

Electrochemical Reduction of Zirconocene Dihalides and Dialkyls Studied by Electron Spin Resonance

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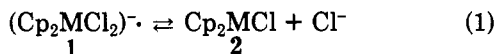
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An electrochemical cell designed to work in the cavity of an ESR spectrometer at variable temperatures was used to study the electrochemical reduction of zirconocene compounds Cp_2ZrX_2 ($X = \text{halogen (hal)}$); $Cp = \eta^5-C_5H_5$) and $Cp_2Zr(CH_3)_2$ in THF. It is shown that in each case zirconocenium(III) species are formed. On the basis of their spectral parameters they are characterized as the anion radicals $(Cp_2ZrX_2)^{\cdot-}$ for $X = Cl, Br,$ and CH_3 and as the monohalide Cp_2ZrX for $X = I$. Halogen hyperfine interactions are resolved for the first time. For $X = Cl$ and Br , electrochemical reduction in the presence of PMe_3 and $PMePh_2$ yields spectra attributable to the species $Cp_2ZrX(PMe_3)$ and $Cp_2ZrX(PMePh_2)$.

In spite of the rapidly growing importance of zirconocene compounds in organic synthesis and catalysis, very little attention has been devoted to their electrochemistry since the early work of Dessy and co-workers,¹ in contrast with the abundant work in this area on their titanium analogues.

The dihalides and some of their organic-substituted derivatives, Cp_2ZrX_2 ($X = \text{hal}, CH_3, C_6H_5$), are the most common starting materials in all reactions involving zirconocene-mediated substrate transformations. Since such transformations proceed mostly through electron transfer on the metal, it is of primary importance to gain insight into the nature of the species formed by the stepwise electron addition or abstraction. Electrochemical methods can therefore be of great help in the understanding of such mechanisms.

Several studies have been devoted to the electrochemistry of the pseudotetrahedral early transition metallocene dihalides.²⁻⁹ It is now well established by cyclic voltammetry that Cp_2MCl_2 ($M = Ti, V$) ($Cp = \eta^5-C_5H_5$) show perfectly reversible first reduction waves for which two schemes were proposed: (a) formation of a radical anion $(Cp_2MCl_2)^{\cdot-}$ as the only stable reduced species^{6,8} and (b) an EC mechanism where a subsequent chemical follow-up step occurs (eq 1).^{5,9}



The fact that the monohalides Cp_2MCl are well-known compounds did not help to completely overrule one process in favor of the other.

On the other hand, $Cp^*_2UCl_2$ ($Cp^* = \eta^5-C_5Me_5$) shows one reversible reduction wave attributed to the formation of the radical anion¹⁰ which was subsequently isolated as a well-defined compound.

Nothing similar has been recorded so far on Cp_2ZrCl_2 . The product of the reversible electrochemical reduction^{6,12} has never, to our knowledge, been hitherto identified and the monochloride Cp_2ZrCl has never been isolated. Lately, however, zirconium(III) metallocene compounds have been receiving increased and well-deserved attention. These compounds are, with one or two exceptions,¹¹ exclusively characterized in solution and produced by either chemical or photochemical methods;¹²⁻²¹ they usually afford well-resolved ESR spectra.

In this work we present our results on the characterization of Zr(III) species produced by electrochemical reduction of Cp_2Zr^{IV} dihalides and dialkyls. This was made possible by the use of an electrochemical cell specially designed to operate within the cavity of an ESR spectrometer at variable temperatures down to 120 K, thus allowing transient species to be identified in situ.

Experimental Section

The cell used a platinum wire provided with a glass sleeve protection to within 1 cm of its lower extremity as working electrode and a silver wire immersed in a suspension of KCl in the solvent containing the electrolyte as the auxiliary electrode. The cell dimensions, especially the lower portion, were adjusted

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Table I. ESR Parameters of Cyclopentadienylzirconium(III) Compounds Characterized in Solution by Electrochemical Methods

compd	<i>g</i>	<i>A</i> (Zr)	<i>a</i> (P)	<i>a</i> (hal)	ΔB
(Cp ₂ ZrCl ₂) ⁻	1.970 <i>g</i> _z = 2.000 <i>g</i> _y = 1.981 <i>g</i> _x = 1.932	29.7			7
(Cp ₂ ZrBr ₂) ⁻	1.989	30.0		2.8	12.6
(Cp ₂ ZrI)	1.992			3.4	20.6
(CpZrCl ₂) ^a	1.979 <i>g</i> = 2.000 <i>g</i> _⊥ = 1.971	37.0			4.9
(Cp ₂ ZrMe ₂) ⁻	1.991	21.9		<i>a</i> (H) = 4.7	
[Cp ₂ ZrCl(PMe ₃)]	1.979	23.0	17.5		4.5
[Cp ₂ ZrCl(PMePh ₂)]	1.979	24.3	19.5		4.8
[Cp ₂ ZrBr(PMe ₃)]	1.994	22.7	19.4		3
[Cp ₂ ZrBr(PMePh ₂)]	1.991	24.3	21.9		3.2

^aFrom CpNa + ZrCl₃. The formulas are related to assumed structures. Hyperfine coupling constants (isotropic) and ΔB in gauss; 1 G = 10⁻⁴ T. The isotropic *g* values are given unless stated otherwise.

to optimize the Q-load of the cavity and the ohmic drop between cathode and anode. Electrolysis was done at constant current generated by a TACUSSEL-CEAM D 6 amperostat, and the initial current flow was set at the minimal value to produce the signal. ESR measurements were done on a Bruker ER-10 spectrometer with dpph as internal standard. The 0.3 M (NBu₄)PF₆ (Fluka, recrystallized in methanol and melted under vacuum before use to ensure efficient dehydration) was employed as supporting electrolyte for ESR electrochemical and cyclic voltammetry studies.

Cp₂ZrCl₂ (Alfa Ventron) was recrystallized before use. The other dihalides were prepared from this compound as described in the literature,²² and their purity controlled by NMR to ensure complete absence of the dichloride. They were used at 5 × 10⁻³ M concentrations. THF was used as solvent; it was freshly distilled from sodium benzophenone ketyl and then on LiAlH₄ and introduced into the cell under argon.

Cyclic voltammetry used a platinum disk electrode; potentials were measured vs. Ag/AgCl system (saturated KCl in THF, NBu₄PF₆); experiments were carried out with a PAR 362 potentiostat using IR compensation.

Blank experiments were performed on the phosphines used in order to check the absence of electroactivity in the potential range studied.

Reaction of ZrCl₃ with CpNa. A solution of CpNa in THF was added to a suspension of ZrCl₃ (gray powder) in THF in 2/1 molar ratios at -20 °C. A dark brown color developed immediately. The decanted solution gave an intense ESR signal consisting of a singlet with Zr satellites. Evaporation of THF and extraction of the solid residue with toluene gave only Cp₂ZrCl₂ as a characterizable product, whereas sublimation under vacuum gave a yellowish, microcrystalline solid which gave a powder ESR spectrum identical with the frozen solution spectrum (Table I). The mass spectrum showed the presence of Cp₂ZrCl₂ in substantial amounts and attempts to purify this powder by recrystallization or a second sublimation led only to Cp₂ZrCl₂.

Results

All spectral parameters are gathered in Table I.

(1) **Cp₂ZrCl₂.** This is the only compound in the dihalide series on which electrochemical studies have been reported.^{6,12} Only one cathodic wave was detected at -*E*_{1/2} = 1.8 V (curve A, Figure 1), reversible at scan rates up to 1 V/s. A careful reinvestigation revealed to us an additional cathodic wave (curve B), which is irreversible, and also that the first wave is perfectly reversible only if the potential is reversed before the second reduction wave; otherwise it loses reversibility if the voltage sweep is al-

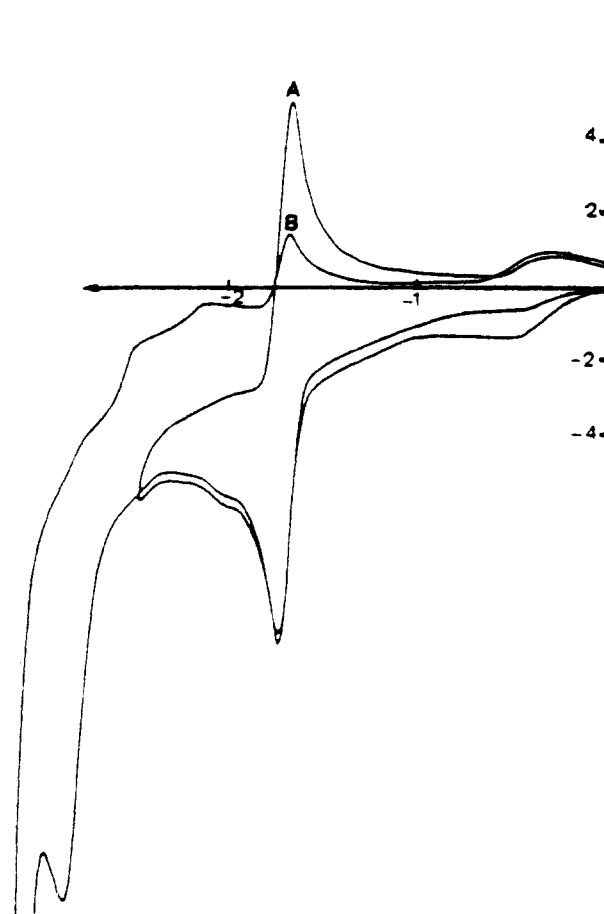


Figure 1. Cyclic voltammogram of Cp₂ZrCl₂ in THF at 200 mV/s. The scan is reversed at -2.5 V (curve A) and -3.2 V (curve B).

lowed to span the whole cathodic potential range as shown in the figure.

Electrolysis in the ESR cavity at 20 °C affords almost immediately a signal consisting of a sharp singlet which increases in intensity under continuous current flow. The expected Zr satellites are neatly resolved, especially on the low field side. This signal remains stationary for several minutes when the current flow is stopped. The solution in the proximity of the cathode is wine red. No other signal is observed upon continued electrolysis.

At 140 K a well-resolved frozen solution spectrum with three *g* values is observed.

(2) **Cp₂ZrBr₂.** Our study by cyclic voltammetry showed two reduction waves at the same potentials as the dichloride except that the second wave at -2.9 V is less well-defined. The first wave shows an appreciable scan rate dependence; it is reversible at 200 mV/s and almost irreversible at 20 mV/s, with intermediary features inside this interval which clearly reflects an EC mechanism. At high scan rates the reversibility is affected by the potential sweep range in the same manner as the dichloride. The overall behavior does not seem to undergo modifications at temperatures down to -20 °C.

At room temperature, the signal generated in the ESR cavity is weak and of rather short lifetime (a few seconds). The best results were obtained by electrolysis at 253 K when an intense well-resolved spectrum (Figure 2) was obtained. This signal is composed of a central septet, the relative line intensities being consistent with the interaction of the unpaired electron on Zr with two bromine nuclei; this superhyperfine structure is also resolved on the Zr satellites on both sides of the *I* = 0 multiplet. At high field a signal is observed whose intensity increases at room

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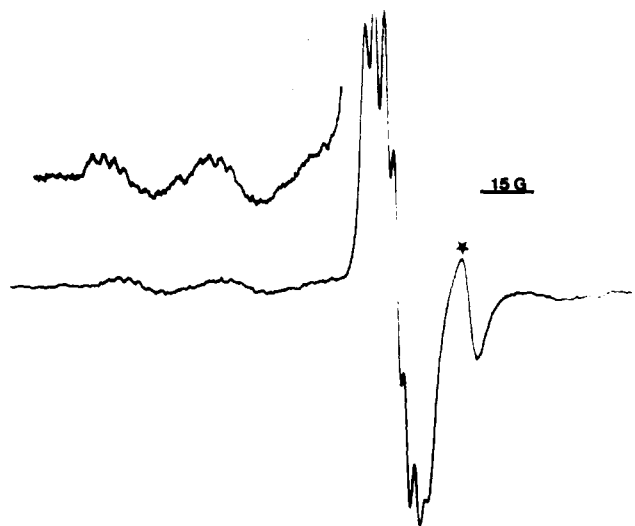


Figure 2. ESR spectra at 253 K of Cp_2ZrBr_2 in THF under reductive current (asterisk (*) = minor secondary product).

temperature and is probably due to a secondary product produced by a chemical follow-up reaction. The color of the electrolyzed solution is wine red.

The frozen solution spectrum is rather complex and could not be analyzed.

(3) Cp_2ZrF_2 . The ESR signal under reductive current exhibited a complex coupling pattern which did not allow definitive assignments to be made. The cyclic voltammogram is rather obscure and has no defined features.

(4) Cp_2ZrI_2 . The voltammogram exhibits an irreversible reduction wave with complications due to the formation of I_2 as revealed by additional waves characteristic of the I_2/I^- system.²³

Reductive electrolysis in the ESR cavity at 273 K gives a broad signal with a resolved hyperfine structure. Computer simulation allows us to attribute it unambiguously to the interaction of the unpaired electron on zirconium with one iodine nucleus (Figure 3). Due to the broadness of the signal, the Zr hyperfine structure is not resolved on the satellites and the frozen solution spectrum is not clearly resolved either.

(5) Cp_2ZrMe_2 . Cyclic voltammetry does not yield interpretable results, the reduction wave probably lies at low potentials at close proximity to the electrolyte discharge. However, electrolysis in the ESR cavity with a cathodic current gives a neat, well-resolved signal at 190 K, consisting of a central septet due to interaction of the unpaired electron with six methyl hydrogens. This superhyperfine structure is also clearly resolved on the zirconium satellites on both sides of the central signal (Figure 4).

Reduction in Presence of PMe_3 . Cp_2ZrCl_2 . The same experiment as above performed in the ESR electrochemical cell in presence of an excess of PMe_3 yielded under reductive current a strong central doublet with satellites, due to interaction of the unpaired electron with one ^{31}P nucleus. A singlet on the higher field side of the doublet appears also and is attributed from its g value without difficulty to the reduction product of Cp_2ZrCl_2 described above which is obviously unaffected by the presence of PMe_3 . The solution becomes red and is stable for hours without a significant loss in the ESR signal intensity.

Cp_2ZrBr_2 . The same result was observed with a more neat spectrum showing only a sharp doublet with clearly

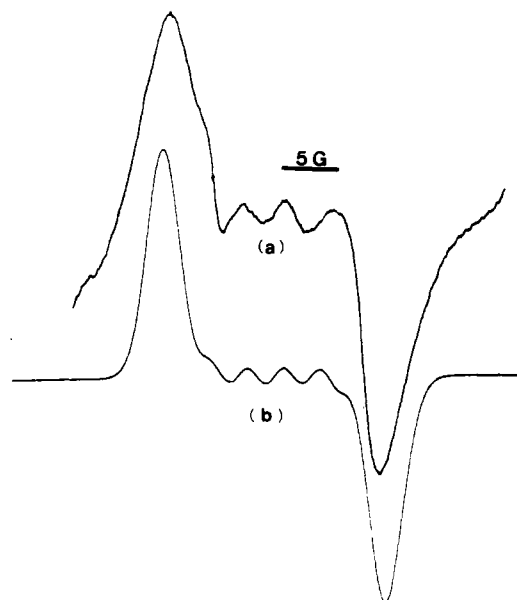


Figure 3. ESR spectrum at 273 K of Cp_2ZrI_2 in THF under reductive current: (a) experimental; (b) computer simulation assuming electron interaction with one iodine nucleus $I = 5/2$, 100%, and identical bandwidth ($\Delta B = 5.7$ G) for each of the six lines.

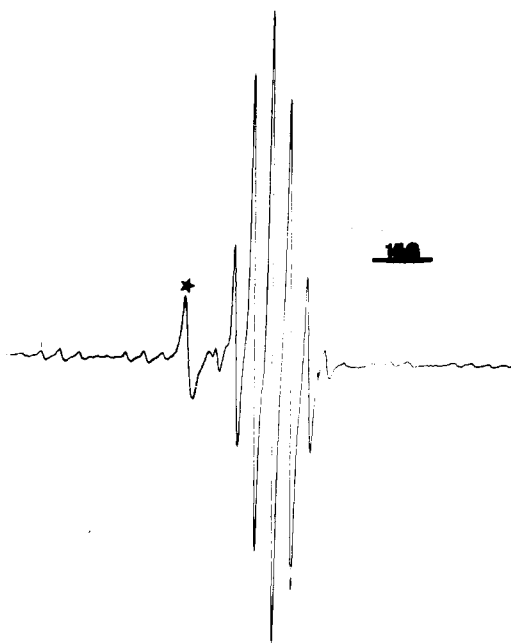


Figure 4. ESR spectrum at 190 K of Cp_2ZrMe_2 after electrochemical reduction (asterisk (*) = dpph).

resolved Zr satellites which indicates that the reaction with PMe_3 was complete. Frozen solution spectra for these phosphine species were complicated to analyze due to the resolution of the phosphorus anisotropy.

Cyclic voltammetry in presence of a small excess of PMe_3 (molar ratios slightly above 1/1) exhibits dramatic changes. For the dichloride, the first reduction wave (-1.8 V) partially disappears, whereas it disappears totally for the dibromide. Instead two irreversible waves at -0.8 and -2.6 V common to both compounds appear, along with other anodic waves ($+1.0$ V for $X = \text{Cl}$ and $+0.45$ and $+0.85$ V for $X = \text{Br}$).

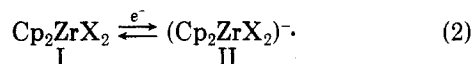
Discussion

The electrochemical device described in this paper allowed us for the first time to reveal the existence of Zr(III)

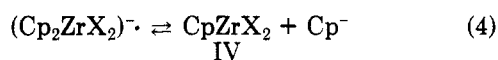
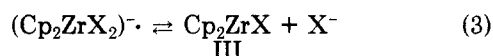
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species obtained directly by electrochemical reduction of zirconocene(IV) compounds. Although no well-defined products could be isolated by bulk electrolysis, the ESR data presented in this study provides a considerable amount of information about the structure of the paramagnetic species formed.

Reduction involving transfer of one electron per molecule on a d^0 Cp_2Zr^{IV} species as is assumed throughout this work would obviously lead in a primary process to the radical anion (eq 2), and if a chemical follow-up reaction



(EC) occurs, it is likely to proceed as shown in eq 3 and 4.



II, III, and IV should be ESR active if they have a long enough half-life and are expected to exhibit spectral patterns essentially dependent on the nature of X if the unpaired electron hyperfine interaction with the cyclopentadienyl hydrogens is not resolved. With very few exceptions,²⁴⁻²⁶ such resolution has never been observed in the ESR spectra of the pseudotetrahedral early transition d^1 metal compounds.

However, we have good reasons to believe that reactions 3 and 4 are not occurring with X = Cl or Br.

(1) For X = Cl, the first CV reduction wave (-1.8 V) is perfectly reversible at the accessible scan speed of our instrument. The voltammogram is clean up to the initial potential, and no anodic wave at -0.2 V is observed. The latter was previously reported to be present in the voltammogram of some titanocene compounds and assigned to the oxidation of the $C_5H_5^-$ anion, generated by reductive cleavage.²⁷

(2) The Zr hyperfine constant (29.7 G) is different from the value (40.3 G) obtained upon photolysis of Cp_2ZrRCl (R = H or Me) and thought to be due to Cp_2ZrCl .¹⁵ Furthermore, this product shows a signal with a half-life of 1 min at room temperature, whereas our electrochemical signal is stable for several minutes in the absence of current flow.

(3) The frozen solution spectrum of the electrochemically generated product (X = Cl) shows a three-component *g* tensor with values in perfect agreement with rhombic symmetry of the molecule and a d_{z^2} ground state as observed with the isoelectronic Cp_2NbCl_2 compound²⁸ (Cp_2NbCl_2 , $g_z = 2.0019$, $g_y = 1.9396$, $g_x = 1.9752$).

In order to have a clear view of the situation, we attempted to prepare Cp_2ZrCl from $ZrCl_3$ and $CpNa$. The reaction in stoichiometric proportions did not allow us to isolate a pure paramagnetic compound, but the spectrum of the solution after the reactants were mixed gave a strong signal (a singlet) with $A(Zr) = 37$ G. Furthermore, the frozen solution showed a clean spectrum of quasi-axial symmetry with only two *g* values (Table I). This spectrum was obtained also with the sublimed solid. We assign this spectrum to $CpZrCl_2$. In support of this hypothesis, a similar situation was observed with $CpTiCl_3$: both the

electron addition compound $(CpTiCl_3)^{\cdot-}$ and the one believed to result from the reductive cleavage of Cl^- , $(CpTiCl_2)$, have two-component *g* tensors.²⁹ On these grounds we conclude that reaction 2 is occurring in the electrochemical reduction of Cp_2ZrCl_2 .

The formation of a radical anion (reaction 2) finds further support from the ESR spectrum obtained by electrolytic reduction of Cp_2ZrBr_2 which exhibits the exact expected pattern for a $(Cp_2ZrBr_2)^{\cdot-}$ radical, with good resolution of the Br hyperfine interaction.

The situation with the iodide is more clear-cut. Computer simulation of the ESR spectrum on the assumption that the unpaired electron interacts with only one iodine nucleus was in good agreement with the experimental spectrum ($a(I) = 3.4$ G). The fact that reaction 3 prevails during the electrochemical reduction of Cp_2ZrI_2 leaves little doubt, and this experimental evidence does not allow for further alternatives.

Radical anions II are to our knowledge the first examples in early transition metallocenes where halogen hyperfine structure is resolved. Speculations on the magnitude of the Cl hyperfine constant can be deduced from comparison with known data on isostructural $(Cp_2MoCl_2)^+$ and $(Cp_2MoBr_2)^+$ cations;³¹ the ratio of $a(Br)/a(Cl)$ is approximately fivefold ($a(Cl) = 3$ G; $a(Br) = 15.8$ G). This gives roughly a constant of about 0.5 G for $a(Cl)$ in our zirconium compound, a value too low for resolution to be revealed in the observed bandwidth of the $(Cp_2ZrCl_2)^{\cdot-}$ spectrum. A similar situation was discussed for Ti by Krusic, who estimated this constant to have a value of 0.8 G in the methylene-bridged compound $[(\mu-CH_2)(\mu-Cl)-(Cp_2Ti)_2]$.³²

Comparison of our ESR parameters for the species generated under identical experimental conditions allows us to make some further interesting observations.

(a) The Zr hyperfine interaction constant is practically the same in the chloride and the bromide; it is substantially reduced in the phosphine compounds due to partial shift of electron spin density on phosphorus. In contrast, there is an increasing trend of the *g* isotropic value in the halide series Cl < Br < I, which could be due to several factors,³⁰ but the available data are not sufficient to explain its true significance.

(b) The phosphine adducts show some remarkable peculiarities. Their signals are evidently due to the coordination of one phosphine ligand to a Zr(III) species, but they do not give a straightforward answer about their nature. The Zr hyperfine interaction is substantially reduced in comparison with the dihalide radical anions as a consequence of a partial electron density shift onto the phosphorus nucleus. The bromine hyperfine interaction is also reduced to below resolution, and the linewidth becomes surprisingly sharp ($\Delta B \approx 5$ G for the phosphine compounds vs. 9.5 and 13 G for X = Cl and X = Br, respectively, in the radical anions). The halogen dependence of the ESR parameters is reflected by the slight difference in the $a(P)$ values (see Table I) and especially the significant difference in the *g* isotropic values in the same manner as in (a) above ($g(Br) > g(Cl)$). Taken together, these results show that electron distribution around zirconium in the dihalide radical anions is considerably modified by reaction with phosphines so that formulation of these products as simple phosphine adducts such as

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$[\text{Cp}_2\text{ZrX}_2(\text{PR}_3)]^-$ becomes rather unreasonable; added to this is the fact that such a structure formally implies a 19-electron configuration and a highly crowded metal environment. We therefore formulate them as the mono-halide compounds $\text{Cp}_2\text{ZrX}(\text{PR}_3)$ formed by halogen cleavage following electron addition on the starting dihalides. This structural assignment is further supported by the irreversible character of the cathodic waves which appear in the cyclic voltammetry upon addition of phosphines and the appearance of electroactive species in the anodic region. However, our data with PMePh_2 do not agree with earlier reports²⁰ on compounds obtained by the reactions of alkyl halides with $\text{Cp}_2\text{Zr}(\text{PMePh}_2)_2$ in pure phosphine and identified by ESR as $\text{Cp}_2\text{ZrX}(\text{PMePh}_2)$ (X = Cl, Br). The reported spectral parameters do not exhibit any significant halogen dependence ($a(\text{P}) = 21$ G for X = Cl and Br; $A(\text{Zr}) = 17$ G for X = Cl and, surprisingly $g = 1.998$ for X = Cl, very close to $g = 1.995$ for X = Br) as is the case with our compounds.

Finally, it may be argued that the species arising from the electrolytic reduction of Cp_2ZrMe_2 could be due to either metal radicals arising from reaction 2 or 4. ESR signals of the same pattern were obtained with a series of compounds (Cp_2MR_2) (M = Ti, Zr; R = CH_2Ph , CHPh_2 , CH_2SiMe_3) by chemical and electrochemical methods for which both types of radicals were postulated.^{12,33} On the

other hand, electrochemical oxidation of $\text{Cp}_2\text{W}(\text{CH}_3)_2$ was reported to yield the cation $[\text{Cp}_2\text{W}(\text{CH}_3)_2]^+$ identified by ESR.³⁴ We believe that the radical anion structure (Cp_2ZrMe_2)⁻ is more likely for our electrochemically reduced compound than the highly electron-deficient CpZrMe_2 formulation.

Electrolytic reduction of hafnocene compounds along the same lines as above did not generate signals attributable to hafnium(III) paramagnetic species, and the only signals observed were those due to reduction of the accompanying zirconium analogues usually present.

Acknowledgment. We are grateful to Dr. Gourier for computer simulation and discussions on ESR and to Mrs. Hénique for efficient technical assistance.

Registry No. $[\text{Cp}_2\text{ZrCl}_2]^-$, 75699-43-3; $[\text{Cp}_2\text{ZrBr}_2]^-$, 95765-30-3; Cp_2ZrI , 95765-31-4; CpZrCl_2 , 80042-49-5; $[\text{Cp}_2\text{ZrMe}_2]^-$, 95765-32-5; $[\text{Cp}_2\text{ZrCl}(\text{PMe}_3)]$, 95765-33-6; $[\text{Cp}_2\text{ZrCl}(\text{PMePh}_2)]$, 80642-23-5; $[\text{Cp}_2\text{ZrBr}(\text{PMe}_3)]$, 95765-34-7; $[\text{Cp}_2\text{ZrBr}(\text{PMePh}_2)]$, 80642-24-6; Cp_2ZrCl_2 , 1291-32-3; Cp_2ZrBr_2 , 1294-67-3; Cp_2ZrF_2 , 11090-85-0; Cp_2ZrI_2 , 1298-41-5; Cp_2ZrMe_2 , 12636-72-5; Cp_2ZrCl , 86665-14-7; ZrCl_3 , 10241-03-9; PMe_3 , 594-09-2; PMePh_2 , 1486-28-8.

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Paramagnetic Organometallic Molecules. 18.¹ Redox Chemistry of the Flyover Complexes $\text{R}_6\text{C}_6\text{Co}_2(\text{CO})_4$

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The redox chemistry of a series of "flyover" complexes $\text{R}_6\text{C}_6\text{Co}_2(\text{CO})_4$ has been investigated by electrochemical and ESR techniques in a variety of solvents. The compounds all undergo reversible one-electron reduction to a radical anion, the stability of which is dependent on the solvent system. In acetone or dichloromethane, the radical anion $(\text{CF}_3)_6\text{C}_6\text{Co}_2(\text{CO})_4^-$ decomposes by ring closure of the flyover bridge to give hexakis(trifluoromethyl)benzene, $(\text{CF}_3)_6\text{C}_6$, via the radical anion $(\text{CF}_3)_6\text{C}_6^-$. In contrast the radical anion $(\text{CF}_3)_6\text{C}_6\text{Co}_2(\text{CO})_4^-$ shows exceptional stability in THF solvent. A second reduction step producing an inherently unstable dianion is also observed in all solvents. Unusual scan rate dependence of this second step under conditions of cyclic voltammetry may be consistent with a homogeneous electron-transfer reaction between the dianion and the neutral "flyover" complex. In acetonitrile, rapid electron-transfer-catalyzed substitution of the radical anions leads to the formation of acetonitrile complexes. The ESR spectra of electrolytically generated radical anions of several of the flyover complexes were observed in THF solutions. The isotropic spectra show coupling to two equivalent cobalt nuclei. Isotropic ESR spectra of $(\text{CF}_3)_6\text{C}_6\text{Co}_2(\text{CO})_4^-$ in acetone solution again showed coupling to two equivalent cobalt nuclei, but slow decomposition of the radical anion of the flyover complex led to the observation of the radical anion $(\text{CF}_3)_6\text{C}_6^-$.

Introduction

Complexes of the general formula $(\text{alkyne})_3\text{Co}_2(\text{CO})_4$ in which three acetylenic moieties oligomerize in a "head to tail" fashion to form a "flyover" bridge to the cobalt-cobalt

bond are well-characterized,³ and structural information has been reported for three of them.⁴⁻⁶ Our interest in the redox chemistry of capped tricobalt⁷ and dicobalt^{8,9}

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