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An ESR Study on the Reaction between Dicarbonyl Titanocene and Aryl-Tin Halides

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ABSTRACT

The oxidation elimination reaction between dicarbonyl titanocene and aryltin halides was studied by means of paramagnetic resonance spectroscopy. The radical intermediates containing Ti(III) were discovered from the ESR spectra to be $(Cp_2TiSnAr_nX_{3-n})$, $Cp_2Ti(CO)X$, *and* Cp_2TiX, *and a radical mechanism for the reaction is proposed. © 1996 John Wiley & Sons, Inc.*

INTRODUCTION

It was found that dicarbonyl titanocene reacted with aryl-tin halides through the oxidation-elimination pathway to form Ti-Sn binuclear compounds. [1] In this reaction, Ti(II) was oxidized to Ti(IV). Thus, Ti must have gone through a trivalent stage, which could presumably be detected by the ESR method. This was found to be true, since the Ti(III) intermediate was detected in the reaction between $Cp_2Ti(CO)_2$ and RX [2]. The ESR parameter of Ti(III) species became the focus of our investigation, and here we wish to report the ESR study of the reaction between $Cp_2Ti(CO)_2$ and Ar_nSnX_{4-n}:

$$Cp_2Ti(CO)_2 + Ar_nSnX_{4-n} \rightarrow Cp_2Ti(X) - SnA_{rn}X_{3-n} + 2CO$$

Cp = C_5H_5, MeC_5H_4; Ar = Ph, *p*-Me-Ph, *p*Cl-Ph;

X = Br, Cl, I; $n = 2, 3$

The preceding reaction does not include $ArSnX_3$ or Ar_2SnI_2, the possible cause of which will be discussed later.

EXPERIMENTAL

The preparation and analysis of reactants and the identification of the stable products have been recounted in a previous article [1].

ESR spectra were obtained on a JES-FE1XG ESR spectrometer, made by Jeol Co., using Mn^{2+} (MgO) as an external reference. The experimental conditions were set at room temperature, microwave power: 1 mW; modulation frequency: 100 KHz; modulation width: 0.1–0.63 Gauss; magnet field sweep width: 3400 ± 250 Gauss; sweep time: 8 min/360 mm.

A benzene solution of dicarbonyl titanocene (about 10^{-3} mol/L) was introduced into an ESR sample tube with a diameter of 5 mm by means of a cannular tube under the protection of an argon atmosphere. The tube was closed by a latex stopper. A benzene solution of twice the molar amount of organotin halide Ph_2SnCl_2 was injected into the tube, and the mixture was immediately examined by ESR spectroscopy.

The simulated spectra were drawn with the help of our own program erected on an IBM computer.

RESULTS AND DISCUSSION

ESR signals of the reactants were recorded. At g = 1.975, there was a conspicuous peak, accompanied by weak peaks at both sides. The signal gradually became intense as the reaction proceeded. When the accompanying peaks were magnified, eight hyperfine lines specific to Ti(III) could be perceived, cor-

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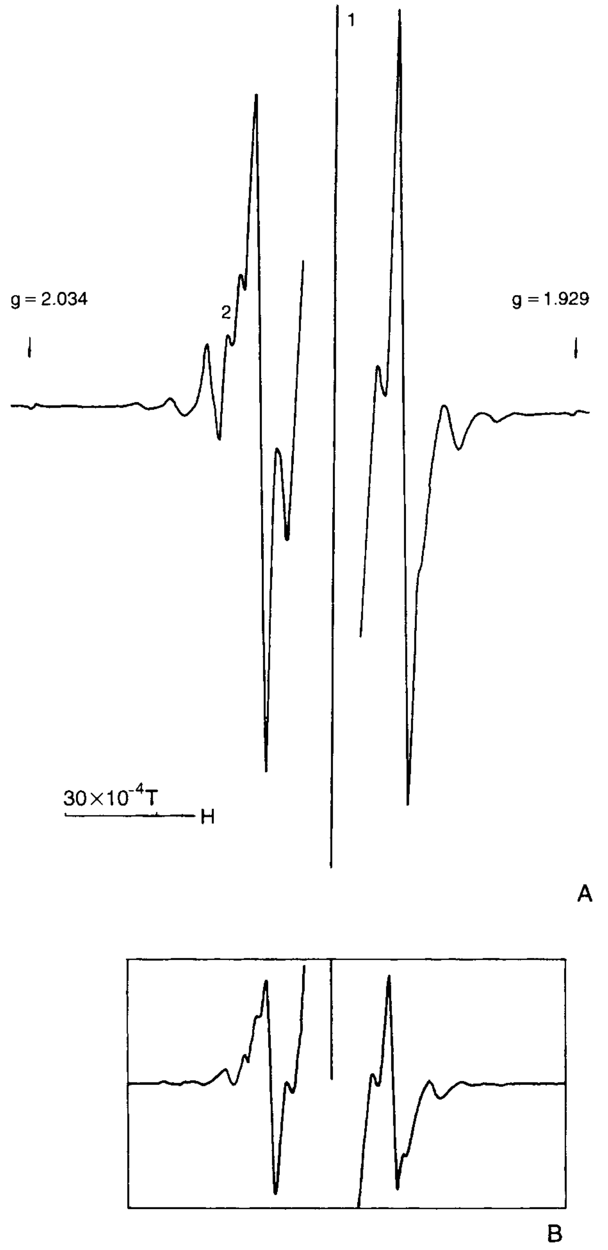


FIGURE 1 (a) ESR spectrum obtained by addition of Ph_2SnCl_2 to $Cp_2Ti(CO)_2$ in benzene and (b) the computer-simulated spectrum: 1. $[Cp_2TiSnPh_2Cl]$; 2. $[Cp_2Ti(CO)Cl]$; the arrows indicate the positions of the Mn marker.

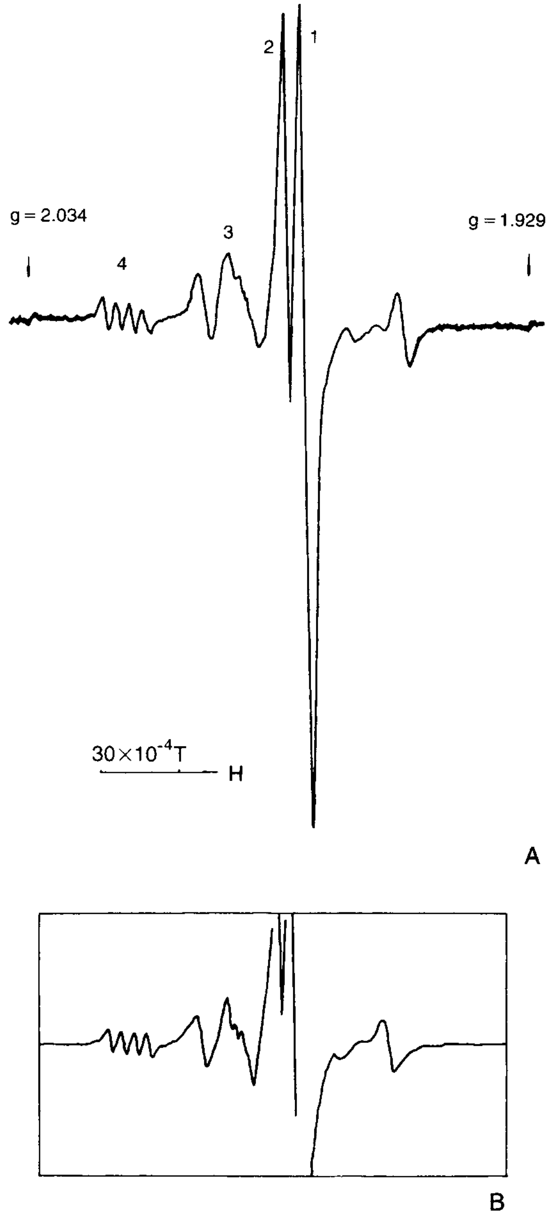


FIGURE 2 ESR spectrum arising from (a) Ph_3SnBr and $Cp_2Ti(CO)_2$ and (b) the computer-simulated spectrum: 1. $[Cp_2TiSnPh_3]$; 2. an impurity peak; 3. $[Cp_2TiBr]$; 4. $[Cp_2Ti(CO)Br]$.

responding to ^{47}Ti: I = 5/2, abundance 7.73%; ^{49}Ti: I = 7/2, abundance 5.51%. Besides these peaks, there were two other, stronger peaks (see Figure 1). Since the Sn nucleus having I = 1/2 includes three isotopes—^{115}Sn, ^{117}Sn, and ^{119}Sn whose abundance is 0.35%, 7.67%, and 8.68%, respectively, the stronger peaks could be assigned to the hyperfine structure of Sn in the intermediate Ti(III)–Sn species. At g = 1.993, one weak peak could be perceived when the reaction time was prolonged 1 hour more, and it might be identified to be attributable to the radical intermediate $[Cp_2Ti(CO)Cl]$ [3]. The radicals were found to be stable for at least a week under conditions of protection from air. It is hard to tell whether the signal at g = 1.975 should be assigned to $[Cp_2TiSnPh_2Cl]$ or to $[Cp_2Ti(CO)SnPh_2Cl]$. To resolve this problem, the following experiment was carried out. Dipentadienyltitanium chloride $(Cp_2TiCl)_2$, a dimer in toluene in equilibrium with its monomer, was used instead of $Cp_2Ti(CO)_2$ to react with Ph_2SnCl_2. When the reactants were mixed with Ph_2SnCl_2 in tol-

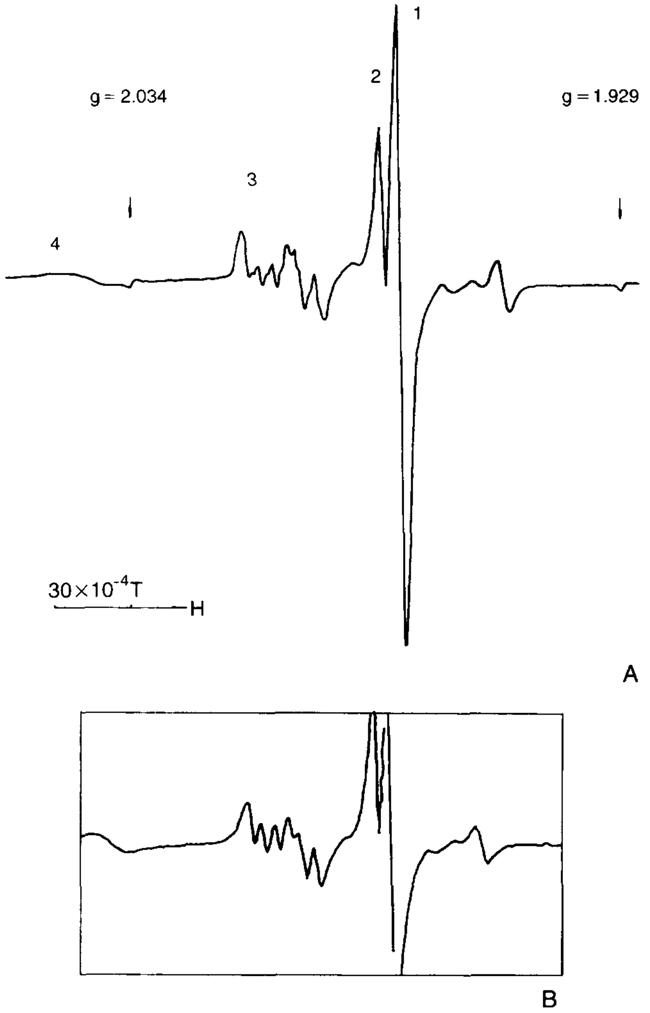


FIGURE 3 ESR spectrum arising from (a) Ph_3SnI and $Cp_2Ti(CO)_2$ and (b) a computer-simulated spectrum: 1. $[Cp_2TiSnPh_3]$; 2. impurity peak; 3. $[Cp_2TiI]$; 4. $[Cp_2Ti(CO)I]$.

uene, the ESR spectrum showed a peak at g = 1.975 that was instantly perceived. This signal clearly showed the presence of the intermediate $[Cp_2Ti\text{-}SnPh_2Cl]$, and the weak peak of $[Cp_2Ti(CO)Cl]$ at 1.993 did not appear.

With respect to the I-values and abundance of the Ti and Sn nuclei, we developed a computer-simulated program to check the experimental results. After having been fitted repeatedly, simulated spectra coinciding very well with the experimental spectra were obtained. In consequence, for the intermediate $[Cp_2Ti\text{-}SnPh_2Cl]$, the hyperfine coupling constants of Ti and Sn nuclei, $a(Sn) = 46.58 \times 10^{-4}T$ and $a(Ti) = 2.12 \times 10^{-4}T$, respectively, were assigned. The ESR spectral data for other organo-tin halides reacting with $Cp_2Ti(CO)_2$ are all listed in Table 1. These are, so far, the first parameters reported for the Ti(III)–Sn radical. Some experimental and simulated spectra are shown in Figures 1 through 3.

From the data listed in Table 1, it is shown that Ph_2SnI_2 does not form the free radical [Ti(III)–Sn], and $PhSnCl_3$ gives evidence of the radical but of no Ti–Sn product. These results may be attributed to the abundance of iodine atoms and chlorine atoms on either of the metals causing dissociation of the unstable products, such as $Cp_2Ti(I)SnPh_2I$ and $Cp_2Ti(Cl)SnPhCl_2$.

In the case wherein Ph_3SnX was used, $Cp_2Ti(X)\text{-}SnPh_3$ was obtained as the main product in addition to $Ph_3Sn\text{-}SnPh_3$ as a byproduct; however, no $[Ph_3Sn]$. ESR signal was detected. Bis(methylcyclopentadienyl) dicarbonyl titanium reacted with the aryl-tin halide, as in the case of $Cp_2Ti(CO)_2$, to give the corresponding [Ti(III)–Sn] and $(MeCp)_2Ti(CO)X$ signals.

Other ligands present on the tin complexes instead of the halogens were studied for their effect in the reaction with dicarbonyl titanocene. As shown in Table 1, $SnCl_3(CH_2CH_2COOMe)$ gave a Ti–Sn intermediate but no stable product, and $Ph_2Sn(S_2COEt)_2$ gave no [Ti–Sn] intermediate but rather an intermediate $Cp_2Ti(S_2COEt)$ signal. Among the ESR parameters shown in Table 1, it is worthy of note that the $a(Sn)$ values vary greatly according to the ligands present on the tin. It is known that "*a*", a hyperfine coupling constant, is a measure of unpaired electron density on Sn. In a Ti–Sn intermediate, the lone electron is drawn from Ti toward Sn, and this delocalization varies with the substitution on Sn. A phenyl group is a more electron-attracting group than a butyl group, causing a stronger delocalization effect, and in such an intermediate, the *a* of Ph–Sn is larger than that of Bu–Sn. Greater substitution of Ph on Sn resulted in the enlargement of the *a* value. A para-chlorophenyl substituent on tin exerts a larger *a* effect than the presence of a phenyl or *p*-tolyl substitutent on the tin intermediate. The presence of an electron donation methyl group on the cyclopentadienyl ring produced the opposite effect of delocalization through Ti toward Sn and also gives a larger *a* value.

The ESR study of the reaction reveals the nature of the reaction mechanism. As we have reported, in the reaction between dicarbonyl titanocene and alkyl halides [2], we found the radical intermediates of $Cp_2Ti(CO)X$ and Cp_2TiX, which were also found in the reaction between dicarbonyl titanocene and aryl tin halides. Could this be a manifestation of the same reaction pathway? In the case of alkyl halides or trityl halides, the reactions with $Cp_2Ti(CO)_2$ were different from those of aryl tin halides in the following respects. In the case of the alkyl halides, the velocity of the reaction depends on the nature of the halogen: RI> RBr> RCl; while for the organo-tin

TABLE 1 The ESR Spectral Parameters of Ti(III) Intermediates[a]

	$Cp_2Ti(CO)X$		Cp_2TiX		$Cp_2TiSnAr_nX_{3-n}$		
Ar_nSnX_{4-n}	g	$a(X)$	g	$a(X)$	g	$a(Ti)$	$a(Sn)$
Ph_2SnCl_2	1.994				1.975	12.12	46.58
$(p\text{-}ClPh)_2SnCl_2$	1.993				1.974	11.59	50.71
Bu_2SnCl_2	1.993				1.975	11.96	23.92
Ph_2SnBr_2	2.013 [4]	4.82			1.976	10.38	47.22
Bu_2SnBr_2	2.013	4.89			1.975	11.95	23.90
Ph_2SnI_2	2.044						
$(p\text{-}Me\text{-}Ph)_3SnCl$	1.994		1.979[b]		1.975	10.84	67.15
Ph_3SnCl	1.994		1.979		1.975	10.25	68.98
					1.976[c]		72.70
Ph_3SnBr	2.014	4.81	1.987	2.50	1.975	10.73	69.65
	2.012	4.41			1.976[c]		75.53
Ph_3SnI	2.044		2.001	5.19	1.975	11.13	73.61
	2.040				1.976[c]		78.50
$PhSnCl_3$					1.974[d]		111.46
$SnCl_3(CH_2CH_2CO_2Me)$					1.976[d]		105.70
$Ph_2Sn(S_2COEt)_2$			1.984	9.72[e]			

[a] The unit of "a" is 10^{-4} T.

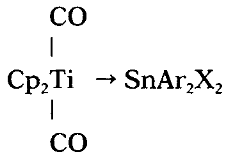
[b] A composite of Cp_2TiX and the oxidation impurities.

[c] $Cp = MeC_5H_4$.

[d] The life of the radicals is about 10 minutes.

[e] $a = a(Ti)$.

halides, the reaction velocity does not vary with the nature of the halogen. Tin has a vacant d orbital that can serve as a Lewis acid, while Ti has paired electrons serving as a Lewis base. They approach each other in the following manner:



$$\begin{array}{l} CO \\ \; | \\ Cp_2Ti \rightarrow SnAr_2X_2 \\ \; | \\ CO \end{array}$$

In the case of Ph_2SnCl_2, the free radical intermediate $Cp_2TiSnPh_2Cl$ forms by loss of CO and Cl and gives an ESR signal at g = 1.975. In the same way, Ph_3SnCl would react with $Cp_2Ti(CO)_2$ in the following manner:

$$Cp_2Ti(CO)_2 + Ph_3SnCl \rightarrow [Cp_2Ti(CO)SnPh_3Cl]$$

$$[Cp_2Ti(CO)SnPh_3Cl] - CO \rightarrow [Cp_2Ti\text{-}SnPh_3Cl]$$

$$[Cp_2Ti\text{-}SnPh_3Cl] - Cl \rightarrow [Cp_2Ti\text{-}SnPh_3]$$

$$[Cp_2Ti\text{-}SnPh_3] + Cl \rightarrow Cp_2Ti(Cl)SnPh_3$$

with $[Cp_2TiCl]$ as the starting material, the sequence of reactions is

$$Cp_2TiCl + Ph_2SnCl_2 \rightarrow [Cp_2Ti\text{-}SnPh_2Cl] + Cl$$

$$[Cp_2Ti\text{-}SnPh_2Cl] + Cl \rightarrow Cp_2Ti(Cl)SnPh_2Cl$$

The following is a by-product formed by use of Ph_3SnCl:

$$[Cp_2Ti\text{-}SnPh_3] + Cl \rightarrow [Cp_2TiCl] + [Ph_3Sn]^\bullet$$

$$2[Ph_3Sn]^\bullet \rightarrow Ph_3Sn\text{-}SnPh_3$$

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