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Electrochemical and Chemical Reduction of Titanocene Dihalides—An EPR Study

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Electrolysis in the cavity of an EPR spectrometer was used to study in situ the species generated by electroreduction of bis(cyclopentadienyl)titanium(IV) dihalides [$(\eta^5\text{-}C_5H_5)_2TiX_2$] (X = Cl, Br, I) in THF (tetrahydrofuran). Careful analysis of the spectra showed that the only species formed were the respective Ti(III)-solvated monohalides. It is concluded that the radical anion $[(\eta^5\text{-}C_5H_5)_2TiX_2]^-$ formed upon one-electron addition by electrolytic reduction is rapidly followed by halogen cleavage, so that it is not detectable as such by EPR. The role of residual water present in purified THF is discussed. In the light of these results the formation of aquatitanocene(III) species as well as titanocene(III) monocation is postulated. Hyperfine interaction of the unpaired electron in titanocene monohalides with bromine (A_{Br} = 2.1 G) and with iodine (A_I = 5.1 G) nuclei is reported for the first time.

Introduction

For several years, the reaction steps involved in the electrochemical reduction of titanocene dichloride have been the subject of extensive investigations.[1-15] The intriguing problem that arose from the outset and was at the origin of controversial speculations was whether the uptake of one electron per molecule in aprotic solvents leads to the formation of a stable radical anion or is rapidly followed by halogen cleavage to give the well-known monochloride. The main reason for this difficulty in finding a satisfactory answer to an apparently simple question is the perfect reversibility of the first reduction wave (out of the three reduction waves observed) and the failure to isolate a well-defined species resulting from electrochemical reduction.[16] Evidence for the radical anion mechanism relied essentially on EPR data that were used to confirm polarography or voltammetry experiments.

In a previous study we used electrochemical reduction inside the cavity of an EPR spectrometer to establish the in situ formation of [Cp_2ZrX_2] (X = Cl, Br) radical anions,[17] and subsequent studies supported these findings.[18] In this work we present our results on the identification by EPR of the species obtained upon reduction of [Cp_2TiX_2] (X = Cl, Br, I) (I, II, and III, respectively) in THF (tetrahydrofuran) by both chemical and electrochemical methods. We show that a careful comparison of the spectra obtained by these two methods sheds some light on this somewhat enigmatic and important subject, since these dihalides are precursors in the syntheses of a host of compounds used in various areas of organometallic chemistry[19] and recently in biology[20] so that comprehension of some of their basic reactions is of fundamental importance. We also show that although it is tempting to use arguments based on EPR to confirm the radical anion hypothesis, this technique in the present case contains some pitfalls so that our current knowledge of the problem has to be reconsidered.

We report also the observation by EPR of hyperfine interaction in the paramagnetic titanocene monohalides [$(Cp_2TiX)_2$] (X = Br, I) of the unpaired electron on Ti with Br and I nuclei, which, to the best of our knowledge, has not been reported earlier.

Experimental Section

All manipulations and cyclic voltammetric measurements were performed under argon. For routine experiments, and unless otherwise stated, THF was dried by conventional methods and distilled over $AlLiH_4$ under argon before use. The EPR electrochemical cell and apparatus were previously described,[17] and the same procedure was followed to generate the signals of the reduction products. The signal, once generated (usually after electrolysis for about 40 s at 50 μA), is stable for appreciable lengths of time (about an hour) after the current flow is stopped. I was purchased from Alfa Inorganics; II and III were prepared by literature methods[21] by reacting I with BBr_3 and BI_3, re-

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(1) Dessy, R. E.; King, R. B.; Waldorf, M. *J. Am. Chem. Soc.* **1966**, *88*, 5112.

(2) Valcher, S.; Mastragostino, M. *J. Electroanal. Chem.* **1967**, *14*, 219.

(3) Gubin, S. P.; Smirnova, A. *J. Organomet. Chem.* **1969**, *20*, 229.

(4) Doisneau, R. G.; Marchon, J. C. *J. Electroanal. Chem.* **1971**, *30*, 487.

(5) Kadlec, V.; Kadlecova, H. *J. Organomet. Chem.* **1979**, *82*, 113.

(6) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219.

(7) Laviron, E.; Besançon, J.; Huq, F. *J. Organomet. Chem.* **1978**, *159*, 279.

(8) Chaloyard, A.; Dormond, A.; Tirouflet, J. *J. Chem. Soc., Chem. Commun.* **1980**, 214.

(9) El Murr, N.; Chaloyard, A.; Tirouflet, J. *J. Chem. Soc., Chem. Commun.* **1980**, 446.

(10) Mugnier, Y.; Moïse, C.; Laviron, E. *J. Organomet. Chem.* **1981**, *204*, 61.

(11) Mugnier, Y.; Moïse, C.; Laviron, E. *J. Organomet. Chem.* **1981**, *210*, 69.

(12) El Murr, N.; Chaloyard, A. *J. Organomet. Chem.* **1981**, *212*, C39.

(13) El Murr, N.; Chaloyard, A. *J. Organomet. Chem.* **1982**, *231*, 1.

(14) Symons, M. R. C.; Mishra, S. P. *J. Chem. Soc., Dalton Trans.* **1981**, 2258.

(15) Mugnier, Y.; Fakhr, A.; Fauconnet, M.; Moïse, C.; Laviron, E. *Acta Chem. Scand., Ser. B.* **1983**, *B37*, 423.

(16) Connelly, N. G.; Geiger, W. E. *Adv. Organomet. Chem.* **1984**, *23*, 2.

(17) Samuel, E.; Guery, D.; Vedel, J.; Basile, F. *Organometallics* **1985**, *4*, 1073.

(18) Fakhr, A.; Mugnier, Y.; Gautheron, B.; Laviron, E. *Nouv. J. Chim.* **1986**, *10*, 601.

(19) *Comprehensive Organometallic Chemistry*; pergamon: Oxford, 1982; Vol. 3.

(20) Koepf-Maier, P.; Koepf, H. *Chem. Rev.* **1987**, *87*, 1137 and references therein.

(21) Druce, P. M.; Kingston, B. M.; Lappert, M. F.; Spalding, T. R.; Srivastava, R. C. *J. Chem. Soc. A* **1969**, 2106.

0276-7333/89/2308-0237$01.50/0

spectively, and their purity was controlled by NMR. They were used in the electrochemical cell at 0.02 M concentrations and in cyclic voltammetry at 0.005 M. The halide-bridged dimers $[(Cp_2TiX)_2]$ (X = Cl, Br, I; IV, V, and VI, respectively) were prepared according to literature methods by reducing the corresponding dihalides with activated aluminum in THF.[22]

In order to measure under controlled conditions the EPR spectra of the reaction products obtained by chemical reduction, a special device was conceived. About 30 mg of the compound were placed together with activated aluminum foil,[22] 2 mL of dry THF, and a magnetic bar in an apparatus made of a Pyrex tubing 16 cm high and 9 mm in diameter, to which was sealed in the same plane at midheight and in a parallel direction, bottom upward, an EPR Pyrex tube. The large tube was sealed under vacuum after introduction of the reactants and the solution stirred. Formation of the monohalide was monitored by tilting the apparatus so as to introduce some of the solution into the EPR tube and then recording the spectrum. No signal other than that of the solvated monohalide $[(Cp_2TiX(THF)]$ was observed.

Results

The electrochemical reduction of I in various solvents and especially in THF has been carefully studied.[9] As a reminder, the compound exhibits by cyclic voltammetry in THF/NBu_4PF_6 three reduction waves at 0.77, 2.0, and 2.2 V (vs Ag/AgCl), respectively. The first wave is perfectly reversible at room temperature irrespective of scan speed throughout the full potential range; however, it was found to split into two waves[15] at −54 °C. The other two are slightly reversible.

The electrochemistry of II was only briefly discussed earlier,[9] though comparison of I and II for the present purposes is very instructive as will be shown later. The voltammogram under the same conditions as in I exhibits also three cathodic waves at roughly the same potentials and having exactly the same shapes provided that the solvent is very carefully dried. It is remarkable that the first reduction wave is also perfectly reversible.

III exhibits an ill-defined irreversible cathodic wave at low potentials followed by broad features attributable to chemical reactions due to dissociation and loss of halogen.

Reduction of these three halides by well-known chemical methods gives the monohalides $[(Cp_2TiCl)_2]$, $[(Cp_2TiBr)_2]$, and $[(Cp_2TiI)_2]$ (IV, V, and VI), respectively. These compounds are well characterized and known to be paramagnetic dimers in the solid phase exhibiting antiferromagnetism.[23] This dimeric structure is conserved in hydrocarbon solvents, but in donor organic solvents such as THF, pyridine, or DMF, the solvated monomers $[Cp_2TiX(S)]$ are obtained.[24] To our knowledge, little is known about their EPR behavior apart from a few elementary data on the monochloride.

The important question we are attempting to elucidate is whether the uptake of one electron in the dihalides proceeds by the formation of a stable anion radical

$$Cp_2TiCl_2 \rightleftarrows [Cp_2TiCl_2]^- \quad (1)$$

or is accompanied immediately by halide cleavage

$$Cp_2TiCl_2 \overset{THF}{\rightleftarrows} Cp_2TiCl(THF) + Cl^- \quad (2)$$

In other words, the radical anions $[Cp_2TiX_2]^-$ are the stable species which can be well characterized spectroscopically, albeit isolated, or IV, V, and VI are actually the only detectable species formed as the solvate monomers $[Cp_2TiX(THF)]$ by electrochemical reduction. For this purpose it is quite convenient to monitor the electrochemical reactions by EPR and evaluate the results by comparison with those obtained by chemical reduction under similar conditions (solvent, temperature, concentration). Different species would evidently give different spectra.

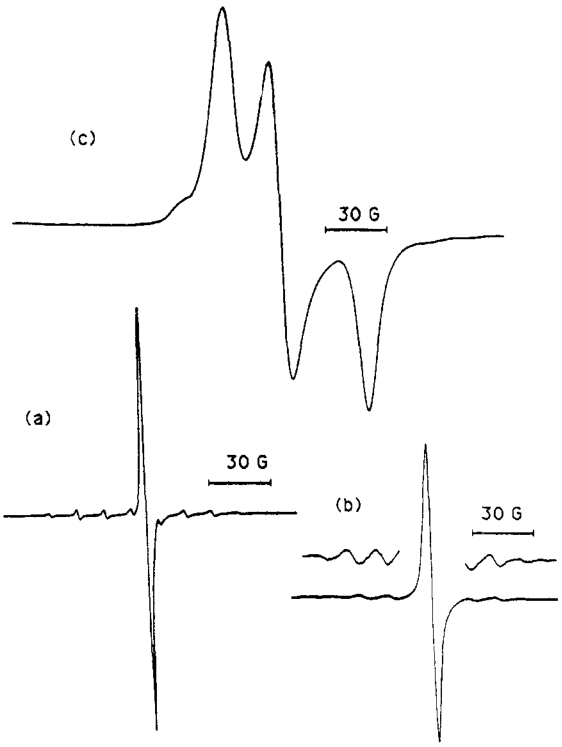

Figure 1. (a) Room-temperature spectrum of electrochemically reduced $[Cp_2TiCl_2]$ in THF in situ or of pure $[Cp_2TiCl]_2$ in THF dried electrolytically. (b) $[Cp_2TiCl]_2$ in THF without electrolytic treatment. (c) Frozen solution spectrum of (a) or (b).

Electrochemical reduction of I, II, and III in an EPR-electrochemical cell yielded within a few seconds intense signals due to the formation of Ti(III) compounds as follows; these we shall henceforth call Ie, IIe, and IIIe, respectively.

Compound Ie. The signal is a very sharp singlet flanked by satellites (due to ^{47}Ti and ^{49}Ti; $I = {}^5/_2$ and ${}^7/_2$ in their respective natural abundance) with exceptionally good resolution (Figure 1a). This is the only signal that appears at room temperature or at temperatures down to −50 °C. At lower temperatures the signal broadens and resolution is lost progressively. The same signal was also obtained by exhaustive electrolysis at controlled potential corresponding to the first reduction wave.[9] Cooling down to 130 K gives the anisotropic frozen solution spectrum shown on Figure 1c.

Compound IIe. By proceeding in the same manner, a signal is immediately obtained which is best resolved at −30 °C. This signal is reproducible and consists of a central manifold of a poorly resolved sextet; the same pattern was also observed, especially at the low-field side, on the satellites flanking the central multiplet (Figure 2a). This signal splitting is obviously due to hyperfine interaction with Br nuclei ($^{79,81}Br$:$I = {}^3/_2$, 100%) and will be discussed later. It is sometimes accompanied by another signal, a singlet at higher field ($g = 1.974$). The frozen solution spectrum of the multiplet presents complicated features that cannot be rationalized by a first-order analysis.

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[22] Coutts, R. S. P.; Wailes, P. C.; Martin, R. L. *J. Organomet. Chem.* **1973**, *47*, 375.

[23] Coutts, R. S. P.; Wailes, P. C. *Adv. Organomet. Chem.* **1970**, *9*, 162.

[24] (a) Green, M. L. H.; Lucas, C. R. *J. Chem. Soc. Dalton Trans.* **1972**, 1000. (b) Coutts, R. S. P.; Kautzner, B.; Wailes, P. C. *Aust. J. Chem.* **1969**, *22*, 1137.

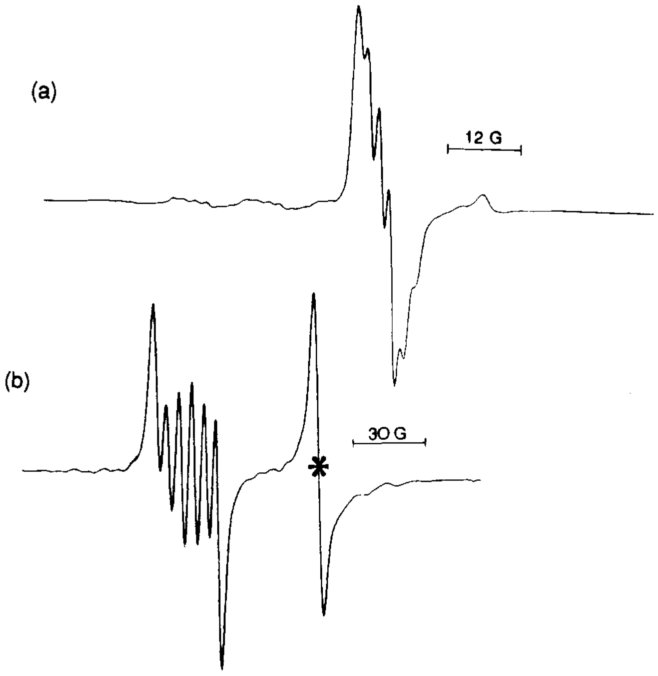

Figure 2. EPR spectra at −20 °C of (a) electrochemically reduced [Cp_2TiBr_2] and (b) [Cp_2TiI_2] in THF in situ. Singlet at high-field marked with asterisk is presumably due to the [$Cp_2Ti(S)]^+$ cation.

Table I. EPR Parameters of Cp_2Ti^{III} Halides

compd	g_{iso}	g_z	g_y	g_x	A_{iso}(Ti)	A_{iso}(X)	ΔB
[$Cp_2TiCl\cdot THF$]	1.976	1.9981	1.977	1.955	14.6		2.0
[$Cp_2Ti(S)]^{+a}$	1.974	2.000	1.980	1.945	14.6		4.2
[$Cp_2TiBr\cdot THF$]	1.988				12.9	2.1 (q)	7.3
[$Cp_2TiI\cdot THF$]	2.008				12.16	5.1 (s)	

[a] Solvated cation obtained from solutions of [$Cp_2TiX]_2$ in toluene/methanol. Other entries in THF. Abbreviations: q, quartet; s, sextet. g factors relative to dpph (diphenylpicrylhydrazyl). Hyperfine constants and bandwidth values (ΔB) in gauss (1 G = 10^{-4} T). X = halide.

Compound IIIe. The signal is a neatly resolved sextet with lines of equal intensities (Figure 2b). These can be attributed unambiguously to hyperfine interaction of the unpaired electron on titanium with one iodine nucleus (^{127}I:I = $^5/_2$, 100%). Another intense peak that is a singlet is sometimes observed at high fields at exactly the same field as for IIe (see below).

We now compare the results obtained for Ie, IIe, and IIIe with those for IV, V, and VI.

Ie and IV. This case deserves special attention since most of the electrochemical literature on titanocene deals with the dichloride.

Although the isotropic spectra of the two compounds have practically the same g and A(Ti) (hyperfine splitting) values, they have slightly different bandwidths (Table I). The central peak in Ie is sharp (Figure 1a), and satellite splitting is resolved very clearly all through the different M_I values, whereas in IV the broadened band profile obscures the splitting at $M_I = \pm^1/_2$ (Figure 1b). As for the frozen solution spectra, they are rigorously identical for both compounds (Figure 1c). From this result it can be reasonably concluded that the two compounds having identical ground states, are one and the same, and therefore electrochemical reduction under the conditions described above yields only the monochloride. Thus the reason for the small difference in the isotropic spectra should be sought elsewhere.

In this context, it should be mentioned that the same frozen solution spectrum (Figure 1c) was obtained[14] upon γ-irradiation of I in THF at 77 K and was attributed to the formation of the radical anion by simple electron capture. However, by operating in methanol, the same authors obtained a slightly different spectrum at 77 K whose features show practically the same g_z and g_y values as the former, but a slightly lower g_x value. For this reason they attributed the spectrum to the formation of the monochloride by loss of a Cl^- ion from the initially formed radical anion.

Figure 3. Frozen solution spectrum of [$Cp_2TiX]_2$ in THF or toluene containing 20% methanol. The spectrum is attributed to the [$Cp_2Ti(S)]^+$ cation.

This point requires some elaboration, and as we shall see later, this small difference in the g_x value is a fundamental criterion in characterizing the titanium(III) species by EPR. Our results show that the frozen solution spectrum of γ-irradiated I in THF is that of the monochloride (Ie or IV). Therefore, the other spectrum mentioned above could be only due to a different compound formed by treatment of the monochloride with methanol. This is proved by the following.

Dissolution of IV in a mixture of toluene/THF (30/70) gives the isotropic spectrum (Figure 1b) and the frozen solution spectrum (Figure 1c). If methanol is added at about 20%, the frozen solution spectrum Figure 3 is obtained. This spectrum is also obtained if V or VI are dissolved in a mixture of THF/methanol. Consequently the spectrum is due to a titanocene compound which does not contain a halogen. We attribute it to the solvated [$Cp_2Ti(S)]^+$ cation (S = methanol or THF). This hypothesis is supported by our previous EPR–ENDOR studies[25] on the trimetallic compound [$(Cp_2TiCl)_2(ZnCl_4)$] where we could demonstrate that in THF an ionic structure predominates in which the unpaired electron strongly interacts with a coordinated solvent molecule and for which we proposed the formula [$\{Cp_2Ti(THF)\}_2][ZnCl_4]$. Indeed this trimetallic compound in very dilute THF solution shows an anisotropic spectrum at 130 K identical with the one shown in Figure 3. We therefore believe that the assignment of this spectrum to a titanocene cation is very reasonable.

We now have to account for the difference in the isotropic spectra of Ie and IV (parts a and b of Figure 1), which according to the above results should belong to the same compound. Upon careful study it can be shown that this subtle difference is only of form rather than of substance and is due solely to solvent effects for the following reasons.

THF containing only supporting electrolyte (0.1 M) was electrolyzed for about 2 hours with cathodic current in an electrolytic cell under argon by using a platinum gauze cathode and an Ag/AgCl/KCl anode and then introduced in the sealed system described above together with

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(25) Gourier, D.; Vivien, D.; Samuel, E. *J. Am. Chem. Soc.* **1985**, *107*, 7418.

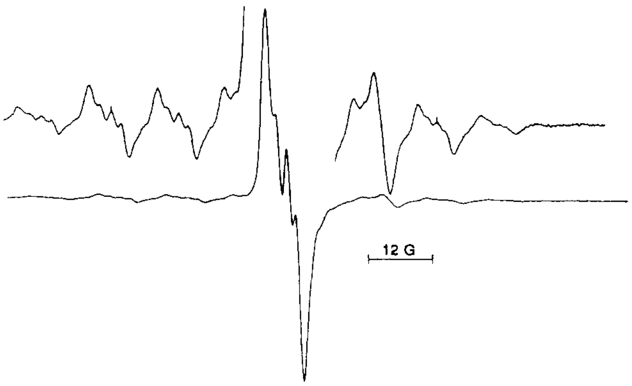

Figure 4. Isotropic spectrum at -20 °C of $[Cp_2TiBr_2]$ reduced electrochemically in situ in THF dried by electrolytic treatment. The same spectrum is obtained with pure $[Cp_2TiBr]_2$ in similarly treated THF.

$[Cp_2TiCl_2]$ and Al foil. The EPR spectrum of the paramagnetic compound formed and normally supposed to be IV was identical with the spectrum of Ie (Figure 1a), exhibiting in particular the same sharp signal contrasting with the relatively broad signal obtained when THF not previously submitted to electrolysis was used (Figure 1b). The frozen solution spectrum was of course that of IV (Figure 1c). This experiment provides a convincing proof that trace amounts of water in THF, which cannot be removed by conventional chemical treatment, are sufficient to modify the isotropic line shape. It is quite plausible that a solvated species such as $[Cp_2TiCl(H_2O)]$ is formed along with $[Cp_2TiCl(THF)]$. These two compounds, having the same symmetry around titanium, would have nevertheless very slightly different isotropic g values so that their isotropic signals overalp, thus causing the band broadening, and their ground state being essentially the same, resolution of the frozen solution spectra is not sufficient to allow the separation of their respective components.

IIe and V. We mentioned earlier that the signal of IIe, which first appears upon the flow of cathodic current and which most probably corresponds to the first reduction wave, is a sextet (Figure 2a). This signal was mistakingly taken to be a septet (interaction of the unpaired electron with two bromine nuclei), thus confirming the radical anion nature of the electroreduced species. However, this confusion is easily dissipated by the following observation: (i) dissolution of V in a mixture of toluene/THF gives an EPR signal identical in all respects with that of IIe, so that this signal cannot be that of a radical anion which should in any case be a septet, and (ii) even if this signal were a septet due to the radical anion, the relative intensities of the individual components should be those predicted for such a system (1:2:3:4:3:2:1). No such thing is observed, and moreover, the relative intensities of the outside peaks of the central multiplet vary from one preparation to another. Also computer simulation based on an $s = {}^1/_2$ electron spin interacting with two equivalent $I\ {}^3/_2$ nuclear spins gave an EPR spectrum definitely different from the experimental one.

Again the following experiment helps to clarify the situation: preelectrolyzed THF (see above) was used in the EPR electrochemical cell to reduce II. Instead of the sextet, a *quartet* was obtained with features in full agreement with those of a titanocene monobromide monomer (interaction of the unpaired electron with one Br nucleus with the appropriate signal intensities), Figure 4 and Table I. Introduction of water (to make 0.25 M) in the cell and electrolysis again with cathodic current under the same conditions regenerate the sextet obtained above. This sextet can therefore be interpreted as being due to the overlap of two quartet signals having very close g values, the one due to $[Cp_2TiBr(THF)]$ and the other probably to $[Cp_2TiBr(H_2O)]$.

The spectrum of V now becomes clear, and in order to provide a further confirmation, preelectrolyzed THF together with II and Al foil were introduced in the EPR device (see Experimental Section) and the tube was sealed. The signal that is obtained from this reaction is a clean well-resolved *quartet* as shown on Figure 4, so that here again residual water in THF seems to be associated with the EPR spectra of the reduction products, whether obtained by chemical or electrochemical methods, and consequently the radical anion hypothesis in this case also is not justified.

It should be mentioned in this context that when preelectrolyzed THF is used in cyclic voltammetry, the first reduction wave of II, which otherwise has a lower peak oxidation current intensity, becomes perfectly reversible and resembles in every respect to the voltammogram of I.

IIIe and VI. The situation in this case is more straightforward. Both species give identical spectra easily attributable to the monoiodide (Figure 2b). Although neat spectra were obtained only when working with the sealed device, traces of water do not seem to have the same dramatic effect as with the above two compounds. It is quite possible that the aqua species eventually formed is spontaneously hydrolyzed to give the monocation, giving thus the high-field signal observed sometimes.

All EPR parameters are gathered in Table I.

Discussion

The EPR criteria detailed above, brought to light by comparison of electrochemical and chemical reduction methods, provide a strong support to the mechanism which postulates that the first electrochemical reduction wave observed by cyclic voltammetry in the case of I and II involves rapid halide loss subsequent to the one-electron uptake (the case of III is clear and does not need comment). This contrasts with the isostructural zirconocene compounds where it was shown by EPR[17] that radical ions are formed without halogen cleavage upon electrochemical reduction of the corresponding dihalides. The only features in common are the results obtained by electrochemical (or chemical) reduction of the dimethyl compounds where EPR spectra consistent with the formation of the corresponding radical anions were obtained (hyperfine interaction with protons of the two methyl groups); this structure, however, was disputed and rapid ring cleavage was postulated.[26]

Another feature revealed in the above study is the role of residual water in purified THF. The quantity of this residual water was estimated[27] to be about 0.05 M. It was found to interfere also in the electrolytic reduction of zirconocene and hafnocene dichlorides,[18] and its role in voltammetry studies of these compounds was already recognized.[4]

A third particularity revealed in this work is the action of methanol on the halogen-bridged dimers. EPR parameters of liquid and frozen solutions are the same in all three cases (X = Cl, Br, I; Table I), indicating the formation of a single species, presumably the solvated tianocene monocation $[Cp_2Ti(S)]^+$. This cation has been described already, and stable compounds derived from it have been isolated.[24] However, a structure such as solvated

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[26] Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organozirconium and -hafnium compounds*; Wiley: New York, 1986; p 61.

$[Cp_2Ti(OH)]$ should not be excluded.

As for the EPR parameters, a survey of Table I shows that the isotropic g values of the three halides examined show a uniform positive shift from Cl to I. A similar situation was found with the electroreduced zirconocene dihalides. In both cases no adequate information can be gathered from the anisotropic spectra of the bromides or the iodides because either of poor resolution or of the noncoaxial nature of the **A** and **g** tensors, so that all attempts to rationalize this phenomenon become purely speculative. Futhermore, similar information on d^1 metallocenes do not seem to be mentioned in literature, for example, in the case of the vanadocene dihalides. It is surprising, however, that this trend is exactly the opposite to that observed in the monomeric monohalides of the bis(pentamethylcyclopentadienyl)titanium compounds where the g values were reported to be 1.956, 1.953, and 1.939 for X = Cl, Br, and I, respectively.[28] It should be noted, however, that these measurements were made in pentane, and the bandwidths observed were over 60 G at room temperature. It is very unlikely that a difference in the ground state is responsible for this abnormally high negative shift compared to that for our compounds. Obviously a more detailed study in this area is needed.

Finally, the second and third reduction waves observed in the voltammogram of I call for some comments. Although a few speculations have been made about their significance, no conclusive evidence was provided in support. Our measurements on the ring-substituted analogues where Cp is replaced by Me-Cp or tetrahydroindenyl show not only that these two waves are always present but also that their reversibility is much more pronounced and is almost perfect in the latter substituted ring.[29] Strangely enough, both waves are absent in the voltammogram of $[\{Si(CH_3)_2(C_5H_4)_2\}TiCl_2]$[30] which exhibits only one reversible cathodic wave at −0.793 V against −0.800 V for I measured under the same conditions (ferrocene/ferrocenium couple as internal standard, $E°$ = 0.51 V vs SCE). It is surprising that bridging the rings in this case has such drastic effects on the electronic property of the metal so as to shift these two waves to much more negative potentials (below the solvent discharge) if they really exist. The reasons therefore should be sought elsewhere, and more studies are needed on this important feature in the chemistry of this family of compounds.

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Registry No. I, 1271-19-8; Ie, 65466-17-3; II, 1293-73-8; IIe, 117469-83-7; III, 12152-92-0; IIIe, 117469-84-8; IV, 1271-18-7; V, 39333-86-3; VI, 39333-90-9; $[Cp_2Ti(MeOH)]^+$, 117469-85-9.

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(27) Corriu, R. J. P.; Dabosi, G.; Martineau, M. *J. Organomet. Chem.* **1981**, *222*, 195.

(28) Pattiasina, J. W.; Heeres, H. J., van Bolhuis, F.; Meetsema, A.; Teuben, J. H. *Organometallics* **1987**, *6*, 1004.

(29) Guery, D. Dissertation, University of Pierre and Marie Curie, Paris, 1982.

(30) Bajgur, C. S.; Tikkanen, W. R.; Petersen, J. L. *Inorg. Chem.* **1985**, *24*, 2539.

A Comparison of the Structures of *exo*- and *endo*-(η^5-Cyclopentadienyl)(η^3-2-methylallyl)ruthenium Carbonyl

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Crystal structure determinations of both the exo and endo isomers of $(C_5H_5)(C_4H_7)Ru(CO)$ reveal differences in interligand crowding which reflect the relative thermodynamic stability of the two conformers. In the less stable endo isomer, there are short hydrogen–hydrogen contacts between the C_5H_5 and C_4H_7 ligands, causing the Ru–C(Cp) distances to be unequal and the Ru–C distance to the central methylallyl carbon to lengthen [2.187 (7) Å] relative to the exo isomer [2.140(4) Å]. Another close contact between the allyl methyl and the CO ligand in the endo isomer forces nonlinearity [174.0 (8)°] in the Ru–C–O group. There is no significant intramolecular crowding in the exo isomer. The 2-methylallyl ligand is nonplanar in both structures, with the methyl carbon displaced 0.141 (9) Å from the allyl plane, toward the metal atom. *exo*-$(C_5H_5)(C_4H_7)RuCO$: monoclinic, space group $P2_1/c$, a = 13.512 (2) Å, b = 6.004 (1) Å, c = 12.526 (4) Å, β = 108.42 (2)°, Z = 4, R = 0.028 for 1734 reflections with $I > 3\sigma(I)$. *endo*-$(C_5H_5)(C_4H_7)RuCO$: orthorhombic, space group $Cmca$, a = 8.814 (1) Å, b = 7.854 (1) Å, c = 27.659 (4) Å, Z = 8, R = 0.041 for 1013 reflections with $I > 3\sigma(I)$.

Introduction

The capacity of some (η^5-cyclopentadienyl)(η^3-allyl)metal complexes to exist in endo and exo conformationally isomeric forms has been known for a number of years,[1] and the interconversions of some such isomers have been studied by dynamic NMR techniques.[2] Relative thermodynamic stabilities have been inferred from thermal isomerization data or observed concentration ratios for the

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(1) (a) Faller, J. W.; Incorvia, M. J. *Inorg. Chem.* **1968**, *7*, 840. (b) King, R. B.; Ishaq, M. *Inorg. Chim. Acta* **1970**, *4*, 258; (c) Faller, J. W.; Johnson, B. V.; Dryja, T. P. *J. Organomet. Chem.* **1974**, *65*, 395.

(2) See: Faller, J. W. *Adv. Organomet. Chem.* 1977, 16, *211*, for a review of this work.

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