

Investigation of the Trimetallic Compounds $[(\eta^5\text{-C}_5\text{H}_5)_2\text{TiX}]_2\text{ZnX}_2$ (X = Cl, Br) by ESR and ENDOR Spectroscopies

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Abstract: A detailed study of the trimetallic compounds $(\text{Cp}_2\text{TiX})_2\text{ZnX}_2$ (X = Cl, Br) in solution by ESR and ENDOR is presented. In toluene at 130 K, both compounds exhibit ESR spectra typical of electron triplet states ($S = 1$). For X = Cl the magnetic parameters derived from analysis of the ESR spectra are in good agreement with previous magnetic and structural measurements in the solid compound; ENDOR measurements show that dissolution in THF provokes rupture of the trimetallic edifice and formation of a species which shows electron doublet state $S = 1/2$ to which we assign the structure $(\text{Cp}_2\text{Ti}\cdot\text{THF})^+$.

The reduction of Ti(IV) organometallic compounds to lower oxidation states is a step of fundamental importance in the promotion of their reactivity toward homogeneous catalysis and synthetic organic chemistry.

It is well-known that titanocene dihalides can be reduced to monohalides by various methods. Whereas it was recognized very shortly after the discovery of Cp_2TiCl_2 [$\text{Cp} = (\eta^5\text{-C}_5\text{H}_5)$] that this compound can be reduced by zinc dust to Ti(III) species,¹ it was not until many years later that the chemistry of this reaction was studied in enough detail.²⁻⁴ It was found, in particular, that this reduction yields under certain conditions the trimetallic compound $[(\text{Cp}_2\text{TiCl})_2\text{ZnCl}_2\cdot 2\text{C}_6\text{H}_6]$ the crystal structure of which was determined by G. Stucky and co-workers.⁵ The trinuclear molecule was shown to be formed of two titanocene units linked by a ZnCl_4 tetrahedron through chlorine bridges. Studies of the magnetic properties of the crystalline solid showed that the compound exhibits antiferromagnetic behavior with a J value of -8.9 cm^{-1} and $\theta = 0.49 \text{ K}$.⁶

Curiously enough, no mention to our knowledge is made in the literature about ESR studies of this compound in solution, apart from the trivial measurement of the g value and the Ti isotropic hyperfine interaction constant. Such a study is of undeniable interest because it provides an opportunity to explore the extent to which the physical molecular properties in the solid state are preserved in solution.

We present in this work the results of our investigations on the behavior of the two compounds $[(\text{Cp}_2\text{TiX})_2\text{ZnX}_2]$ (X = Cl, Br; **1** and **2**, respectively) in solution at low temperatures using both ESR and (for **1**) ENDOR (electron nuclear double resonance) spectroscopies. The latter technique, which adds a further dimension to the former in the study of paramagnetic molecules, has been used on various occasions to study organic radicals but thus far has known a very limited extension to the area of transition-metal sandwich compounds.⁷ In this work we demonstrate by this technique the existence of strong titanium-tetrahydrofuran interaction and doublet-triplet state species equilibria of **1** in THF solution.

Experimental Section

All manipulations were conducted under argon. Solvents were rigorously dried and distilled under argon. **1** (light green) was prepared by reduction of Cp_2TiCl_2 (Alfa-Ventron) with Zn dust in benzene according to the published procedure.⁸ Cp_2TiBr_2 was prepared from Cp_2TiCl_2 by halogen exchange with BBr_3 in methylene chloride; purity of the product was determined by NMR. **2** was prepared as a brownish powder by reduction of Cp_2TiBr_2 with Zn powder in benzene containing about 5% of THF.

ESR and ENDOR spectra were recorded on a Bruker ER 220D spectrometer equipped with the Aspect 2000 computer monitored ENDOR unit. The maximum radio frequency power in the ENDOR coil

Table I. ESR Parameters of $(\text{Cp}_2\text{TiX})_2\text{ZnX}_2$ in Toluene (X = C, Br)

	g_{iso}	g_{\parallel}	g_{\perp}	D (cm^{-1})
$(\text{Cp}_2\text{TiCl})_2\text{ZnCl}_2$	1.9765	1.9831	1.9732	83.4×10^{-4}
$(\text{Cp}_2\text{TiBr})_2\text{ZnBr}_2$	1.987	1.984	1.989	37.0×10^{-4}

was 100 W. The spectrometer was also equipped with the microprocessor ER 031 Bruker field control device, which ensures good stability and accuracy of the field setting. A Systron Donner frequency counter was used to measure the microwave frequency. In order to cool the samples to the liquid helium temperature range, the spectrometer was fitted with a helium flow cryostat ESR 9 from Oxford Instrument.

Electron Spin Resonance

Figures 1a and 2 show the low-temperature ESR spectra (-130°C) of **1** and **2** in glassy toluene matrix. They are unambiguously attributed to triplet state ($S = 1$) spectra of molecules with two interacting $S = 1/2$ Ti^{3+} ions. This conclusion is essentially based on the observation of "forbidden" $\Delta M_s = 2$ mid-field transitions and on the typical shape of the $\Delta M_s = 1$ spectrum, particularly for **1**. The ESR of this compound is well described by using the spin Hamiltonian of a triplet state with axial symmetry

$$\mathcal{H} = \beta[g_{\parallel}(B_z S_z) + g_{\perp}(B_x S_x + B_y S_y)] + D[(S_z)^2 - S(S+1)/3] \quad (1)$$

in which the hyperfine terms describing the interaction with the ^{47}Ti ($I = 5/2$, 7.28%) and ^{49}Ti ($I = 7/2$, 5.51%) nuclei have been omitted. The corresponding spin Hamiltonian parameters are given in Table I. A detailed analysis of the g tensor, the isotropic exchange coupling term J , and the anisotropic interaction term D will show that the molecular structures of these trinuclear complexes are identical in frozen toluene matrix and in the solid state (see the molecular structure for X = Cl in ref 5).

First of all the g and D tensors have axial symmetry, which is consistent with the D_2d symmetry of the trinuclear species **1**. In this point group $d(xz)$ and $d(yz)$ belong to the degenerate representation E while the $d(z^2)$, $d(x^2 - y^2)$, and $d(xy)$ orbitals belong respectively to the nondegenerate representations A_1 , B_1 , and B_2 . The observed g values with $g_{\perp} < g_{\parallel}$ indicate that the

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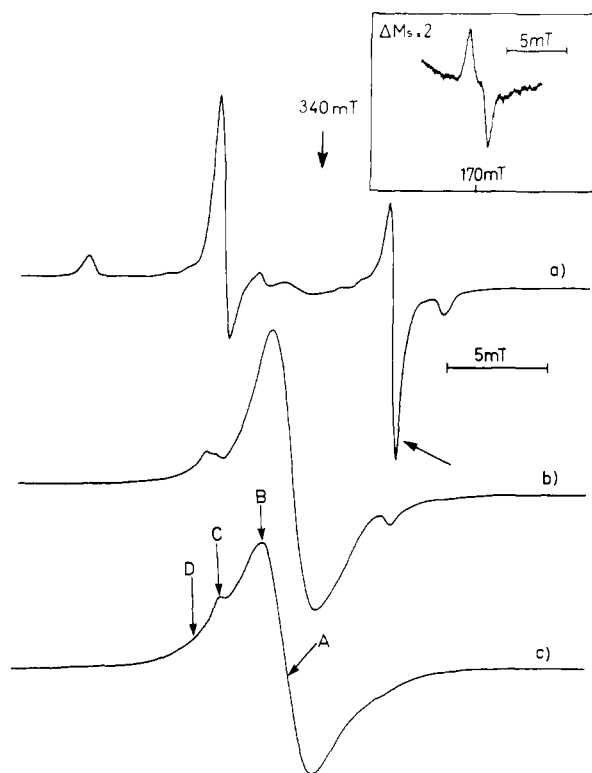


Figure 1. X-band ESR spectra at 130 K of the $(\text{Cp}_2\text{TiCl})_2\text{ZnCl}_2$ trimetallic complex diluted in frozen toluene and THF matrix. (a) ESR in toluene. The arrow indicates the magnetic field setting used in ENDOR experiments. The spectrum in the upper right is the $\Delta M_s = 2$ transition. (b) ESR in toluene with traces of THF. (c) ESR in pure THF. The letters indicate the magnetic field settings used in ENDOR experiments.

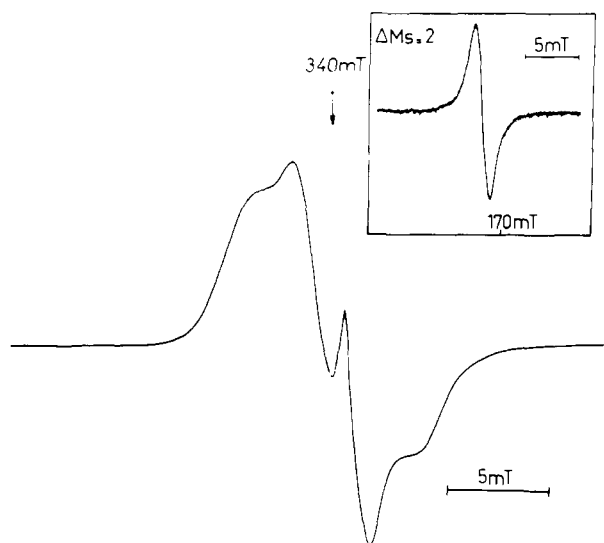


Figure 2. X-band ESR spectrum at 130 K of $(\text{Cp}_2\text{TiBr})_2\text{ZnBr}_2$ diluted in frozen toluene matrix. The $\Delta M_s = 2$ transition is also shown.

unpaired electron lies in $d(z^2)$ orbitals of titanium, whose axis lies along the Ti–Zn–Ti direction. For a purely $d(z^2)$ ground state the g values to second-order perturbation are given by⁹

$$g_{\parallel} = g_e$$

$$g_{\perp} = g_e - \frac{3\lambda(\text{eff})}{\Delta} \quad (2)$$

in which λ_{eff} is the effective spin–orbit coupling constant and Δ the energy separation between the A_1 and E levels, which are respectively the ground and excited states mixed by spin–orbit coupling. It could be possible to account for the observed negative

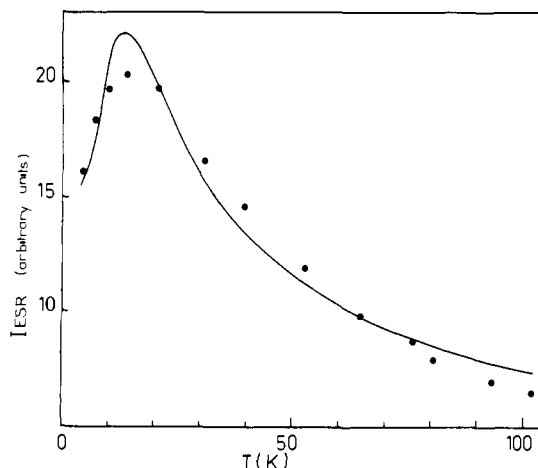


Figure 3. Variation with temperature (4 to 100 K) of the intensity of the $\Delta M_s = 1$ transition of $(\text{Cp}_2\text{TiCl})_2\text{ZnCl}_2$ in toluene. Heavy dots, experimental; full line, calculated for $J = -9.2 \text{ cm}^{-1}$, $\theta = 4.1 \text{ K}$, $A = 611$.

parallel g -shift, Δg_{\parallel} , by considering the ground state $\psi_0 = \alpha[d(z^2) + \beta]d(x^2 - y^2)$. However, this situation is not possible without a lowering of the molecular symmetry, which will destroy the axial character of both g and D tensors. In contrast covalency effects could account for the observed parallel g -shift. Since the electronic ground state is no longer of purely metallic $d(z^2)$ character, but is a symmetry adapted linear combination of titanium $d(z^2)$ and chlorine p orbitals, this ligand admixture could be responsible for the observed parallel g -shift.

An estimation of the isotropic exchange coupling constant J has been obtained from the variation with temperature of the intensity of the $\Delta M_s = 1$ spectrum. The results are depicted in Figure 3. Taking the singlet–triplet separation equal to $2J$, the J value can be deduced from a least-squares fitting of the ESR amplitude to an expression of the form

$$I(\text{ESR}) = A/(T - \theta) [1 + 1/3 \exp(-2J/kT)]^{-1} + B \quad (3)$$

adapted from the expression of the magnetic susceptibility of two exchange coupled spin $1/2$ centers. The best fit gives the value $J = -9.2 \text{ cm}^{-1}$ and $\theta = 4.1 \text{ K}$. This result shows that the singlet state lies lowest, and this J value derived by ESR is very close to the value $J = -8.9 \text{ cm}^{-1}$ obtained in the solid state by susceptibility measurements.⁶ The discrepancy between the value of θ in toluene and the value $\theta = 0.49 \text{ K}$ obtained for the solid⁶ could be due to inaccuracies in our measurements of the spectrum intensities at low temperature.

The zero-field splitting term D is calculated from the spacing ΔB_{\parallel} between the two parallel components of the $\Delta M_s = 1$ spectrum

$$\Delta B_{\parallel} = 2D/g_{\parallel}\beta \quad (4)$$

It gives $D = 83.4 \times 10^{-4} \text{ cm}^{-1}$. Such a small zero-field splitting is related to a large Ti–Ti distance, which is consistent with the trinuclear structure of the compound.⁵ The observed D value arises from a combination of a dipole–dipole interaction D_d , which depends on the Ti–Ti distance, and from a pseudodipolar interaction D_E resulting from spin–orbit admixture of excited states into the ground state

$$D = D_d + D_E \quad (5)$$

For a purely $d(z^2)$ ground state, D_E is given by¹⁰

$$D_E = J(g_{\perp} - 2)^2/36 \quad (6)$$

From the experimental J , g_{\perp} , and D values we obtain $D_E = -2.10^{-4} \text{ cm}^{-1}$ and $D_d = 81.4 \times 10^{-4} \text{ cm}^{-1}$. The Ti–Ti distance R

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can be extracted from D_d since these parameters are related by¹¹

$$R = (0.65g_{\parallel}^2/D_d)^{1/3} \quad (7)$$

The value calculated for D_d yields $R = 6.80 \text{ \AA}$, in very good agreement with the value $R = 6.84 \text{ \AA}$ from X-ray diffraction study of the solid.⁵

We may conclude from the ESR results that the trimetallic complex **1** has identical structure and magnetic properties in both solid state and toluene solution. This confirms that magnetic interactions between neighboring trinuclear species are negligible in the solid state. However, it appears from the axial symmetry of both g and D tensors that the angle Ti–Zn–Ti is very close to 180° while it is only 175° in the solid.⁵ The small distortion observed in the solid state could be due, for instance, to steric or van der Waals interactions between neighboring complexes, which disappear in diluted frozen solution.

The structure of **2** in toluene is more difficult to study since the observed $\Delta M_s = 1$ spectrum consists of several overlapping lines (Figure 2). However, the trimetallic character of the molecule is evident from the observation of the half-field $\Delta M_s = 2$ transition. The poor resolution of the $\Delta M_s = 1$ spectrum arises because the anisotropy of the g tensor and the value of the D tensor are smaller than for the chloride compound. From the position of the low- and high-field lines of the spectrum one deduces $g_{\parallel} = 1.984$ and $D \approx 37.10^{-4} \text{ cm}^{-1}$. From g_{\parallel} and the value $g_{\text{iso}} = 1.987$ measured at room temperature the value $g_{\perp} = 1.989$ is obtained. Since g_{\parallel} and g_{\perp} are almost identical, the electronic ground state of Ti^{3+} cannot be inferred from simple crystal-field considerations. However, the quasi-isotropy of the g tensor probably arises from covalency effects. From the value of the zero-field splitting and neglecting the small pseudodipolar contribution, one obtains a Ti–Ti distance $R \approx 8.9 \text{ \AA}$ for **2**. This high value probably requires a wider Ti–X–Zn angle for X = Br than for X = Cl.

The ESR spectra of both compounds exhibit dramatic modifications when traces of THF are present in toluene, as shown in Figure 1b for X = Cl. The intensity of the triplet-state spectrum decreases considerably, but its presence is still exhibited by the two weak perpendicular components of the $\Delta M_s = 1$ transitions, while a new compound characterized by a broad, intense, and structureless signal at $g \approx 1.980$ appears. When the compound is diluted in pure THF, the spectrum exhibits the same broad signal (Figure 1c) but often differs from one sample to another. This is because some triplet-state features, although unresolved, persist together with the broad signal, as will be shown below. Since no information could be gained from the study of such structureless ESR spectra, ENDOR spectroscopy has been used to investigate the new species which is formed by interaction between **1** and THF. It will be shown that the new broad ESR spectrum is due to titanocene–tetrahydrofuran adducts.

ENDOR of $(\text{Cp}_2\text{TiCl})_2\text{ZnCl}_2$ in Toluene and THF Matrixes

In these solvents, the spectra of this compound arise from both doublet and triplet $S = 1/2$ electron states, the ENDOR of which differ significantly. The characteristics of $S = 1/2$ state ENDOR are well documented.¹² The spectra consist of two lines for each set of equivalent nuclei coupled to the electron spin. Two situations can be distinguished, depending upon which of ν_n or $|A|/2$ (respectively the nuclear Zeeman frequency and half the hyperfine constant) is the smaller. For $\nu_n > |A|/2$ the two lines are centered at ν_n and separated by $|A|$ and for $\nu_n < |A|/2$ they are centered at $|A|/2$ and separated by $2\nu_n$.

To our knowledge, there are few studies reported in the literature on $S = 1$ state.^{7,12} The energy level diagram of a $S = 1$, $I = 1/2$ system in a static magnetic field is given in Figure 4a. One could expect three transitions at ν_n and $|\nu_n \pm A|$. However, the $|+1\rangle \leftrightarrow |-1\rangle$ electronic transition is strongly forbidden, hence there are no efficient relaxation mechanisms which link these two

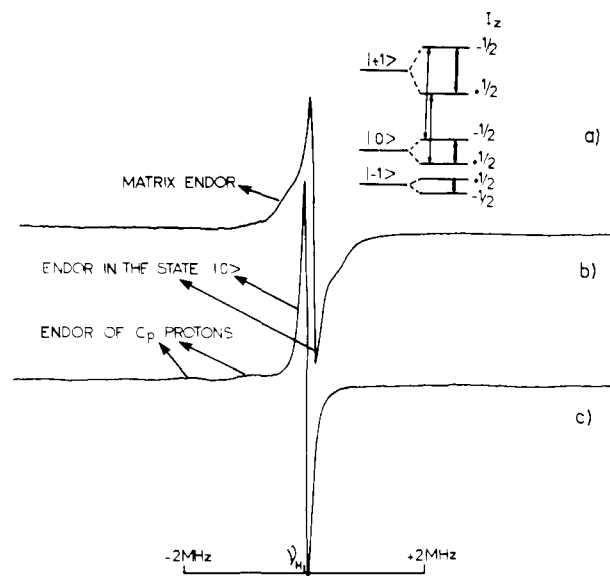


Figure 4. (a) Energy level diagram of a $S = 1, I = 1/2$ system showing the ESR transitions (single lines) and the ENDOR transitions (double lines). (b and c) ^1H ENDOR spectra at 10 K of $(\text{Cp}_2\text{TiCl})_2\text{ZnCl}_2$ in toluene (b) and deuteriotoluene (c) solvents. The magnetic field setting corresponds to the arrow on Figure 1a.

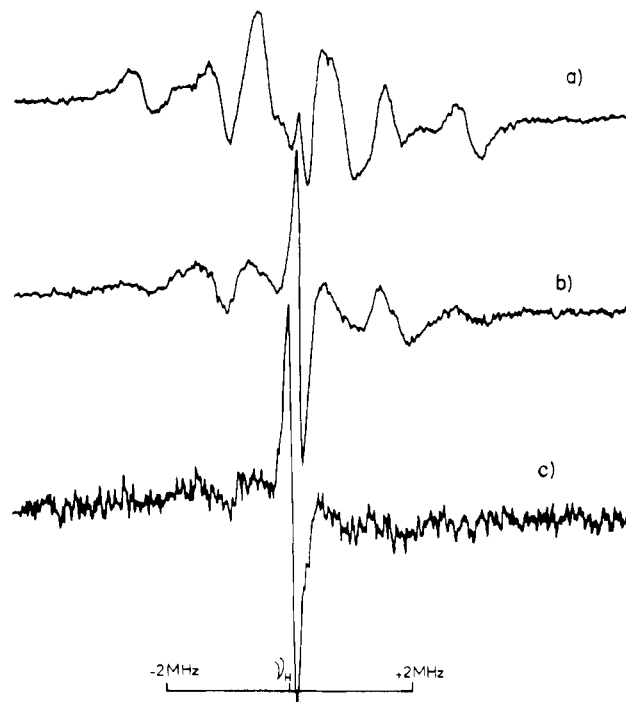


Figure 5. ^1H ENDOR spectra at 10 K of $(\text{Cp}_2\text{TiCl})_2\text{ZnCl}_2$ diluted in deuterio-THF matrix. Spectra a, b, and c were recorded, respectively, at the field settings A, C, and D of Figure 1c.

states. Therefore the ENDOR spectra of a triplet state consists of two lines, one at the nuclear frequency and the other either at $|\nu_n + A|$ or $|\nu_n - A|$ depending upon which ESR transition is observed.

(1) Triplet-State ENDOR. We have performed ENDOR measurements on the trimetallic complex **1** in frozen toluene and deuteriotoluene (Figure 4) by observing the high-field perpendicular ESR transition (marked by an arrow in Figure 1a). In deuteriotoluene (Figure 4c) the spectrum consists mainly of a strong and sharp line centered at the proton nuclear frequency attributed to the ENDOR transition in the $|0\rangle$ electronic state. This ENDOR is obviously not a matrix line because the solvent contains no protons. Furthermore, in toluene, one observes a broad matrix line (Figure 4b) which could easily be distinguished from

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the narrow ENDOR transition in $|0\rangle$ state. Observation of such a narrow line at ν_H will be used in the following section to detect the presence of small amounts of trimetallic complex **1** in THF matrix. Besides the strong ENDOR line at ν_H , which is observed when the ESR transition is saturated, there are also observed several weak and broad lines flanking the central one (Figure 4c). These lines are more easily detected on the low-frequency side of the spectrum. They correspond to interactions with the protons of the Cp rings and are broadened because the proton hyperfine tensor axes are not co-linear to the principal axes of the zero-field tensor.¹² Owing to their weakness, these lines have not been considered further, and we have turned our attention to the spectra of $(\text{Cp}_2\text{TiCl})_2\text{ZnCl}_2$ in THF.

(2) ^1H ENDOR of $(\text{Cp}_2\text{TiCl})_2\text{ZnCl}_2/\text{THF}$ Reaction Product.

(a) ^1H ENDOR Spectra in $(^2\text{H})\text{THF}$. Figure 5 shows the proton ENDOR spectra of **1** in frozen deuterio-THF matrix, for different magnetic field settings. When the observing field is at the center of the broad ESR line (position A in Figure 1c), the spectrum exhibits pairs of lines of similar intensities characteristic of a doublet state ENDOR. Shifting the observing magnetic field gradually from the center to the wings of the broad ESR line (positions B to D in Figure 1c) leads to a drastic change of the ENDOR spectrum (Figure 5b,c). There is a decrease of the intensity of the doublet state ENDOR transitions while a narrow line appears at the proton frequency. This line corresponds to the ENDOR transition in the $|0\rangle$ state of the trinuclear complex **1**. The occurrence of a doublet-state ENDOR indicates that magnetic interactions between titanium ions no longer exist, showing that the trimetallic species has been partially destroyed by reaction with THF molecules. Since THF is fully deuterated, the pairs of lines depicted in Figure 5a arise from interactions of the titanium unpaired electron with protons of Cp rings. Therefore, the skeleton of the reaction product is probably $(\text{Cp}_2\text{Ti})^+$. In the following discussion this unknown species will be labeled X. It should be pointed out that trimetallic complex molecules are still present in small quantities, together with the mononuclear species X. This shows that ENDOR is able to separate spectra of doublet and triplet states when they are present simultaneously in the same solution, while ESR cannot in this case because of the overlapping of the spectra. Returning to the doublet-state ENDOR spectrum of X depicted in Figure 5a, it should be noticed that all the orientations of the molecules with respect to the static magnetic field B_0 contribute to the spectrum. This corresponds to the situation of the so-called powder ENDOR spectra.¹² The spacing between the outer pair of lines gives the parallel component of the hyperfine tensor $A_{\parallel}(\text{Cp}) = 5.7$ MHz while the inner doublets give the two other components. Neglecting the departure from axial symmetry of the hyperfine tensor, the perpendicular part of the interaction is approximately $A_{\perp}(\text{Cp}) \approx 1.9$ MHz. These parameters are related to the isotropic $A(\text{iso},\text{Cp})$ and anisotropic $A(\text{aniso},\text{Cp})$ terms of the hyperfine coupling by

$$\begin{aligned} A(\text{iso},\text{Cp}) &= 1/3[A_{\parallel}(\text{Cp}) + 2A_{\perp}(\text{Cp})] \\ A(\text{aniso},\text{Cp}) &= 1/3[A_{\parallel}(\text{Cp}) - A_{\perp}(\text{Cp})] \end{aligned} \quad (8)$$

Since the g shift is small, $A(\text{aniso},\text{Cp})$ is assumed to be essentially due to a dipole-dipole interaction and thus positive. Usually, in metallocene compounds, the largest contribution to the hyperfine tensor comes from $A(\text{iso},\text{Cp})$.⁷ Therefore $A_{\parallel}(\text{Cp})$ and $A_{\perp}(\text{Cp})$ should be of the same sign, and one obtains $A(\text{iso},\text{Cp}) = +3.2$ MHz and $A(\text{aniso},\text{Cp}) = +1.3$ MHz. This leads to an unpaired electron spin density at Cp protons of 0.23%. Similar values have been reported for titanium(III) sandwich complexes. For instance in the case of $\text{Ti}(\text{C}_5\text{H}_5)_2\text{C}_8\text{H}_8$,¹³ $A(\text{iso},\text{Cp}) = +4.15$ MHz and $A(\text{aniso},\text{Cp}) = +0.80$ MHz, giving a spin density at Cp protons of 0.29%. We have checked our assumption concerning the relative signs of $A(\text{iso},\text{Cp})$ and $A(\text{aniso},\text{Cp})$ by simulating the ESR spectrum at room temperature. This is possible since previous

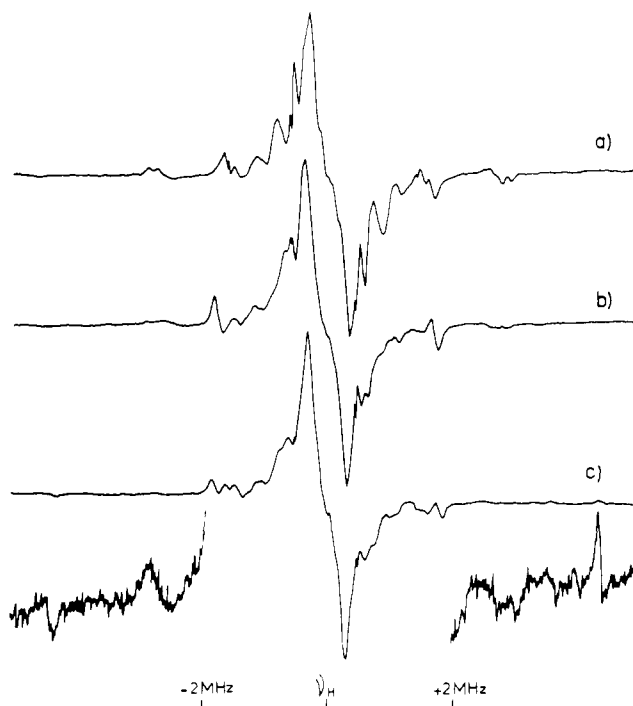


Figure 6. ^1H ENDOR spectra at 10 K of $(\text{Cp}_2\text{TiCl})_2\text{ZnCl}_2$ diluted in THF matrix. Spectra a, b, and c were recorded, respectively, at the field settings A, B, and C of Figure 1c.

work on the $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{C}_8\text{H}_8)$ complex¹³ has shown that the ESR line shape in liquid solution is determined by the isotropic hyperfine coupling with ring protons. We have simulated the ESR spectrum of a $S = 1/2$ electron coupled to 10 equivalent protons corresponding to two Cp rings, taking either $|A(\text{iso},\text{Cp})| = 3.2$ MHz (same sign for $A_{\parallel}(\text{Cp})$ and $A_{\perp}(\text{Cp})$) or $|A(\text{iso},\text{Cp})| = 0.6$ MHz (opposite signs for $A_{\parallel}(\text{Cp})$ and $A_{\perp}(\text{Cp})$). The stick diagram is fairly well superimposed to the experimental ESR line, which exhibits a peak-to-peak line width of 0.4 mT, by using the largest value for $A(\text{iso})$. There is a complete disagreement when taking the other $A(\text{iso})$ value.

(b) ^1H ENDOR Spectra in $(^1\text{H})\text{THF}$: The use of $(^1\text{H})\text{THF}$ instead of $(^2\text{H})\text{THF}$ as a solvent leads to a dramatic complication of the ENDOR spectra, because of hyperfine interactions with a number of THF protons. It is worth noting that these Ti-THF interactions dominate the ENDOR spectra. When the magnetic field is set at position A (Figure 1c and 6a) one recognizes easily the 5.7 MHz spacing doublet corresponding to the parallel components of the proton hyperfine interaction with Cp rings. It is not clear at present why these ENDOR transitions are split (Figure 6a) in THF but not in $(^2\text{H})\text{THF}$. The strong group of ENDOR lines near the proton frequency are mainly due to interactions with inner solvent sphere THF molecules. Several modifications occur in the ENDOR spectrum when the magnetic field setting is modified. For the field setting labeled B (Figures 1c and 6b) a pair of narrow and intense lines with a spacing of 3.5 MHz is observed. For other field settings these lines split into several components. When setting B_0 at the position labeled C (Figures 1c and 6c) at the low-field side of the ESR spectrum, a weak and narrow pair of lines corresponding to a coupling of 8.7 MHz is observed.

All these ENDOR lines, which are absent in $(^2\text{H})\text{THF}$ matrix, suggest that at least one THF molecule is bonded to titanium in the X compound. In contrast with the "powder" character of the interactions with Cp rings, the ENDOR lines corresponding to interactions with THF molecules exhibit some "orientation selection".⁷

(3) ^2H ENDOR of $(\text{Cp}_2\text{TiCl})_2\text{ZnCl}_2/(^2\text{H})\text{THF}$ Reaction Product. ^2H ENDOR spectra of nuclei with small g_N factors are difficult to observe because the very strong oscillating radio frequency field B_2 , required to saturate the nuclear transition

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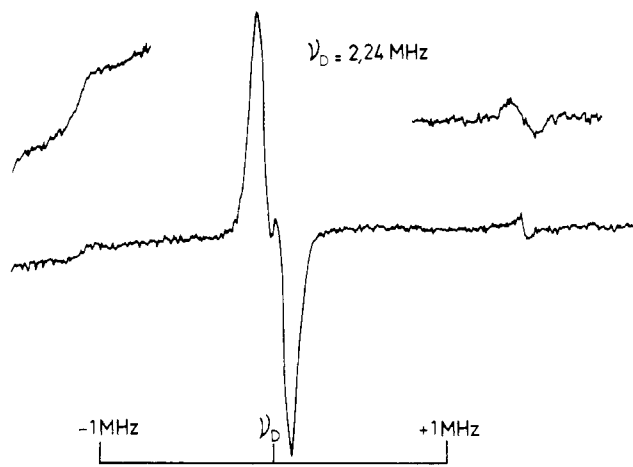


Figure 7. ^2H ENDOR spectrum at 10 K of $(\text{Cp}_2\text{TiCl})_2\text{ZnCl}_2$ diluted in deuterio-THF matrix. The magnetic field was set at the middle of the broad ESR spectrum (point A) of Figure 1c.

($\gamma_N^2 B_2^2 T_1 T_2 \gg 1$), is far beyond the maximum B_2 value of our spectrometer. However, if the hyperfine interaction exhibits a large isotropic component, there is a significant enhancement of the effective oscillating magnetic field B_2 at the nucleus.¹²

The ^2H ENDOR spectrum of **1** in $(^2\text{H})\text{THF}$ frozen solution recorded with the magnetic field setting A (Figure 1c) is shown in Figure 7. It consists of a pair of weak lines separated by 2.6 MHz and a pair of strong lines separated by 0.12 MHz centered at the nuclear frequency ν_D of deuterium. The two pairs of lines probably correspond to the parallel and perpendicular components of a strong titanium– ^2H hyperfine interaction. In that case the isotropic coupling constant is $A(\text{iso}, \text{THF}) \approx +0.8$ to 0.9 MHz, which corresponds to a spin density at deuterium of 0.4%. $A(\text{iso})$ has been taken as positive because such a high value is probably due to a direct interaction between the unpaired electron and the deuterium. This large $A(\text{iso})$ could explain why this deuterium coupling has been detected.

All the other titanium–THF interactions observed in ^1H ENDOR present isotropic hyperfine interactions that are too small to be detectable as titanium– ^2H interactions in ^2H ENDOR. The A_{\parallel} value of 2.6 MHz measured in ^2H ENDOR should correspond to a coupling of 16.9 MHz in ^1H ENDOR (ratio of the g_N factors for proton and deuterium = 6.51). Such a large coupling has not been observed in the ^1H ENDOR spectra, probably because the corresponding ENDOR transitions are too broad or too weak (ν_N and $A/2$ bearing similar values). It follows that in the present case ^1H and ^2H ENDOR spectra are complementary in revealing the interactions between titanium and its surroundings. It has already been pointed out that the ESR line width of the compound **X** changes from 0.4 to 10 mT going from liquid to frozen THF solution. It is evident that in liquid solution the large hyperfine interaction which is observed at low temperature no longer exists. This phenomenon can result either from a fast rotation (compared to the hyperfine interaction in frequency units) of the THF molecules around the Ti–O bond or from a chemical exchange of THF molecules between the free and bound states.

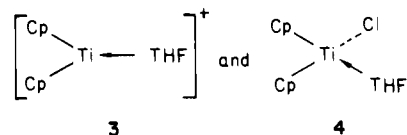
Discussion

The above study gives a more detailed picture of the species formed in solution by the reduction of Cp_2TiX_2 ($\text{X} = \text{Cl}, \text{Br}$) with metallic Zn than previously available. In toluene, the trimetallic molecular units, which were shown from crystal structure to be present in the solid crystalline state, are entirely preserved. The magnetic properties deduced from susceptibility measurements on the solid⁶ are in complete agreement with those presently deduced from ESR variable-temperature studies in frozen toluene solutions. Furthermore, the Ti–Ti distance calculated from the magnitude of the zero-field splitting is very close to the value obtained from the crystal structure data⁵ of $(\text{Cp}_2\text{TiCl})_2\text{ZnCl}_2 \cdot 2\text{C}_6\text{H}_6$. The situation with the bromide is less clear. The poor resolution of the ESR frozen solution spectrum did not allow

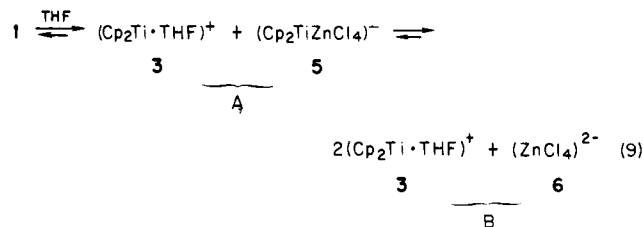
measurement of the zero-field splitting with good precision.

The nature of the species obtained upon dissolution of **1** in THF is clarified by ENDOR. Although the frozen solution ESR spectrum contains on either side of the broad central band sharp and weak signals that could be intuitively attributed to remnants of an $S = 1$ spectrum, the ENDOR experiments provide convincing evidence in support of this speculation. At the same time greater understanding of the nature of the species responsible for the broad, central signal is gained. ENDOR spectra in THF and $(^2\text{H})\text{THF}$ reveal, besides some weak interactions of Ti with several THF molecules, strong interaction by orbital overlap with THF at close proximity. But these spectra did not allow determination of the number of THF molecules coordinated to Ti (one or two). The coordination of two molecules of THF, although allowed in order to achieve tetrahedral coordination around Ti, is sterically unfavored. Because the free rotation of the two molecules will then be hindered, the strong Ti–H coupling due to direct overlap of a Ti orbital with a THF proton should persist at high temperature. No such coupling was observed in the room-temperature ESR spectra.

Two structures (**3** and **4**) appear to be likely on the basis of these considerations: ENDOR measurements alone cannot decide between these two possibilities since ENDOR transitions due to Cl nuclei were not detected. It should, however, be stressed that no modifications in the ENDOR spectra were observed by replacing Cl with Br, a result in favor of formula **3**. Furthermore,

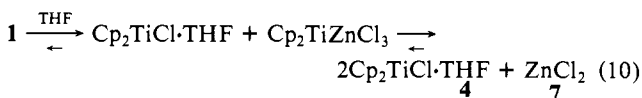


X-ray studies on **1**⁵ revealed that the bridging Cl atoms are bonded more tightly to Zn ($\text{Zn–Cl} = 2.25 \text{ \AA}$) than to Ti ($\text{Ti–Cl} = 2.59 \text{ \AA}$) so that the molecule can be viewed as an association of a $(\text{ZnCl}_4)^{2-}$ tetrahedron with two $(\text{Cp}_2\text{Ti})^+$ entities. In this case, cleavage of the two Ti–Cl bonds of each titanocene unit by the Lewis base THF to give an ion pair is not unreasonable to assume. This may occur according to the following stepwise mechanism:



The intermediate species **A** is an association of two paramagnetic complex ions (**3** + **5**) of opposite charge which should give by ESR a signal due to two $S = 1/2$ states having very close g values and superimposed on the signal of the $S = 1$ state due to small amounts of **1** still present. The ion pair **A** is also possibly responsible for the observation of a variable ESR line shape from one sample preparation to another due to small variations in the relative concentrations of **1**, **A**, and **B** and for the splitting of the signal at 5.7 MHz in the H ENDOR spectrum of **1** in $(^1\text{H})\text{THF}$, Figure 6a. This splitting could be related to two sets of equivalent Cp ring protons belonging to the two different species. In addition, this scheme provides a rational explanation to the possibility of isolating compound **1** in THF; the $(\text{ZnCl}_4)^{2-}$ tetrahedron lying at close proximity to cation **3** in the ion pair **B** will easily recombine to form compound **1** in a saturated solution.

The following scheme offers the other alternative to the scrambling of the trimetallic skeleton of **1** in THF,



but it is less likely since it requires preferential cleavage by THF of a tightly bound Zn–Cl bond on the one hand and implies the

formation of two neutral species **4** and **7** which will recombine less easily in dilute THF on the other hand, so that the persistence of the spectrum of **1** in THF would be rather unexpected.

Finally, the titanocene cation was found by X-ray studies to be associated with one molecule of DME in the structure of $(Cp_2Ti \cdot DME)_2Zn_2Cl_6 \cdot C_6H_6$.⁵ It is also formed by dissolution of $(Cp_2TiCl)_2$ in water.⁸ Its possible existence in THF, as we tried

to demonstrate in this work, is then not unusual.

Further studies by ESR on the species formed in solutions containing titanocene (III) compounds is currently in progress.

Registry No. **1**, 12308-91-7; **2**, 54004-69-2; A, 98689-79-3; B, 98689-80-6; Cp_2TiBr_2 , 1293-73-8; Cp_2TiCl_2 , 1271-19-8; BBr_3 , 10294-33-4; Zn, 7440-66-6.

A New Type of Transition-Metal Dimer Based on a Hexaphosphine Ligand System: $Co_2(CO)_4(eHTP)^{2+}$ ($eHTP = (Et_2PCH_2CH_2)_2PCH_2P(CH_2CH_2PEt_2)_2$)

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Abstract: The synthesis and characterization of a new hexa-*tert*-phosphine ligand system, $(Et_2PCH_2CH_2)_2PCH_2P(CH_2CH_2PEt_2)_2$, **1**, is described. This ligand has the ability to both tris-chelate and bridge two transition metals, either in a closed-mode, M–M bonding geometry, or in an open-mode configuration in which the two metal atoms are 6–7 Å apart. Reaction of **1** with 2 equiv of $CoCl_2$ initially produces, in high yields, the paramagnetic, binuclear, red-brown $Co(II)$ compound, $Co_2Cl_4(eHTP)$, **4**, where $eHTP = 1$. An Extended X-ray Absorption Fine Structure (EXAFS) spectrum of **4** shows Co–P and Co–Cl bond distances in the 2.2–2.4-Å region and no Co–Co contact distance less than 4.0 Å, indicating that **4** is in an open-mode geometry. On standing, **4** dissociates two chloride ligands to form the green, paramagnetic $Co_2Cl_2(eHTP)^{2+}$ complex, **5**, which precipitates out of the reaction mixture, either as the chloride or, if an extra equivalent of $CoCl_2$ is used, the $CoCl_4^{2-}$ salt. The EXAFS spectrum on the $CoCl_4^{2-}$ salt of **5** is very similar to that of **4**, indicating that **5** is also in an open-mode geometry. Reaction of **4** or **5** (alone or mixed) with H_2/CO (33% CO) and an extra equivalent of $CoCl_2$ at 50 bar and 80 °C forms, in high yields, the yellow-green, diamagnetic $Co(I)$ binuclear carbonyl/ $eHTP$ complex, $[Co_2(CO)_4(eHTP)^{2+}][CoCl_4^{2-}]$, **6a**, which can be metathesized with aqueous $NaPF_6$ to give the yellow PF_6^- salt, **6b**. **6b** has been characterized by ¹H and ³¹P NMR, EXAFS, mass spectroscopy, IR, and a crystal structure. Crystals of **6b** belong to the monoclinic space group $C2/c$, with unit cell parameters $a = 26.464$ (4) Å, $b = 12.562$ (2) Å, $c = 14.380$ (3) Å, $\beta = 99.04$ (1)°, $V = 4721$ (3) Å³, and $Z = 4$. The structure was refined to give $R = 0.070$ and $R_w = 0.106$. The molecule lies on a 2-fold axis, passing through the bridging methylene group of the $eHTP$ ligand. The complex has the central bis(phosphino)methane portion of the $eHTP$ ligand adopting a unique inverted coordination geometry to give an open-mode complex with the two cobalt atoms separated by 6.697 (1) Å. The cobalt atoms have a distorted trigonal-bipyramidal geometry with one carbonyl ligand and two terminal phosphorus atoms of the $eHTP$ ligand in the equatorial plane.

Despite the large amount of interest in utilizing transition-metal dimers and clusters as homogeneous catalysts, few such systems have been discovered,¹ while even fewer have been demonstrated to be more effective than mononuclear systems already known. Two major problems traditionally associated with research into polynuclear complexes have been difficulties in synthesizing new species in a stepwise and rational fashion and the often ready fragmentation of these polynuclear systems into mononuclear complexes which can lead to confusion about the nature of the reactive species in solution.

In the last few years, however, there has been an increasing amount of work directed at solving these problems. Stone,² Osborn,³ and Vahrenkamp,⁴ for example, have developed a variety of elegant synthetic routes for preparing homo- and heterometallic clusters. The general strategy in each of these methods has been to use a ligand system that cannot only act as a template for building up a cluster in a stepwise synthesis but has also been designed to have the proper geometric and steric factors needed to constrain the metal centers in proximity, even in the event of M–M bond-breaking reactions which often lead to fragmentation.

The fragmentation of polynuclear systems is a particularly severe problem when dealing with medium-to-high-pressure carbon monoxide reaction conditions, as found in the homogeneously

catalyzed ethylene glycol process,⁵ or in studying the potentials for photocatalysis. An ideal type of ligand system would be one which cannot only bridge two or more metal atoms, but also chelates the metal centers in some way to give a polynuclear complex which is extremely resistant to M–M and M–L-induced fragmentation reactions.

We have decided to start with the simplest of cluster systems, i.e., transition-metal dimers, and would like, therefore, to report the design and synthesis of a new hexaphosphine ligand system for the assembly of binuclear complexes and the structural characterization of a novel open-mode dicobalt carbonyl complex based on this ligand system.

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