a bridging ligand, the infrared, isomer-shift, and temperature-dependence data are all consistent with the presence of essentially independent $Sn(N_3)_6^{2-}$ moieties.

From the present results it is clear that Mössbauer isomer shift systematics for a given structure type (*i.e.*, O_h, C_{3v}, D_{4h}, etc.) can be used to give useful estimates of group electronegativities for polyatomic ligands and that, moreover, such data are sensitive enough to reflect subtle changes in bonding and structure of these species.

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Electron Capture Reactions of Group IVb Dicyclopentadienylmetal Dichlorides in the Gas Phase

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Resonance electron capture and dissociative electron capture reactions have been observed for the principal negative ions produced from $M(C_5H_5)_2Cl_2$ (M = Ti, Zr, Hf) in the mass spectrometer. Parent negative ions are formed in each metal compound at low electron energies by direct capture of thermal electrons. Fragment negative ions are detected in dissociative resonance capture reactions.

Introduction

Interest in mass spectrometry of organometallic compounds[1,2] has prompted a study of the negatively charged species produced *via* electron capture processes in the mass spectrometer. Since little is known about the negative ion mass spectra of organometallic compounds, a study of the formation of negative ions by electron bombardment may lead to a better understanding of electron capture reactions and dissociative capture reactions. In addition such studies may suggest the usefulness of negative ion mass spectrometry as an aid in elucidating molecular structures. In this paper an investigation of the electron capture and dissociative electron capture reactions for group IVb dicyclopentadienylmetal dichlorides is reported.

Experimental Section

The compounds used in this study $Ti(C_5H_5)_2Cl_2$, $Zr(C_5H_5)_2Cl_2$, $Hf(C_5H_5)_2Cl_2$, $C_6H_5NO_2$, and SF_6 were purchased from commercial sources and were used without additional purification. The zirconium compound contained about a 1% impurity of $Hf(C_5H_5)_2Cl_2$ and the hafnium compound contained about a 5% impurity of $Zr(C_5H_5)_2Cl_2$.

The investigation was carried out using an Hitachi Perkin-Elmer RMU-7E double-focusing mass spectrometer. The samples were introduced into the ionization chamber using the direct inlet probe. The solid inlet heater was maintained at 100° and the ionization chamber temperature was held at 150° for the electron capture studies.

Thermal stability of the compounds in the ion source was examined by measuring the intensity of the most abundant positive ions as a function of chamber temperature (100–300°) while the solid inlet temperature was kept at 100°. The values of the fractional intensity for the $M(C_5H_5)_2Cl_2^+$, $M(C_5H_5)_2Cl^+$, and $M(C_5H_5)Cl_2^+$ ions (M = Ti, Zr, and Hf) were determined as a function of chamber temperature. No thermal dependence of the intensity of the positive ions was noted as indicated in Figure 1 for $Zr(C_5H_5)_2Cl_2$. Similar temperature behavior was noted for positive ions from $Ti(C_5H_5)_2Cl_2$ and $Hf(C_5H_5)_2Cl_2$.

The pressure in the analyzer tube was maintained at less than 3.0×10^{-6} Torr in all experiments. It is assumed that the pressure in the ionization chamber differed by less than an order of magnitude from the analyzer tube pressure. In the determination of the dependence of the ion current in the electron capture reaction on pressure the solid inlet temperature was increased to provide a higher pressure in the ionization chamber and the electron capture curve for the ion in question was determined. The maximum in the ion capture curve was taken as the intensity of a particular ion for the measured analyzer tube pressure.

Mass calibration at 0.08 and 50 eV was accomplished by introducing perfluorokerosene (PFK) into the mass spectrometer simultaneously with the compounds studied. The identity of the negative ionic species was established by comparing the spectra of PFK[3] with the compound of interest. Identification of the parent negative ions was confirmed at 0.08 eV also by a comparison of calculated and observed isotopic abundances. The comparison is presented in Table I.

The electron energy was provided by a pair of 10.3-V mercury batteries and was varied using a 25-turn Helipot precision potentiometer. Since low-energy processes were of interest in this study, a positive bias was applied in the electron-accelerating circuit to obtain a suitable electron energy. Because the electron beam possesses a thermal energy distribution, the positive bias effectively allows only electrons with energy greater than the bias to enter the ionization chamber. In this way essentially

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(1) R. W. Kiser and R. E. Sullivan, *Anal. Chem.*, **40**, 273R (1968).

(2) J. Lewis and B. F. G. Johnson, *Accounts Chem. Res.*, **1**, 245 (1968).

(3) R. S. Gohlke and L. H. Thompson, *Anal. Chem.*, **40**, 1004 (1968).

Table I

Calculated and Observed Isotopic Abundances for $M(C_5H_5)_2Cl_2^-$ Ions

	$Ti(C_5H_5)_2Cl_2^-$ m/e									
	246	247	248	249	250	251	252	253	254	255
Calcd	4.10	4.22	41.06	9.80	28.23	5.29	6.01	0.93	0.33	0.03
Obsd	4.40	4.63	41.18	9.48	28.00	5.24	5.93	0.77	0.37	...

	$Zr(C_5H_5)_2Cl_2^-$ m/e											
	290	291	292	293	294	295	296	297	298	299	300	301
Calcd	26.22	8.76	26.55	6.63	17.86	2.56	8.24	0.91	1.88	0.21	0.16	0.02
Obsd	26.28	8.82	26.48	6.79	17.54	2.74	8.08	1.06	1.82	0.22	0.17	...

	$Hf(C_5H_5)_2Cl_2^-$ m/e												
	374	375	376	377	378	379	380	381	382	383	384	385	386
Calcd	0.09	0.01	2.68	9.82	16.72	14.96	28.86	8.63	13.78	2.22	2.01	0.21	0.01
Obsd	...	...	2.79	9.76	16.89	14.81	28.86	8.89	13.80	2.20	2.00	...	...

zero-energy electrons can be introduced into the ionization chamber and the complete electron capture curve for SF_6^- or $C_6H_5NO_2^-$ obtained. The electron energy scale was calibrated using SF_6^-, SF_5^- (SF_6); $C_6H_5NO_2^-$, NO_2^- ($C_6H_5NO_2$), which show resonance capture maxima at 0.08, 0.16;[4] 0.08, 1.07 (3.50) eV,[5] respectively. Calibrating gases were introduced into the ionization chamber along with the organometallic compounds. In all experiments the potential on the repellers and on the electron grid was maintained at zero.

Results and Discussion

The abundant ions in the negative ion mass spectra of the dicyclopentadienylmetal dichlorides are presented in Table II. The reported abundances include the contributions from all isotopes in a given ion measured at 50 eV. The abundance of the parent negative ions varies in an irregular fashion; *i.e.*, the relative abundance of $Zr(C_5H_5)_2Cl_2^-$ is significantly greater than the abundance of the other parent ions. The mass spectra were determined repeatedly over about a 6-month period and were reproducible each time. At present no explanation for this observation can be given. The electron energies at which maxima occurred in the electron capture ionization efficiency curves are given in Table II.

Table II

Negative Ions in Dicyclopentadienylmetal Dichlorides

	Rel abund (50 eV)	Resonance capture max, eV
	$Ti(C_5H_5)_2Cl_2$	
$Ti(C_5H_5)_2Cl_2^-$	0.2	0.08
$Ti(C_5H_5)_2Cl^-$	2.0	0.25
$Ti(C_5H_5)Cl_2^-$	29.0	2.95
$C_5H_5^-$	32.0	3.6
Cl^-	100.0	0.1, 2.55, 8
	$Zr(C_5H_5)_2Cl_2$	
$Zr(C_5H_5)_2Cl_2^-$	92.0	0.08
$Zr(C_5H_5)Cl_2^-$	0.8	3.75
$C_5H_5^-$	45.0	4.7
Cl^-	100.0	0.3, 4.2, 8.5
	$Hf(C_5H_5)_2Cl_2$	
$Hf(C_5H_5)_2Cl_2^-$	0.1	0.08
$C_5H_5^-$	60.0	1.7, 5.0, 8.1
Cl^-	100.0	0.8, 4.4, 8.8

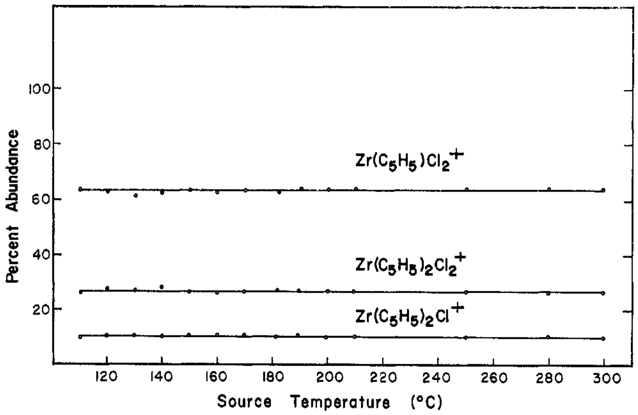

Figure 1.—Per cent abundance of selected $Zr(C_5H_5)_2Cl_2$ positive ions *vs.* temperature.

It is well known that a large thermal energy distribution on the electron beam and space charge effects can lead to broadened and distorted electron capture ionization efficiency curves. In the measurements of the electron capture ionization efficiency curves, adequate precautions were taken to ensure that the thermal energy distribution indicated no distortion due to space charge effects and had a Maxwellian-shaped distribution. An optimum-energy half-width was selected which permitted adequate negative ion current to be measured. To accomplish this the rhenium filament was operated at a constant current in the range from 2.0 to 2.5 A. When operating the filament at these currents, the energy width at half-height on the electron beam ranged from about 0.27 to 0.6 eV. Since the electron capture process for the $M(C_5H_5)_2Cl_2$ molecules is similar to that for nitrobenzene, *i.e.*, thermal electron capture, the determination of the electron capture ionization efficiency curve for $M(C_5H_5)_2Cl_2^-$ corresponds to the thermal energy distribution of the electron beam.[4,5] Once the nature of the electron capture by $M(C_5H_5)_2Cl_2^-$ had been established by comparison with the electron capture in SF_6^- or $C_6H_5NO_2^-$, the formation of the $M(C_5H_5)_2Cl_2^-$ ion served as an internal standard for obtaining the desired electron energy distribution profile and for calibrating the electron energy scale at low energies.

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[4] W. M. Hickam and R. E. Fox, *J. Chem. Phys.*, **25**, 642 (1956).

[5] L. G. Christophorou, R. N. Compton, G. S. Hurst, and P. W. Reinhardt, *ibid.*, **45**, 536 (1966).

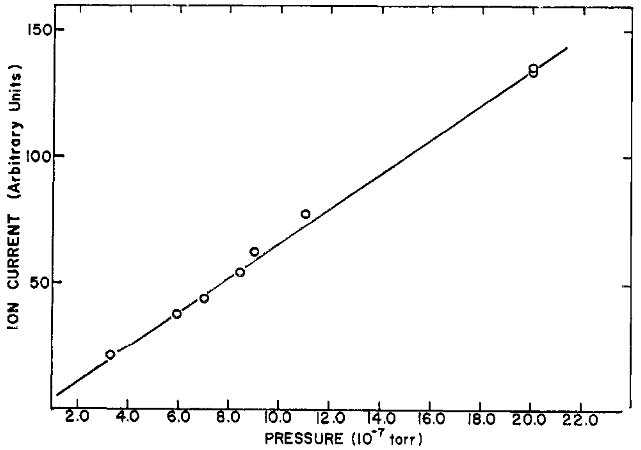

Figure 2.—Variation of $Zr(C_5H_5)_2Cl_2^-$ ion current at 0.08 eV with pressure.

Negative ions may form in the ion source of the mass spectrometer upon electron bombardment by three processes:[6] resonance electron capture

$$AB + e^- \longrightarrow AB^- \qquad (1)$$

dissociative electron capture

$$AB + e^- \longrightarrow A + B^- \qquad (2)$$

and ion-pair production

$$AB + e^- \longrightarrow A^+ + B^- + e^- \qquad (3)$$

Processes indicated by eq 1 and 2 occur at low electron energies (0–8 eV) while ion-pair reactions may occur above about 8 eV, depending on the onset energy for the formation of the accompanying positive ion. It is often stated[7–9] that the formation of parent negative ions (reaction 1) is rare under the conditions existing in the ion source of the mass spectrometer. However, parent negative ions may form by secondary electron capture[10] and in some instances at near-zero eV[4,5,11,12] by direct electron capture. In this study it was observed that in each of the dicyclopentadienylmetal dichlorides parent negative ions were formed.

The formation of the parent negative ions at low electron energies could occur in three ways: (1) by dissociative electron capture from a polymeric species $[M(C_5H_5)_2Cl_2]_2$ (reaction 2), (2) by secondary electron capture or collisional stabilization of the parent negative ion, or (3) by resonance electron capture (reaction 1). In the formation by dissociative electron capture, the "parent negative ion" would be produced from a polymeric species in the gas phase

$$[M(C_5H_5)_2Cl_2]_2 + e^- \longrightarrow M(C_5H_5)_2Cl_2^- + M(C_5H_5)_2Cl_2 \qquad (4)$$

A search for polymeric species was made in this study by measuring the positive and negative ion mass spectrum to about 1200 amu. No polymeric ionic species were detected. If such polymers exist, their abundance in the gas phase must be less than about 0.0001%. It appears that the "parent negative ions" are not formed by dissociative electron capture.

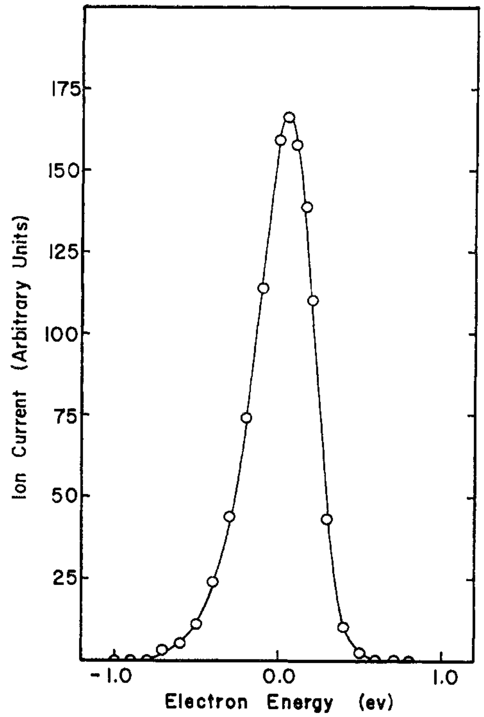

Figure 3.—Electron capture ionization efficiency curve for $Zr(C_5H_5)_2Cl_2^-$.

The formation of the parent negative ions by secondary electron capture appears not to be the process since the electron energy is well below that required to produce positive ions and secondary electrons. If secondary electron capture were a significant process for the formation of the parent negative ions, the ion current should be second order in pressure in accord with the reactions

$$M(C_5H_5)_2Cl_2 + e^- \longrightarrow M(C_5H_5)_2Cl_2^+ + e^- + e^- \qquad (5)$$

$$e^- + M(C_5H_5)_2Cl_2 \longrightarrow M(C_5H_5)_2Cl_2^- \qquad (6)$$

The intensity of the negative ions $M(C_5H_5)_2Cl_2^-$ is first order with pressure as indicated in Figure 2 for $Zr(C_5H_5)_2Cl_2^-$. The formation of $M(C_5H_5)_2Cl_2^-$ at 50 eV is no doubt due to capture of secondary electrons.

It appears, therefore, that the $M(C_5H_5)_2Cl_2^-$, parent negative ions, are produced by direct electron capture. The electron capture ionization efficiency curve for $Zr(C_5H_5)_2Cl_2^-$ is shown in Figure 3, where the electron energy axis was calibrated with nitrobenzene. Similar ionization curves were obtained for $Ti(C_5H_5)_2Cl_2^-$ and $Hf(C_5H_5)_2Cl_2^-$. It is perhaps not surprising that the $M(C_5H_5)_2Cl_2^-$ negative ions are formed in the mass spectrometer since paramagnetic $V(C_5H_5)_2Cl_2$, which is isoelectronic with $Ti(C_5H_5)_2Cl_2^-$, is stable in solution.[13] Nevertheless, the observation of these negative ions suggests that in organometallic systems parent negative ions may be more important in unimolecular ion de-

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(6) R. W. Kiser, "Introduction to Mass Spectrometry," Prentice-Hall Inc., Englewood Cliffs, N. J., 1965, p 192.

(7) See ref 6, p 131.

(8) C. A. McDowell, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1963, p 526.

(9) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957, p 145.

(10) J. C. J. Thynne, *Chem. Commun.*, 1075 (1968).

(11) R. M. Reese, V. H. Dibeler, and F. H. Mohler, *J. Res. Natl. Bur. Std.*, **57**, 367 (1956).

(12) D. F. Munro, J. E. Ahnell, and W. S. Koski, *J. Phys. Chem.*, **72**, 2682 (1968).

(13) J. C. W. Chien and C. R. Boss, *J. Am. Chem. Soc.*, **83**, 3767 (1961).

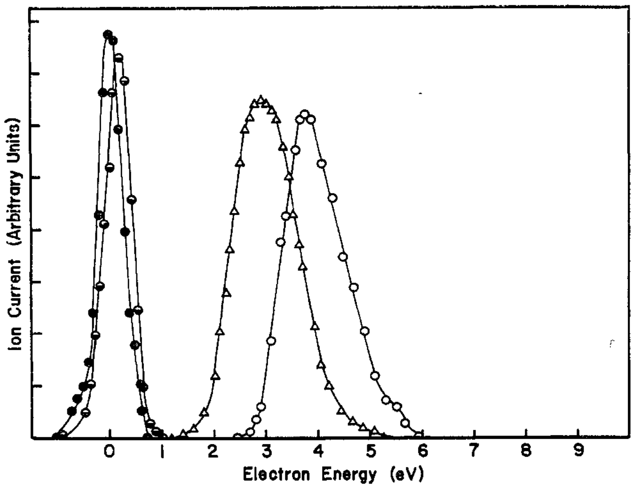

Figure 4.—Dissociative electron capture ionization efficiency curves for metal-containing ions: ●, $C_6H_5NO_2^-$ (calibrant); ◓, $Ti(C_5H_5)_2Cl^-$; △, $Ti(C_5H_5)Cl_2^-$; ○, $Zr(C_5H_5)Cl_2^-$.

composition reactions in the mass spectrometer than has been recognized.

According to the Franck–Condon principle[9] the formation of $M(C_5H_5)_2Cl_2^-$ ions at near-zero electron energies by resonance electron capture can be represented as

$$M(C_5H_5)_2Cl_2 + e^- \longrightarrow [M(C_5H_5)_2Cl_2^-]^* \quad (7)$$

where $[M(C_5H_5)_2Cl_2^-]^*$ represents the ion in an excited or ground state. Formation of the parent negative ion in its ground-state configuration implies exact coincidence of the ground-state potential energy surfaces for the neutral molecule and for the negative ion. Since it is extremely unlikely that the $M(C_5H_5)_2Cl_2$ and $M(C_5H_5)_2Cl_2^-$ potential surfaces coincide, the $M(C_5H_5)_2Cl_2^-$ ion is represented as an excited species.

Fragment negative ions are presumed to form *via* unimolecular decomposition of the parent negative ion either in competitive reactions involving the $M(C_5H_5)_2Cl_2^-$ ions or by consecutive reactions of the fragment negative ions formed from the $M(C_5H_5)_2Cl_2^-$ ions. Since it is well known[9] that fragment ions may be formed with excess kinetic energy, certain difficulties arise in assigning a reaction process for the formation of an ion unless the translational energy is measured. It was not possible with the present mass spectrometer to measure translational energies of the fragment negative ions.

The metal-containing fragment negative ions are formed from different energy states of the $M(C_5H_5)_2Cl_2^-$ ions at low electron energies *via* dissociation according to the reactions

$$[M(C_5H_5)_2Cl_2^-]^* \longrightarrow M(C_5H_5)_2Cl^- + Cl \quad (8)$$

$$[M(C_5H_5)_2Cl_2^-]^* \longrightarrow M(C_5H_5)Cl_2^- + C_5H_5 \quad (9)$$

where $Ti(C_5H_5)Cl_2^-$, $Ti(C_5H_5)_2Cl^-$, and $Zr(C_5H_5)Cl_2^-$ were detected in $Ti(C_5H_5)_2Cl_2$ and $Zr(C_5H_5)_2Cl_2$, respectively (Figure 4). In the figure the ion intensities have been adjusted so that all ions could be illustrated in the same figure. No $Zr(C_5H_5)_2Cl^-$, $Hf(C_5H_5)_2Cl^-$, or $Hf(C_5H_5)Cl_2^-$ ions were observed at low or high electron energies.

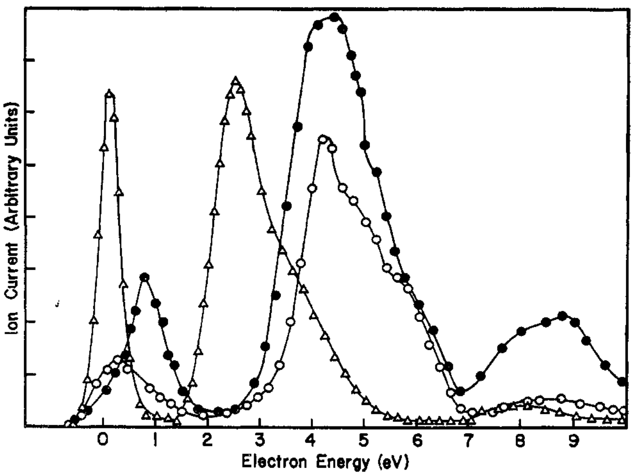

Figure 5.—Dissociative electron capture ionization efficiency curves: △, Cl^- ($Ti(C_5H_5)_2Cl_2$); ○, Cl^- ($Zr(C_5H_5)_2Cl_2$); ●, Cl^- ($Hf(C_5H_5)_2Cl_2$).

$Ti(C_5H_5)_2Cl_2$.—The formation of $Ti(C_5H_5)_2Cl^-$ occurs at low electron energies as indicated in Figure 4. In addition it is noted that Cl^- is also formed at low electron energies in this region as indicated in Figure 5. Because of the similarity of the ionization efficiency curves for Cl^- and $Ti(C_5H_5)_2Cl^-$ it is suggested that competitive reactions occur to form these ions at low energy

$$[Ti(C_5H_5)_2Cl_2^-]^* \longrightarrow Cl^- + Ti(C_5H_5)_2Cl \quad (10)$$

$$[Ti(C_5H_5)_2Cl_2^-]^* \longrightarrow Ti(C_5H_5)_2Cl^- + Cl \quad (11)$$

The negative ions with maxima in the ionization efficiency curves at about 3.0 eV for $Ti(C_5H_5)_2Cl_2$ include $Ti(C_5H_5)Cl_2^-$, $C_5H_5^-$, and Cl^-. It is evident that $Ti(C_5H_5)Cl_2^-$ can only be produced from the parent ion $Ti(C_5H_5)_2Cl_2^-$ in a unimolecular dissociation reaction. However, the formation of Cl^- and $C_5H_5^-$ might occur from $Ti(C_5H_5)_2Cl_2^-$ or from $Ti(C_5H_5)Cl_2^-$. If Cl^- is formed from $Ti(C_5H_5)_2Cl_2^-$, then Cl^- may be formed in an excited electronic state or with translational energy along with neutral $Ti(C_5H_5)_2Cl$. Alternatively Cl^- could be formed in the ground state with different neutral products

$$Ti(C_5H_5)_2Cl_2^- \longrightarrow Cl^- + Ti(C_5H_5)_2 + Cl \quad (12)$$

$$Ti(C_5H_5)_2Cl_2^- \longrightarrow Cl^- + Ti(C_5H_5)Cl + C_5H_5 \quad (13)$$

On the other hand, the reaction leading to the formation of Cl^- from $Ti(C_5H_5)Cl_2^-$

$$Ti(C_5H_5)Cl_2^- \longrightarrow Cl^- + Ti(C_5H_5)Cl \quad (14)$$

is straightforward. A thorough search was made for metastable transitions for a range of low electron energies at which Cl^- was formed and no transition was detected which could be assigned to either process discussed above.

The $C_5H_5^-$ ion forms from each compound *via* a dissociative resonance reaction as shown in Figure 6. At

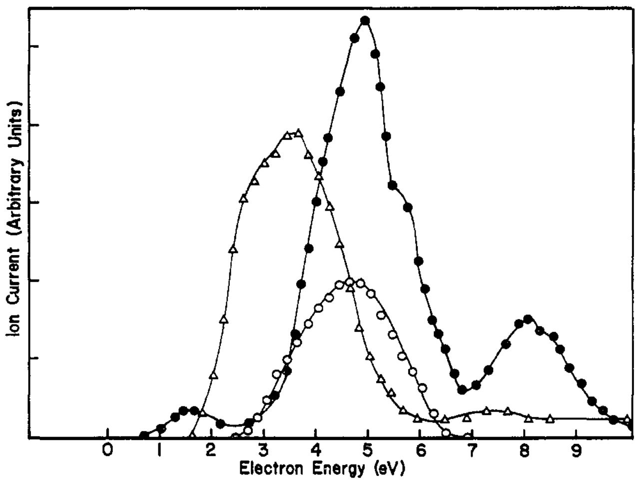

Figure 6.—Dissociative electron capture ionization efficiency curves: △, $C_5H_5^-$ ($Ti(C_5H_5)_2Cl_2$); ○, $C_5H_5^-$ ($Zr(C_5H_5)_2Cl_2$); ●, $C_5H_5^-$ ($Hf(C_5H_5)_2Cl_2$).

least two reactions could account for the formation of $C_5H_5^-$ from $Ti(C_5H_5)_2Cl_2$

$$Ti(C_5H_5)_2Cl_2^- \longrightarrow C_5H_5^- + Ti(C_5H_5)Cl_2 \quad (15)$$

$$Ti(C_5H_5)Cl_2^- \longrightarrow C_5H_5^- + TiCl_2 \quad (16)$$

As with Cl^- no metastable transitions were detected to support the process, and the lack of data on heats of formation of the titanium species does not permit selecting either reaction as the probable one.

$Zr(C_5H_5)_2Cl_2$.—The fragment negative ions in $Zr(C_5H_5)_2Cl_2$ are presumed to form *via* unimolecular reactions similar to those postulated for ions from $Ti(C_5H_5)_2Cl_2$. However, no $Zr(C_5H_5)_2Cl^-$ ion was detected. In addition, even though $Zr(C_5H_5)Cl_2^-$ was observed, the intensity of this ion in the dissociative resonance process was about 50 times less intense than that of $Zr(C_5H_5)_2Cl_2^-$ at low energy. By comparison the intensity of the $Ti(C_5H_5)Cl_2^-$ ion was about half as intense as that of $Ti(C_5H_5)_2Cl_2^-$ in the resonance region. A search was made for metastable transitions which would verify the mode of formation of Cl^- (Figure 5) and $C_5H_5^-$ (Figure 6). No metastable transitions were detected which could be associated with the formation process for these negative ions. The probable reactions for the formation of Cl^- and $C_5H_5^-$ are presumed to be like those for $Ti(C_5H_5)_2Cl_2$ (reactions 12–16).

$Hf(C_5H_5)_2Cl_2$.—The only metal-containing ion detected in $Hf(C_5H_5)_2Cl_2$ was $Hf(C_5H_5)_2Cl_2^-$. However, the intensity relative to $Hf(C_5H_5)_2Cl_2^-$ for Cl^- and $C_5H_5^-$ in the resonance capture processes was greater than the relative intensities of the corresponding ions from the titanium and zirconium compounds. The dissociative capture reactions accompanying the formation of Cl^- and $C_5H_5^-$ must only involve the parent ion $Hf(C_5H_5)_2Cl_2^-$. The reactions forming Cl^- and $Hf(C_5H_5)_2Cl^-$ from $Hf(C_5H_5)_2Cl_2^-$ must be limited to the reaction forming Cl^- since no $Hf(C_5H_5)_2Cl^-$ was detected. The case is similar for the competing reactions involving the formation of C_5H_5 or $C_5H_5^-$

$$Hf(C_5H_5)_2Cl_2^- \longrightarrow C_5H_5^- + Hf(C_5H_5)Cl_2 \quad (17)$$

$$Hf(C_5H_5)_2Cl_2^- \longrightarrow Hf(C_5H_5)Cl_2^- + C_5H_5 \quad (18)$$

Reaction 17 is significant since no $Hf(C_5H_5)Cl_2^-$ is observed. The probable processes for the formation of Cl^- and $C_5H_5^-$, assuming that neither ion is formed in an excited state, can best be represented as in eq 19–26.

$$Hf(C_5H_5)_2Cl_2^- \longrightarrow Cl^- + Hf(C_5H_5)_2Cl \; E_e = 0.8 \text{ eV} \quad (19)$$

$$Hf(C_5H_5)_2Cl_2^- \longrightarrow Cl^- + Hf(C_5H_5)_2 + Cl \; E_e = 4.4 \text{ eV} \quad (20)$$

$$Hf(C_5H_5)_2Cl_2^- \longrightarrow Cl^- + Hf(C_5H_5)Cl + C_5H_5 \; E_e = 4.4 \text{ eV} \quad (21)$$

$$Hf(C_5H_5)Cl_2^- \longrightarrow Cl^- + ? \; E_e = 8.8 \text{ eV} \quad (22)$$

$$Hf(C_5H_5)_2Cl_2^- \longrightarrow C_5H_5^- + Hf(C_5H_5)Cl_2 \; E_e = 1.7 \text{ eV} \quad (23)$$

$$Hf(C_5H_5)Cl_2^- \longrightarrow C_5H_5^- + HfCl_2 + C_5H_5 \; E_e = 5.0 \text{ eV} \quad (24)$$

$$Hf(C_5H_5)_2Cl_2^- \longrightarrow C_5H_5^- + Hf(C_5H_5)Cl + Cl \; E_e = 5.0 \text{ eV} \quad (25)$$

$$Hf(C_5H_5)Cl_2^- \longrightarrow C_5H_5 + ? \; E_e = 8.1 \text{ eV} \quad (26)$$

From these results a periodic variation in the reactions leading to the formation of negative ions seems apparent. The negative ion mass spectra of the transition metals of low atomic number are characterized by several ions containing the metal; the mass spectrum of the heavier metals shows few metal-containing ions. Thus, in the competitive reactions between processes leading to the formation of metal-containing ions and processes in which substituents bonded to the metal dissociate to form negative ions, the latter reactions predominate for the heavier metals. Therefore, nonmetal ions are most intense at low electron energies and also at higher electron energies.

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