman active and all but the A_2 modes are infrared active.

Cp_2MMe_2 . The Zr and Hf compounds are much more air and moisture sensitive than the Ti compound, and their infrared spectra have not yet been measured. Three polarized bands are observed in the Raman spectrum for each compound: (a) a medium strong band at 478 (Ti), 462 (Zr), and 475 cm^{-1} (Hf); (b) a medium strong band at 335 (Ti), 318 (Zr), and 299 cm^{-1} (Hf); and (c) a strong band at 255 (Ti), 258 (Zr), and 260 cm^{-1} (Hf).

The bands of type (a) may be readily assigned to $\nu(\text{M-Me})$ A_1 , since they fall in the region expected for this mode by analogy with CpTiMe_3 and other $\nu(\text{M-Me})$ A_1 modes noted above and since there is no band in this region for any of the halides. No other values for $\nu(\text{Zr-Me})$ or $\nu(\text{Hf-Me})$ could be found in literature.

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Table II. Infrared and Raman Spectra of Cp_2MX_2 Compounds

X = Me		X = F		X = Cl		X = Br		X = I	
Infrared	Raman	Infrared	Raman ^a	Infrared	Raman	Infrared	Raman	Infrared	Assignments
Cp_2TiX_2									
557 m									
532 m		564 vs	575 w					216 vw	$\nu(\text{Ti-X}) B_1$
477 w	478 s, p	539 vs	567 w	398 s	400 vw, p	383 ^b m		230 vw	$\nu(\text{Ti-X}) A_1$
464 w									
407 s	407 vw, dp	413 s	415 w	412 m	414 vw, dp	415 m		425 w	$\kappa(\text{Ti-Cp}) B$
333 m	335 s, p	357 w	360 m	300 s	305 s, p	243 ^b m			$\nu(\text{Ti-Cp}) A_1$
				357 m		343 m			
310 w									
280 w		296 w		280 sh	280 br, dp				
250 w	255 s, p	258 m	262 s	254 m	258 s, p	268 w		272 w	$\kappa(\text{Ti-Cp}) A_1$
240 m	240 vw, dp	232 w	217 w	246 m					
205 vw	205 vw, dp			206 m	206 w, dp	208 m		193 m	
185 m	175 w, dp	195 s	195 w	184 w	172 w, dp	172 w		127 m	
		82 m		144 w		152 w			
Cp_2ZrX_2									
		528 s				208 s		175 s	$\nu(\text{Zr-X}) B_1$
	462 s, p	544 s		332 s		222 ^b s	228 m, p	193 m	$\nu(\text{Zr-X}) A_1$
		363 } s, br		356 m	360 w, dp			356 s	$\kappa(\text{Zr-Cp}) B$
		358 }							
	318 m, p	353 m		308 m	312 s, p	356 ^b s	353 m, p	326 w, br	$\nu(\text{Zr-Cp}) A_1$
						312 w			
	288 w, dp			260 s, br	290 m, dp		297 m, d		$\kappa(\text{Zr-Cp}) A_2$
					270 m, p	272 w	278 s, p	272 m	$\kappa(\text{Zr-Cp}) A_1$
		215 w			184 w, dp		187 w, dp		
	212 w, dp	191 m		166 w	172 w, dp			140 m	
		160 m		124 w	150 w, dp	154 m		116 w	
					117 w, dp				
Cp_2HfX_2									
		526 s				196 s		172 m	$\nu(\text{Hf-X}) B_1$
	474 s, p	554 s		325 sh	320 sh	206 s	210 m, p	194 w	$\nu(\text{Hf-X}) A_1$
				357 w				383 w	
	299 m, p	358 m		312 s, br	312 s, p		323 m, p	312 m	$\nu(\text{Hf-Cp}) A_1$
		308 s							
	293 w, dp				295 m, dp	311 s	309 m, dp		
	260 s, p	271 s		264 m		272 w	276 s, p	270 m	$\kappa(\text{Hf-Cp}) A_1$
	217 w, dp	220 m		164 w	158 w, d	154 m		158 s	
		195 s		125 w	125 w, d	84 w		120 w	
		154 w							
		147 w							

^a Solid. Solutions in pyridine showed the bands at 360 and 262 cm^{-1} to be polarized. ^b These frequencies should be more correctly assigned to $\nu[(\text{M-Cp}) + (\text{M-Br})]$ because of coupling.

The frequencies of the bands of type (b) are clearly metal dependent and that for Ti lies close to the frequency observed for $\nu(\text{Ti-Cp}) A_1$ in CpTiMe_3 and close also to $\nu(\text{Fe-Cp}) A_1$ in ferrocene, which is found at 303 cm^{-1} .³² We therefore attribute these bands to $\nu(\text{M-Cp}) A_1$, an assignment consistent with those made below for the halides (Table II). The frequencies of the remaining polarized bands of type (c) are almost metal independent and correspond to similar bands found in all the bis(cyclopentadienyl) compounds examined, but in none of the mono(cyclopentadienyl) compounds. These bands can only be due to $\kappa(\text{M-Cp}) A_1$, which incidentally does not exist for the monocyclic compounds.

All these bands have infrared counterparts, as may be seen from Table II. The weak depolarized band at 407 cm^{-1} in the Raman spectrum of the Ti compound is assigned to one of the asymmetric tilt modes by analogy with the 409- cm^{-1} band in CpTiBr_3 and the 424- cm^{-1} band in CpTiCl_3 ; as already noted, a similar band in the region 400–430 cm^{-1} is found for most mono(cyclopentadienyl)- and bis(cyclopentadienyl)titanium compounds.

Cp_2MHal_2 . (a) Metal-Halide Vibrations. (1) M-F. The assignments of Lappert and coworkers⁹ for the metal-fluorine vibrations are almost certainly correct. The two $\nu(\text{Ti-F})$

bands at 564 and 539 cm^{-1} are observed in the Raman spectra of the solid Cp_2TiF_2 . However, since the relative insolubility of this difluoride allowed the measurement of the solution spectrum only in pyridine, which interferes in the $\nu(\text{Ti-F})$ region and which appears to shift the observed bands toward lower frequencies by about 10 cm^{-1} , we have not been able to establish polarization data to distinguish between the symmetric and asymmetric modes. The intensity of the metal-fluorine stretching bands was very high in the infrared spectrum but very low in the Raman.

(2) M-Cl. The assignment of this band is particularly difficult, since its intensity in the Raman is very low and since in Zr and Hf compounds it lies in a region where $\nu(\text{M-Cp}) A_1$ interferes. For Cp_2TiCl_2 , $\nu(\text{Ti-Cl}) A_1$ is expected to be around 400 cm^{-1} by comparison with CpTiCl_3 , MeTiCl_3 , and TiCl_4 . It is probable that one of the two strong bands observed in the infrared spectrum at 398 and 412 cm^{-1} is due to $\nu(\text{Ti-Cl}) A_1$; the Raman bands in this region were very much weaker than those around 300 cm^{-1} , and only by increasing the gain considerably was it possible to distinguish a polarized band at 400 cm^{-1} and a depolarized band at 414 cm^{-1} (Figure 2). The first is thus assigned to $\nu(\text{Ti-Cl}) A_1$.

For Cp_2ZrCl_2 , $\nu(\text{Zr-Cl}) A_1$ is expected to be rather lower than for Ti, occurring in ZrCl_4 at 377 cm^{-1} .²² The choice of $\nu(\text{Zr-Cl})$ appears to lie between the two strong bands in

(32) E. R. Lippincott and R. D. Nelson, *Spectrochim. Acta*, 10, 307 (1958).

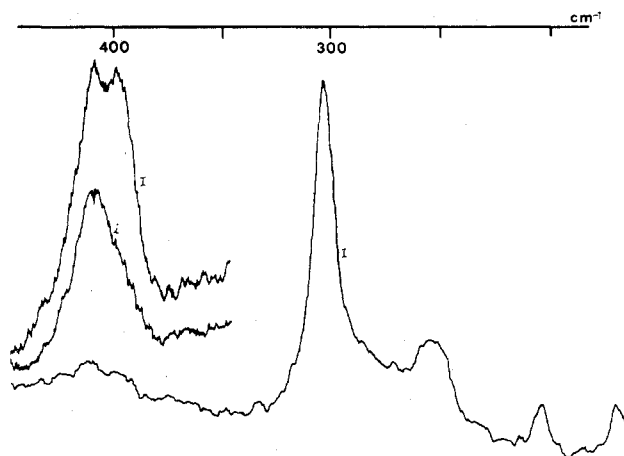


Figure 2. Raman spectrum of Cp_2TiCl_2 . Depolarization ratio = i/I . the infrared spectrum at 360 and 332 cm^{-1} . Since the first of these is depolarized in the Raman spectrum, the second is assigned to $\nu(\text{Zr-Cl}) A_1$. Furthermore, this band is absent in the infrared spectra of the dibromide and the diiodide. However, it was not observed in the Raman, probably due to overlap with the strong broad band at around 300 cm^{-1} .

For Cp_2HfCl_2 , the metal-chloride stretch is expected at around the same frequency as in the Zr compound. The 325- cm^{-1} band in the infrared spectrum is broad in contrast with this band in the spectra of the other dihalides and could contain $\nu(\text{Hf-Cl})$, as could the strong polarized band at 312 cm^{-1} in the Raman, but no definite assignment could be made. This would suggest, however, a weak coupling between Hf-Cp and Hf-Cl vibrations.

(3) **M-Br.** Cp_2TiBr_2 is highly colored and appears to decompose in solution in the laser beam, so no Raman spectra could be obtained. As in the case of CpTiBr_3 , and on the basis of the expected frequencies of $\nu(\text{Ti-Br}) A_1$, $\nu(\text{Ti-Cl}) \times 0.75 = \text{ca. } 300 \text{ cm}^{-1}$, and $\nu(\text{Ti-Cp}) A_1 \text{ ca. } 310 \text{ cm}^{-1}$, we suggest that the bands at 383 and 244 cm^{-1} are due to strong coupling between these two modes; this view is supported by the absence of the expected strong Raman band at 310 cm^{-1} due to $\nu(\text{Ti-Cp}) A_1$.

For Cp_2ZrBr_2 , a polarized Raman band of medium intensity is observed at 228 cm^{-1} , and although there is undoubtedly some mixing with $\nu(\text{Zr-Cp}) A_1$ (see below), this is assigned primarily to $\nu(\text{Zr-Br}) A_1$. Similarly, Cp_2HfBr_2 exhibits a medium polarized Raman band at 210 cm^{-1} , clearly due mainly to $\nu(\text{Hf-Br}) A_1$. Both these assignments agree with those of Lappert, *et al.*⁹

(4) **M-I.** No Raman data could be obtained for any of the iodides because of their color, and little can be added to previous assignments, namely, 193 cm^{-1} for $\nu(\text{Zr-I}) A_1$ and 175 cm^{-1} for $\nu(\text{Zr-I}) B_1$; 175 cm^{-1} for $\nu(\text{Hf-I}) A_1$ and 151 cm^{-1} for $\nu(\text{Hf-I}) B_1$.⁹

(b) **Metal-Ring Vibrations.** (1) $\nu(\text{M-Cp}) A_1$. On the basis of the data for the methyl compounds, a strong and highly polarized band between 300 and 350 cm^{-1} was expected for this mode in the Raman spectrum. All three dichlorides exhibit such a band at 305 (Ti), 310 (Zr), and 312 cm^{-1} (Hf), but Cp_2TiF_2 is somewhat and Cp_2TiBr_2 (judged from infrared) entirely anomalous, $\nu(\text{Ti-Cp}) A_1$ being at 360 cm^{-1} in the former and mixed with $\nu(\text{Ti-Br}) A_1$ in the latter (as explained above). The coupling is less in Cp_2ZrBr_2 , whose band at 353 cm^{-1} is likely to be due essentially to $\nu(\text{Zr-Cp}) A_1$, and small in Cp_2HfBr_2 where the band at 323 cm^{-1} in the Raman spectrum is no doubt due to $\nu(\text{Hf-Cp}) A_1$.

In the absence of Raman data for the diiodides, it seems

reasonable to suggest that the infrared bands at 326 (Zr) and 313 cm^{-1} (Hf) are due to $\nu(\text{M-Cp}) A_1$; the infrared spectrum alone gives no clue to a possible assignment to $\nu(\text{Ti-Cp}) A_1$ in Cp_2TiI_2 .

(2) $\nu(\text{M-Cp}) B_2$. This vibration probably occurs at rather higher frequency than $\nu(\text{M-Cp}) A_1$ (which is the case in ferrocene), and thus we assign the bands where possible as shown in Table II. The difference between $\nu(\text{Ti-Cp}) A_1$ and $\nu(\text{Ti-Cp}) B_2$, where assigned, is almost constant and equal to 50 cm^{-1} .

(3) $\kappa(\text{M-Cp}) A_1$. Strong polarized bands lying in the narrow range 255–278 cm^{-1} are found in all the Raman spectra measured. The relative insensitivity of the band frequency to change either in the metal or in the ligand leads to the assignment of this band to the A_1 tilt $\kappa(\text{M-Cp})$, Figure 1. Where Raman data are not available, it is highly probable that the bands in the infrared spectra lying in this range are due to the $\kappa(\text{M-Cp}) A_1$ and they are thus assigned.

(4) **Asymmetric Ring Tilt Vibrations.** There is no asymmetric metal-ring stretching vibration in CpTiX_3 compounds, so that the bands found at 398 (CpTiBr_3) and 424 cm^{-1} (CpTiCl_3) are assigned to $\kappa(\text{Ti-Cp}) E$, and by analogy the bands at 407 (Cp_2TiMe_2), 413 (Cp_2TiF_2), 412 (Cp_2TiCl_2), 415 (Cp_2TiBr_2), and 425 cm^{-1} (Cp_2TiI_2) are assigned to $\kappa(\text{Ti-Cp}) B_1$ or B_2 . It is surprising that no comparable band is observed for the Zr and Hf compounds.

A band which is weak in the infrared spectra and weak to medium in the Raman spectra is observed for all the Cp_2MX_2 compounds studied, in the range 310–280 cm^{-1} , almost independent of M or X, and is likewise assigned to the asymmetric ring tilt.

(5) **Deformation Vibrations.** No low-frequency polarized Raman bands were observed, although depolarized bands, presumably due to $\delta(\text{X-M-X}) B_1$ or $\delta(\text{Cp-M-Cp}) B_2$ modes, were observed between 100 and 200 cm^{-1} .

Discussion of Band Assignments

From the above assignments it can be seen that the behavior of the different compounds which belong to a homogeneous series (Cp_2MX_2) is consistent (see Figure 3) when going from Ti to Hf, concerning the A_1 modes (symmetric metal-ring, metal-ligand, and ring tilts).

However, an anomaly appears with the Ti derivatives when the asymmetric modes are considered, in that all the Cp-Ti compounds present a band of medium to strong intensity in the region 430–400 cm^{-1} , which is completely absent in the spectra of the Zr and Hf compounds examined. By assuming that this band is due to a skeletal vibration (the frequency being too low to be associated with an internal vibration of the ring) and on the basis of Raman polarization measurements which give the expected number of A_1 bands, it could only be due to an asymmetric mode. Also, its presence in both CpTiX_3 and Cp_2TiX_2 compounds justifies its assignment to the same type of vibration. The previous assignment⁸ of the 453- cm^{-1} band in CpTiCl_3 to Cp-Ti symmetric stretch is not in agreement with ours, and the shift to higher frequencies of this band in $(\text{CH}_3)_5\text{C}_5\text{TiCl}_3$ is probably fortuitous and is not a proof of the donor character of the methyl groups in enhancing the metal-to-ring bonding and consequently increasing the stretching frequency.

Metal-Halogen Bands. On the basis of what has been observed on the Cp_2TiF_2 compound, the Ti-F bands are very strong in the infrared spectra and very weak in the Raman. The disparity in intensity between infrared and Raman bands is even greater for the dichlorides, and the relatively high intensity of the symmetrical metal-bromine bands may well be

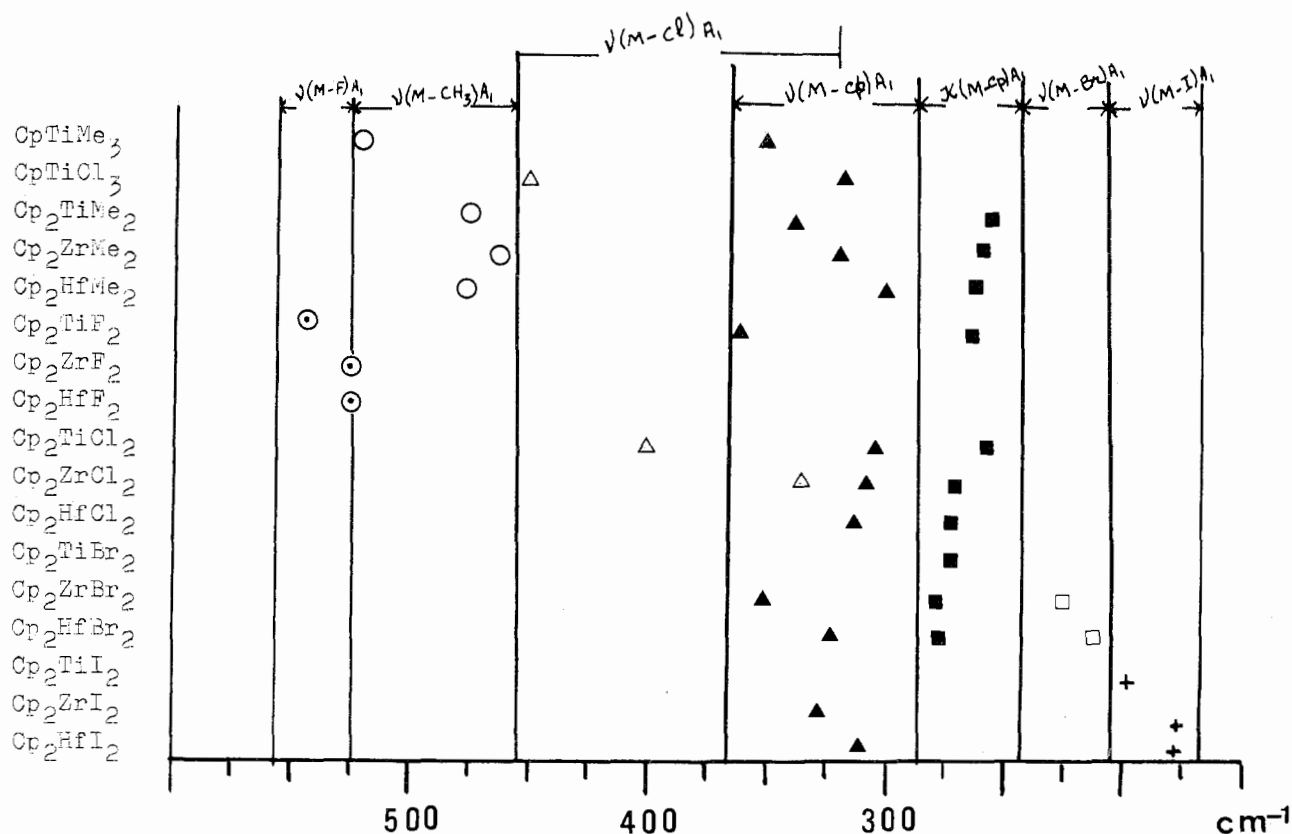


Figure 3.

due to coupling with the $\nu(\text{M-Cp}) A_1$ vibrations.

Metal-Methyl Bands. The Cp_2MMe_2 compounds provide a new homogeneous series containing a metal-methyl bond. The empirical formula and the vibrational spectra indicate that they are isostructural. It was expected that some regularity would be observed in the variation of $\nu(\text{M-CH}_3) A_1$ frequencies on descending the group as has been found for the nmr chemical shifts of the methyl group⁵ (10.17, 10.39, and 10.50 ppm for the Ti, Zr, and Hf compounds, respectively), but this turned out not to be the case. They lie, however, in a narrow range of frequencies and give rise to strong polarized Raman bands which allow them to be identified readily.

Metal-Ring Bands. The assignments proposed above are, in our view, coherent for the following reasons.

(a) The A_1 bands show little dependence on the nature of the metal or the ligand bound to the metal and take values between 300 and 360 cm^{-1} (Figure 3). This result is not surprising since the compounds studied have identical or closely related structures and the metals are in the same oxidation state.

(b) The frequencies are in agreement with those found for the A_1 modes in ferrocene, ruthenocene, $\text{CpMn}(\text{CO})_3$, $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$, and other sandwich compounds in which the assignments are unequivocal.

(c) The A_1 bands have common features: they are intense and strongly polarized in Raman and generally weak in infrared. This observation is purely qualitative.

Although the assignments are straightforward in the methyl compounds, they present some difficulties in the halides and especially in the bromides where it was found necessary to admit some coupling between the M-Cp and M-Br modes. However, if arguments in favor of this coupling are to be rejected, the only alternative would be to reverse the assign-

ments of the M-Cp and M-X symmetrical stretching modes which would lead to the following values.

	$\nu(\text{M-Cp}) A_1, \text{cm}^{-1}$	$\nu(\text{M-X}) A_1, \text{cm}^{-1}$
CpTiCl_3	448	327
CpTiBr_3	424	240
Cp_2TiCl_2	398	300
Cp_2ZrCl_2	332	312

These assignments have the single merit of giving the predicted ratio of $\nu(\text{M-Br})/\nu(\text{M-Cl}) = 0.75$. However, the M-Cp frequencies present two serious shortcomings: (1) They take values in CpTiCl_3 and in Cp_2ZrCl_2 differing by 116 cm^{-1} , which is unexpectedly high even though the two compounds do not have the same molecular symmetry. (2) They decrease by 17 cm^{-1} in the dimethyl compounds and by 66 cm^{-1} in the dichlorides when going from Ti to Zr, so that changing the metal has a very moderate effect in shifting the frequencies in one case and a drastic one in the other.

It can be seen that, by maintaining the original assignments, such discrepancies, which are not easy to justify, are avoided.

In conclusion, it is hoped that the above study will help to rationalize the assignments of the skeletal vibrations in the bent π -cyclopentadienylmetal complexes which cover an important area in metallocene chemistry.

Registry No. CpTiCl_3 , 1270-98-0; CpTiBr_3 , 12240-42-5; CpTiMe_3 , 38386-55-9; Cp_2TiMe_2 , 1271-66-5; Cp_2TiF_2 , 11077-43-3; Cp_2TiCl_2 , 1271-19-8; Cp_2TiBr_2 , 1293-73-8; Cp_2TiI_2 , 12152-92-0; Cp_2ZrMe_2 , 12636-72-5; Cp_2ZrF_2 , 11090-85-0; Cp_2ZrCl_2 , 1291-32-3; Cp_2ZrBr_2 , 1294-67-3; Cp_2ZrI_2 , 1298-41-5; Cp_2HfMe_2 , 37260-88-1; Cp_2HfF_2 , 37260-84-7; Cp_2HfCl_2 , 12116-66-4; Cp_2HfBr_2 , 37260-83-6;

Cp_2HfI_2 , 37260-85-8; Cp_2TiPh_2 , 1273-09-2; HI, 10034-85-2; Br_2 , 7726-95-6.

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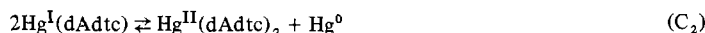
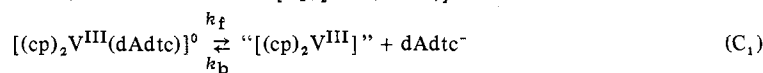
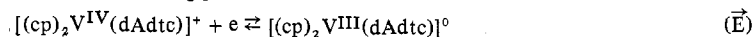
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Polarographic Behavior of Bis(π -cyclopentadienyl)-*N,N*-dialkyldithiocarbamatovanadium(IV) Tetraphenylborates in Acetone. An Example of an $\vec{E}\vec{C}\vec{E}\vec{C}$ Mechanism

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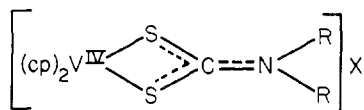
Bis(π -cyclopentadienyl)-*N,N*-dialkyldithiocarbamatovanadium(IV) tetraphenylborates exhibit two one-electron polarographic reduction waves in the potential range +0.75 to -2.2 V relative to a Ag-AgCl(acetone) reference electrode. The first reduction (at ~ -0.4 V) is fully reversible. It is believed that its associated electron is accommodated in a nonbonding orbital of the vanadium atom. The neutral vanadium(III) complexes resulting from this reduction are susceptible to dissociation, releasing free dialkyldithiocarbamate anions—a process which is greatly enhanced in the presence of oxygen. A study of sodium *N,N*-dialkyldithiocarbamates has shown that Hg(0) is oxidized to Hg(I) in the presence of free dialkyldithiocarbamate anions, and since this process occurs at ~ -0.5 V, a novel example of an $\vec{E}\vec{C}\vec{E}$ mechanism results. The terminology $\vec{E}\vec{C}_1\vec{E}\vec{C}_2$ has been used here to describe the following processes associated with the initial reduction step



The second electrode process is not reversible. The system has been investigated by both dc and ac polarography, cyclic and linear sweep voltammetry, and controlled-potential electrolysis.

Introduction

Recently a number of air-stable complexes between the bis(π -cyclopentadienyl)vanadium(IV) moiety and some dialkyldithiocarbamates have been synthesized and characterized in this laboratory.¹ The physical properties of these compounds strongly suggest that they are of the form



where R is hydrogen or an alkyl group and X is either the tetraphenylborate or the tetrafluoroborate anion.

The suggested structure of the cationic species is shown in Figure 1. The vanadium atom is approximately tetrahedrally coordinated by two π -cyclopentadienyl groups and the two sulfur atoms of the dialkyldithiocarbamate, and it is predicted that its unpaired electron resides in a nonbonding orbital directed between the two sulfur atoms.² Epr data collected on the corresponding complexes between the $(\text{cp})_2\text{V}^{\text{IV}}$ moiety and some dialkyl dithiophosphates³ have shown conclusively that the vanadium-sulfur bonds are significantly covalent and

that the unpaired electron does indeed occupy an orbital of the predicted type.

In view of the recent interest shown in the polarographic behavior of transition metal-dithio chelate complexes⁴⁻⁷ and because of the uniqueness of stable complexes between early members of the transition series and dithio chelates, the above system seemed to warrant an electrochemical investigation. Indeed, it can be readily appreciated that the metal atom of these compounds is most favorably disposed toward reduction since it has a d^1 configuration, is involved in a cationic species, and has a partly filled nonbonding orbital as its lowest lying incompletely occupied energy level.

Since the compounds were completely insoluble in water, acetone was chosen as solvent. The complexes are moderately soluble in this solvent and there appears to be no solvolysis. Preliminary investigations on free dialkyldithiocarbamate anions showed an oxidation wave at ~ -0.5 V relative to Ag-AgCl, while a reduction wave at ~ -0.4 V relative to the same electrode was obtained from the complexes. It is clear that if any dissociation of dialkyldithiocarbamate ligands from the complexes occurs as a result of their initial reduction, then

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