Phosphine complexes of Ti(III) and Zr(III): detection in solution by EPR/electrochemical methods [1]

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Abstract

A comparative study by EPR is made on the electrolytic reduction of Cp_2MX_2, $Cp_2M(CH_3)_2$, ($Cp = \eta^5-C_5H_5$, cyclopentadienyl ligand; M = Ti, Zr; X = Cl, Br) and $Ind_2Ti(CH_3)_2$ ($Ind = \eta^5-C_9H_7$, indenyl ligand) in the presence of phosphines. In the case of the dihalides, the monohalo(phosphines) were characterized. In the case of the dimethyl compounds, $Cp_2M(CH_3)(PMe_3)$ and $Ind_2Ti(CH_3)(PMe_3)$ were identified at 230 K from their EPR spectra. At room temperature and for M = Ti, intramolecular rearrangement takes place to yield the presumably chelated dimethylphosphinomethyl compound $Cp_2Ti(III)CH_2PMe_2$ while $Ind_2Ti(CH_3)(PMe_3)$ remains stable.

Keywords: Titanium; Zirconium; Indenyl; ESR; Phosphines; Alkyls; Cyclopentadienyl

1. Introduction

Cyclopentadienyl compounds of Ti and Zr containing neutral phosphine ligands as donors are usually obtained by chemical reduction methods starting from the metal (IV) halides [1]. Thus reduction of $Cp_2M(IV)Cl_2$ (M = Ti, Zr) with Mg metal in THF in the presence of excess trimethylphosphine gives a straightforward method for the formation of the diamagnetic bis-phosphine complexes $Cp_2M(II)(PMe_3)_2$ in good yields. Formation of paramagnetic $Cp_2M(III)E(PR_3)$ compounds (E = one-electron donor ligand, R = alkyl or aryl group) however, is more problematic. Under carefully controlled conditions, $Cp_2TiCl(PMe_3)$ has been isolated and fully characterized [2]. Its formation was also well established by electrochemical one-electron reduction of the starting dichloride in the presence of PMe_3 [3]. Very little is known about alkyl(phosphine) compounds of this family [4]. On the other hand, a series of $Cp_2Ti(III)$ silylphosphine compounds was obtained by the reaction of dimethyltitanocene with primary silanes in the presence of the phosphine ligand [5]. These low-valent stabilized compounds can be used as starting materials

for other synthetic purposes or can be considered as quenched intermediates for catalytic or mechanistic studies.

In this work we report on the characterization in solution by EPR spectroscopy of a series of Ti(III) and Zr(III) halo(phosphine) and methyl(phosphine) compounds using an EPR/electrochemical cell working at variable temperatures to generate the organometallic radicals in situ.

2. Experimental section

The experimental procedure as well as the signals obtained upon in situ electrochemical reduction of titanocene and zirconocene dihalides and dialkyls has already been described in detail [6]. Samples for EPR studies were prepared by dissolving the metal complex (approx. 0.01 M) in THF with two equivalents of phosphine. All abbreviations are conventional.

3. Results

3.1. Cp_2MX_2 (M = Ti, Zr; X = Cl,Br)

Immediately following the flow of reductive current in the EPR/electrochemical cell containing the dihalide

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[1] To M.D.R. -- endowed with an unfailing talent of communicating enthusiasm in search of truth in science.

and PMe_3 at room temperature, a strong signal appears consisting of a central doublet of 1 : 1 intensity characteristic of the interaction of the unpaired electron with a single ^{31}P nucleus. Satellites due to isotopes of Ti and Zr (natural abundance: ^{47}Ti, $I = 5/2$, 7.4%; ^{49}Ti, $I = 7/2$, 5.4%. ^{91}Zr, $I = 5/2$, 11.2%) are also cleanly resolved on both sides of the central doublet. For Ti with X = Br, the band profile is conspicuously broader than the chloride, which indicates non-resolved additional hyperfine interaction with the Br nucleus ($^{79,81}Br$, $I = 3/2$, total 100%). On the other hand, no such band broadening is observed with Zr (M = Zr, X = Br) [6]. The signals thus generated remain stable for a long time when the current flow is stopped.

3.2. $Cp_2M(CH_3)_2$ (M = Ti 1a; Zr 1b)

After a few seconds of cathodic reduction at 200 K an intense septet attributable to the anion radical $[Cp_2M(CH_3)_2]^{-\cdot}$ is observed. This signal is stable up to 240 K. In the case of Ti and at higher temperatures, the signal appears only after several minutes of current flow when the solution around the electrode changes color to become green-black. The signal is stable at room temperature for more than fifteen minutes even in the absence of current. The same experiment conducted in the presence of excess PMe_3 gives, after a few seconds and at 200 K, an intense signal, the central part of which consists of a doublet of quartets easily attributable to the interaction of the unpaired electron with one P nucleus as well as with the three hydrogens of one methyl group bound to the metal.

Additional lines on both sides of the central signal assignable to Ti (or Zr) satellites are also cleanly resolved, which allows one to assign it with certainty to the formation of $[Cp_2M(CH_3)(PMe_3)]$. The signal is more stable with Zr than Ti once the current flow is stopped. Reduction at higher temperatures gives complex signals arising probably from the simultaneous existence of the dimethyl anion radical and the monophosphine compound. From 273 K up to room temperature, no signal is observed for Zr, while with Ti an intense doublet is systematically obtained without any additional hyperfine structure. These data will be discussed below.

Under the same conditions, electrolysis in the presence of PEt_3, $PMePh_2$ or PPh_3 gives no indication of a similar reaction. The signal of the radical anions of 1a and 1b formed by the reductive current remain unaltered.

3.3. $Ind_2Ti(CH_3)_2$ 2

In contrast to the cyclopentadienyl analog mentioned above, electrochemical reduction of this compound at 253 K yields immediately an intense central signal
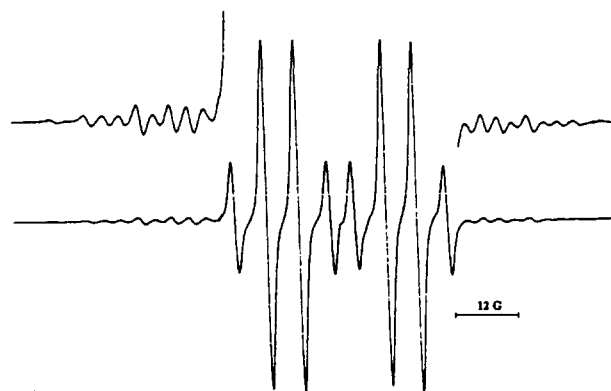

Fig. 1. EPR spectrum of the species $Cp_2Ti(CH_3)(PMe_3)$ generated by electrolysis in the cavity of the spectrometer at 230 K. Gain: 10. Field modulation intensity: 0.1.

consisting this time of a quartet with Ti satellites, the unpaired electron interacting now with the three hydrogens of one methyl group bound to the metal. Cleavage of the other methyl group had therefore occurred subsequent to one-electron addition, and the signal can be attributed to the neutral monomethyl Ti(III) compound $[Ind_2Ti(CH_3)]$. In the presence of excess PMe_3, a doublet of quartets is obtained, the same as above but with slightly different values of the hyperfine coupling. The signal is stable for several minutes in the absence of current flow, even at room temperature.
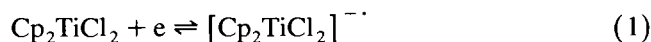
4. Discussion

The above results throw some light on the formation and stability of bis(cyclopentadienyl)Ti(III) and Zr(III) monophosphine compounds. All the data together with the EPR parameters are gathered in Table 1.
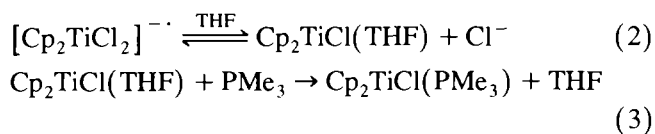
Two sets of results can be extracted from this table, which will be treated successively.

4.1. Halides

Different phosphines, PMe_3, PEt_3, PPh_2Me and PPh_3 were chosen as representative examples to test possible coordination by taking into account the classical criteria of basicity vs. steric hindrance. PEt_3 and PPh_3 did not exhibit any new signals attributable to a phosphine complex, whereas the other two showed clearly the formation of monophosphine complexes in all cases.

In the study of the Cp_2TiCl_2/PMe_3 system by cyclic voltammetry [3], $Cp_2TiCl(PMe_3)$, 3 was isolated by controlled potential electrolysis of Cp_2TiCl_2 at the first reduction potential in the presence of PMe_3, corresponding to the following electrochemical reaction and subsequent equilibria:

$$Cp_2TiCl_2 + e \rightleftharpoons [Cp_2TiCl_2]^{-\cdot} \tag{1}$$

$$[Cp_2TiCl_2]^{-\cdot} \xrightleftharpoons{THF} Cp_2TiCl(THF) + Cl^- \qquad (2)$$

$$Cp_2TiCl(THF) + PMe_3 \rightarrow Cp_2TiCl(PMe_3) + THF \qquad (3)$$

From these results it is clear that PMe_3 enters into the reaction following halide cleavage. This conclusion is unambiguously supported by the observation that the first cathodic wave is unaffected by the presence or absence of phosphine. 3 has been prepared independently by chemical methods [2] and its EPR parameters correspond exactly to the species generated in situ by our electrochemical reduction method. This result can thus be considered as reliable evidence for the identification of the EPR active species generated in the case of the other compounds under study.
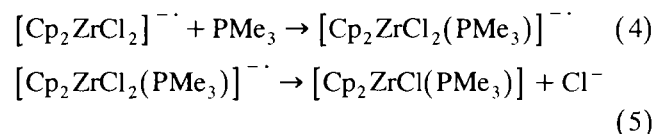
The results and Table 1 show that for encumbered phosphines, $PMePh_2$ is a good compromise between steric hindrance and basicity; it yields stable chloro(phosphine) compounds in all cases. As for the EPR parameters, the a(P) values are slightly higher for the bromide compared to the chloride, and while hyperfine interaction with the halogen nucleus was not resolved for X = Cl, a significant band broadening due to hyperfine interaction with the Br nucleus was observed in the case of Ti only. With regard to the g values, they follow the same trend for Ti and Zr, with higher values for the bromides than the chlorides.

From this knowledge of the electrochemical behavior of the parent dihalides, two different mechanisms can be postulated for M = Ti or Zr:

(1) In the case of Ti, the monochloride formed according to Eq. (2) above is quenched by the phosphine to form the chloro(trimethylphosphine) complex which is responsible for the characteristic EPR signal, the only one observed in the spectrum.

(2) In the case of Zr, we have shown [6] that the anion radical formed according to Eq. (1) is stable, so that it is reasonable to assume that cleavage of one Zr–Cl bond to form the chloro(trimethylphosphine) complex occurs as a second step following coordination of the phosphine on the radical anion metal center to form a pentacoordinate 19-electron species

$$[Cp_2ZrCl_2]^{-\cdot} + PMe_3 \rightarrow [Cp_2ZrCl_2(PMe_3)]^{-\cdot} \qquad (4)$$

$$[Cp_2ZrCl_2(PMe_3)]^{-\cdot} \rightarrow [Cp_2ZrCl(PMe_3)] + Cl^- \qquad (5)$$

Pentacoordination on Zr is not without precedent [7], and is not surprising considering the more diffuse orbitals of this metal compared to Ti. Indeed the signal due to the anion radical ($g_{av} = 1.970$) is always observed along with the chloro(trimethylphosphine) complex. Only the bromide gives a clear spectrum because of the easier cleavage of the Zr–Br bond, or the poor stability of the corresponding dibromide anion radical.

4.2. $Cp_2Ti(CH_3)_2$ 1a, and $Ind_2Ti(CH_3)_2$ 2

For a better understanding of the reactivity of these compounds towards PMe_3, it is relevant to take into consideration their behavior in cyclic voltametry.

In THF at room temperature and with NBu_4PF_6 as supporting electrolyte, 1a exhibits a clean quasi-reversible reduction wave ($\Delta E_p = 120$ mV) at $-2V$ (vs. Ag/AgCl/KCl), see Fig. 2(a). No other cathodic or anodic phenomena are observed. This reduction wave

Table 1

EPR parameters of halo(phosphine) and methyl(phosphine) derivatives of bis-cyclopentadienyl and bis-indenyl Ti and Zr generated in situ by electrochemical methods

Product	a(P)	T(K)	a(H)	A(M) [a]	g(iso)	Ref.
$Cp_2TiCl(PMePh_2)$ [b]	20.5	RT		11.0	1.988	d
$Cp_2TiCl(PMe_3)$	20.2 (d) [c]	RT		11.0	1.986	d
$Cp_2TiBr(PMe_3)$	22.3 (d)	RT		9.7	2.001	d
Cp_2TiMe_2 [e]		210	4.2 (s)	11.2	1.994	d
$Cp_2Ti(Me)(PMe_3)$	23 (dq)	203	6.0	12.3	1.989	d
-id-	20.2 (d)	263		12.0	1.985	d
$Cp_2Ti(Me)(PPh_3)$ [f]	18.9 (dq)	190	6.0		1.999	4
Cp_2ZrMe_2 [e]		190	4.7 (s)	21.9	1.991	6
$Cp_2Zr(Me)(PMe_3)$	21.1 (dq)	203	6.7	17.1	1.989	c
Ind_2TiMe		253	4.8 (q)	12.8	1.975	c
$Ind_2Ti(Me)(PMe_3)$	25.2 (dq)	223	5.9	12.0	1.984	c
$Cp_2ZrCl(PMe_3)$	17.5 (d) [g]	273		23.0	1.979	6
$Cp_2Zr(Br)(PMe_3)$	19.4 (d)			22.7	1.994	6
$Cp_2Zr(Br)(PPh_2Me)$	24.3 (d)	243		21.9	1.991	6

[a] M = Ti or Zr. Coupling constants in Gauss. 1 G = 0.1 mT.
[b] Contains $Cp_2TiCl(THF)$ signal.
[c] d = doublet. dq = doublet of quartets. q = quartet. s = septet.
[d] This work.
[e] As radical anion.
[f] Produced by chemical methods.
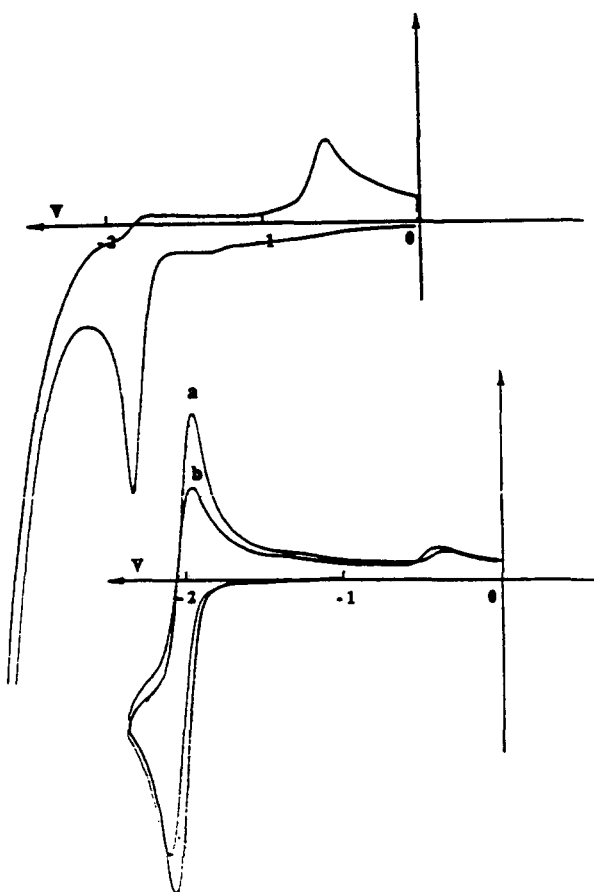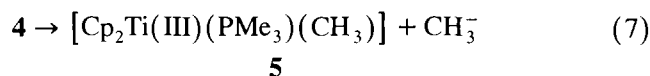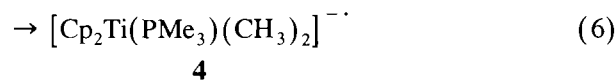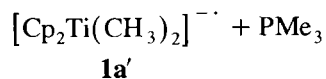[g] Contains Cp_2ZrCl_2 radical anion signal.

Fig. 2. Cyclic voltammograms in THF of: lower inset, $Cp_2Ti(CH_3)_2$ (a) without phosphine and (b) in the presence of PMe_3; upper inset, $Ind_2Ti(CH_3)$. Scan speed, 500 mV s^{-1}.

reasonably corresponds to the formation of the radical anion $[Cp_2Ti(CH_3)_2]^{-\cdot}$ **1a'**, which is responsible for the septet observed by EPR. This indicates that the radical anion formed at the electrode is stable enough to be reoxidized upon anodic scan. The dependance of the EPR signal on temperature is related to the lifetime and diffusion rates of the species generated at the electrode surface with respect to the two techniques (cyclic voltametry and EPR/electrochemical reduction) and the respective rates of accumulation of these species to make their detection possible.

The cyclic voltammogram obtained in the presence of PMe_3 is shown in Fig. 2(b). It can be seen that the reduction potential and the shape of the cathodic wave are unaffected, whereas the anodic wave is substantially reduced in height without shift in potential. This can be explained by the fact that (i) the "chemical" reaction by which the methyl(trimethylphosphine) compound is formed is subsequent to the formation of the five coordinate, 19 electron species $[Cp_2Ti(CH_3)_2(PMe_3)]^{-\cdot}$ **4**

$$[Cp_2Ti(CH_3)_2]^{-\cdot} + PMe_3$$
$$\textbf{1a'}$$

$$\rightarrow [Cp_2Ti(PMe_3)(CH_3)_2]^{-\cdot} \qquad (6)$$
$$\textbf{4}$$

$$\textbf{4} \rightarrow [Cp_2Ti(III)(PMe_3)(CH_3)] + CH_3^- \qquad (7)$$
$$\textbf{5}$$

Here too a five-coordinate intermediate species has to be postulated. (ii) The residual anodic wave can be due to incomplete reaction at the electrode or to the slow diffusion rate of the dimethyl radical anion compared to the reaction product. Also, the latter does not seem to be electroactive within the potential cathodic sweep range.

In a previous study [4], Klei and Teuben identified $Cp_2Ti(III)(CH_3)$ in solution by EPR (a quartet), and by adding PPh_3 obtained a spectrum, (see Table 1) which they attributed to the $[Cp_2Ti(III)(CH_3)(PPh_3)]$ adduct. It can be said that since this phosphine is not reactive in the case under study, a plausible explanation is that it coordinates to Ti only when a vacant site is available. Such a mechanism is not operative here and Eq. (6) is therefore necessary. PPh_3, for steric reasons or donor properties, is not suitable to follow the paths proposed in Eqs. (6) and (7), which lends some support to our argument.

Under the same conditions as used with **1a**, compound **2** exhibits an irreversible cathodic wave, at -1.9 V, followed by an anodic wave at -0.6 V. This result fully explains the EPR spectrum which exhibits a signal due to $Ind_2Ti(III)(CH_3) \cdot THF$ complex. The electrochemical reaction taking place can be described as follows:

$$Ind_2Ti(CH_3)_2 + e \rightarrow Ind_2Ti(III)(CH_3) \cdot THF + CH_3^-$$
$$\textbf{2} \qquad\qquad\qquad \textbf{2a}$$

$$(8)$$
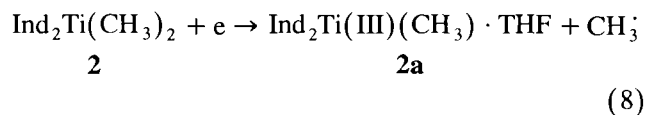
and the anodic phenomenon at -0.6 V is due to the reoxidation of **2a** to Ti(IV). This has been confirmed by reversing the scan before the cathodic wave potential, in which case the anodic wave was completely absent. In this case therefore, the radical anion of **2** is unstable and reaction (8) produces **2a** rapidly. This product is stable, even at room temperature, in contrast to its cyclopentadienyl analog. This difference in behavior may have some bearing on the very high reactivity of bis-indenyl Ti and Zr systems as olefin polymerization catalysts.

The reaction of **2a** with PMe_3 therefore takes place straightforwardly as follows:

$$\textbf{2a} + PMe_3 \rightarrow Ind_2Ti(III)(CH_3)(PMe_3) + THF \qquad (9)$$
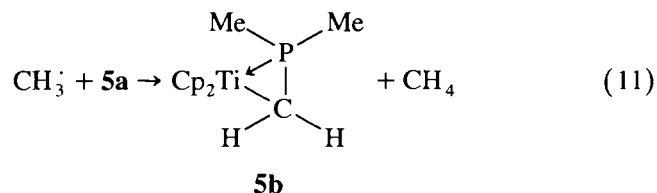$$\textbf{2b}$$
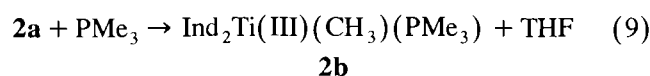
2b is stable at room temperature since the EPR signal decays only slowly when the current flow is stopped.

The situation is different with **1a**. As mentioned above, the low temperature EPR spectrum arising from the methyl(trimethylphosphine) compound **5** degenerates into a doublet at room temperature. This is attributable to the coupling of one ^{31}P nucleus with an electron residing on a Ti center. The disappearance of hyperfine coupling with the methyl hydrogens and the lack of coupling with any other ligand liable to bind to Ti, such as hydrogen, leads us to postulate the following reaction steps:

(a) Reductive cleavage of the Ti-bound methyl group

$$5 \rightarrow [Cp_2Ti(II)(PMe_3)] + CH_3^{\cdot} \qquad (10)$$
$$\mathbf{5a}$$
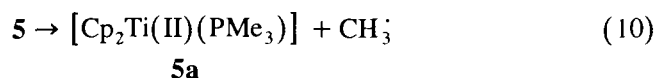
(b) hydrogen abstraction from another P-bound methyl group to yield methane, with oxidative rearrangement to give the chelating phosphinomethylTi(III) complex **3c** as follows:

$$CH_3^{\cdot} + 5a \rightarrow Cp_2Ti\underset{H}{\overset{Me}{\underset{\diagdown}{\overset{\diagup}{P}}}}\overset{Me}{\underset{C}{\diagup}} + CH_4 \qquad (11)$$

$$\mathbf{5b}$$

It is also likely that reactions (10) and (11) proceed by a single concerted reaction rather than by two discrete steps.

It is intriguing that no hyperfine interaction with the methylene protons was observed. However, Schore and coworkers [8] postulated a similar structure for a zirconocene compound obtained by chemical reduction of $Cp_2ZrCl(CH_2PPh_2)$ whereby abstraction of Cl gives a Zr(III) complex having the same EPR features as **5b**, and interestingly hydrogen hyperfine interaction was

also absent. However, it was resolved in the phosphinomethylmonocyclopentadienyl derivatives [9].

Noteworthy is the fact that such a mechanism is not operative with the indenyl analog **2b**. It can be speculated that, since no distinctive feature occurs in the cyclic voltammogram of one compound compared to the other in the presence of the phosphine, the difference in behavior should be attributed only to steric reasons. The indenyl benzo groups, which form an angle extending to contain the methyl and the phosphine ligands, act also as barriers preventing rearrangement according to reaction (11) to take place, thus stabilizing the original structure. Such rearrangement requires a very specific configuration which is much easier to achieve in the relatively unencumbered Cp complex.

Work is in progress with the purpose to isolate alkyl(phosphine) compounds of the series described above.

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