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The Reaction between Dicyclopentadienyl-Dicarbonyl Titanium and Aryltin Halides

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ABSTRACT

The oxidation-elimination reaction between dicyclopentadienyl-dicarbonyl titanium, $Cp_2Ti(CO)_2$ [bis(methylcyclopentadienyl)dicarbonyl titanium, $(MeCp)_2Ti(CO)_2$] and aryltin halides was studied. Nineteen novel complexes containing the Ti–Sn bond were isolated. The reaction was proved to involve free-radical intermediates. © 1996 John Wiley & Sons, Inc.

Dicyclopentadienyl-dicarbonyl titanium, $Cp_2Ti(CO)_2$, has been found to react with many organic compounds. The common feature of these reactions is the loss of CO and the raising of the oxidation state of Ti from d^2 to d^0, i.e., from +II to +IV. The authors have previously investigated the reaction between $Cp_2Ti(CO)_2$ and alkyl halides. These reactions were found to take place by free-radical mechanisms [1]:

$$Cp_2Ti\,(CO)_2 + RX \rightarrow Cp_2Ti(X)C(O)R + CO$$

$$Cp_2Ti\,(CO)_2 + 2RX \rightarrow Cp_2Ti(X)_2 + R\text{–}R + 2CO$$

If RX is a primary alkyl halide, an insertion reaction takes place, and if RX is a tertiary halide [1], both types of reaction shown above can occur. If RX is an allyl halide or a trityl halide, only the latter reaction can be found.

It is our present purpose to investigate whether an aryltin halide behaves in the same way. Generally speaking, Ar_nSnX_{4-n} can be hydrolyzed to give $Ar_nSn(OH)_{4-n}$ in basic solution, like an alkyl halide in an S_N2 or S_N1 reaction. In an aprotic solution, such as toluene, aryltin halides do not undergo ionic processes; the Sn–X bond is more apt to split homolytically.

The following equations illustrate the reactions that occurred in our experiments with aryltin halides and $Cp_2Ti(CO)_2$ in a hydrocarbon solution:

$$Cp_2Ti(CO)_2 + Ar_2SnX_2 \rightarrow Cp_2Ti(X)SnAr_2X + 2CO$$

$$Ar = Ph, MePh, MeOPh; \quad X = Cl, Br$$

$$Cp = C_5H_5, MeC_5H_4$$

$$Cp_2Ti(CO)_2 + Ar_3SnX \rightarrow Cp_2Ti\,(X)\,SnAr_3 + 2CO$$

$$Ar = Ph, MePh, MeOPh; \quad X = Cl, Br, I$$

$$Cp = C_5H_5, MeC_5H_4$$

If $ArSnX_3$ was used as the substrate, products containing the Ti–Sn bond were not found; instead, elementary Sn and the lower valent SnX_2 were isolated:

$$2Cp_2Ti(CO)_2 + 2PhSnCl_3 \rightarrow 2Cp_2TiCl_2 + Ph_2SnCl_2 + Sn$$

$$Cp_2Ti(CO)_2 + 2PhSnCl_3 \rightarrow Cp_2TiCl_2 + Ph_2SnCl_2 + SnCl_2$$

The reactions were monitored by means of ESR spectroscopy. It was found that every time an aryltin halide was added to the substrate solution, an ESR signal was observed. The patterns of ESR spectra were of similar shape that consisted of a main absorption peak at $g = 1.975$; for bromides and iodides, additional weak signals appeared, their locations being scattered between $g = 1.994$ and 2.013. From literature data [3], the ESR signals were assigned as shown in Table 1.

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TABLE 1 ESR Parameters of Ti(III) Intermediates

Tin Halides	*$Cp_2Ti(CO)X$*	*a(X)*	*Cp_2TiX*	*aX*	*$Cp_2TiSn\equiv$*	*aTi*	*a(Sn)*
Ph_2SnCl_2	1.994				1.975	12.12	41.58
Bu_2SnCl_2	1.994				1.975	11.96	23.92
Ph_2SnBr_2	2.013	4.82			1.975	11.06	41.36 a(Br)
Bu_2SnBr_2	2.013	4.98			1.975	11.95	23.90
Ph_2SnI_2	2.044						
Ph_3SnCl	1.994		1.979		1.975	10.25	68.98
(*p*-MePh)$_3$SnCl	1.994		1.979		1.975	10.84	67.15
Ph_3SnBr	2.014	4.95	1.987	2.5	1.975	10.73	69.85
(*p*-MePh)$_3$SnBr	2.012	4.41			1.976		76.20
Ph_3SnI	2.044		2.001		1.975	11.13	71.68
(*p*-MePh)$_3$SnI	2.040				1.976		78.50

Note: The parameters for Cp_2TiX often were mixed with signals of oxidative impurities. That of Ti–Sn complexes was short lived but consistent. The nature of the halogen is immaterial. The last column, a(Sn), shows the unpaired electron density delocalized on Sn from Ti. Additional physical data of the compounds are shown in Tables 2 and 3.

TABLE 2 Some Physical Constants of Complexes containing Ti–X Bonds

Entry	*Complexes* *$Cp_2Ti=$*	*Color*	*m.p. °C*	*Yield%*	*Elemental Data*	
					C%	*H%*
1	–(Cl)SnPh$_2$Cl	deep green	138–40(d)	65	50.42(50.63),	3.78(3.86)
2	–(Br)SnPh$_2$Br	green	142–4(d)	71	42.87(43.24),	3.15(3.30)
3	–(Cl)Sn(PhMe-*p*)$_2$Cl	deep green	150–3(d)	60	52.73(52.36),	4.42(4.36)
4	–(Br)Sn(PhMe-*p*)$_2$Br	green	148–5(d)	75	44.81(45.07),	3.71(3.75)
5	–(Cl)Sn(PhMe-*m*)$_2$Cl	deep green	126–8(d)	74	52.34(52.36),	4.31(4.36)
6	–(Br)Sn(PhMe-*m*)$_2$Br	green	140–2(d)	70	45.58(45.67),	3.89(3.76)
7	–(Cl)SnPh$_3$	deep green	183–5(d)	88	59.22(59.67),	4.53(4.47)
8	–(Cl)Sn(PhMe-*p*)$_3$	deep green	160–2(d)	77	60.90(61.48),	5.18(5.16)
9	–(Cl)Sn(PhMe-*m*)$_3$	deep green	159–61(d)	70	62.07(61.48),	5.23(5.16)
10	–(Cl)Sn(PhOMe-*p*)$_3$	green	156–8(d)	76	57.41(56.91),	4.87(4.80)
11	–(Br)SnPh$_3$	light green	187–90(d)	80	55.19(55.31),	3.99(4.14)
12	–(I)SnPh$_3$	dirty yellow	^{2}20–2(d)	75	50.11(51.33),	3.65(3.84)
	(MeCp)$_2$Ti=					
13	–(Cl)SnPh$_3$	green	162–5(d)	81	60.60(60.91),	4.80(4.94)
14	–(Cl)Sn(PhMe-*p*)$_2$Cl	green	162–4(d)	91	62.30(62.55),	5.63(5.57)
15	–(Cl)Sn(PhMe-*m*)$_2$Cl	green	154–6(d)	89	62.15(62.55),	5.63(5.57)
16	–(Cl)Sn(PhOMe-*p*)$_2$Cl	green	130–2(d)	81	58.48(58.10),	5.07(5.17)
17	–(Cl)Sn(PhCl-*p*)$_2$Cl	green	180–2(d)	77	51.31(51.85),	3.61(3.77)
18	–(Br)SnPh$_3$	light green	164–6(d)	85	57.11(56.65),	5.03(4.60)
19	–(I)SnPh$_3$	dirty yellow	192–4(d)	79	52.61(52.70),	4.24(4.27)

EXPERIMENTAL

Melting points were determined on a PHMK melting point stage under the protection of an inert gas; temperatures were not corrected. ^{119}Sn NMR spectra were taken on a Brucker AC-P200 instrument using Me_4Sn as an internal standard, and ^{1}H NMR on a JEOLFX90NM spectrometer. MS were taken on a VG 7070E-HF mass spectrometer.

Preparation of $Cp_2Ti(CO)_2$

With Cp_2TiCl_2 as the starting material, the reduction was carried out by passing CO into a THF solution containing Cp_2TiCl_2 impregnated with Al foil. The reaction mixture, after absorption of enough CO, was filtered through a column of anhydrous Al_2O_3 under argon protection. The contents of the column were eluted with ligroin. Upon evaporation of the eluent, red crystals of $Cp_2Ti(CO)_2$ were collected, yield 78%.

The $(MeCp)_2Ti(CO)_2$ was prepared by the same procedure.

The Preparation of Aryltin Halides [4]

Triphenyl tin chloride can be taken as an example of the preparation of most of the aryltin halides. Tin chloride was used as the starting material to react with a phenyl Grignard reagent to prepare Ph_4Sn. To prepare the halides of aryl-stannanes, the use of a

TABLE 3 ^{1}H NMR of the Complexes Containing Ti–Sn Bonds

Entry	*Complexes*	δ
1	$Cp_2Ti(Cl)SnPh_2Cl$	6.45(s,Cp,10H), 7.40–7.72(br,Ph,10H)
2	$Cp_2Ti(Br)SnPh_2Br$	6.45(s,Cp,10H), 7.40–7.72(br,Ph,10H)
3	$Cp_2Ti(Cl)Sn(PhMe\text{-}p)_2Cl$	6.38(s,Cp,10H), 2.36(s,Me,6H), 7.24(br,Ph,8H)
4	$Cp_2Ti(Br)Sn(pHMe\text{-}p)_2Br$	6.40(s,Cp,10H), 2.36(s,Me,6H) 7.20–7.60(br,Ph,8H)
5	$Cp_2Ti(Cl)Sn(PhMe\text{-}m)_2Cl$	6.48(s,Cp,10H), 2.38(s,Me,6H) 7.30–7.60(br,Ph,8H)
6	$Cp_2Ti(Br)Sn(PhMe\text{-}m)_2Br$	6.48(s,Cp,10H), 2.40(s,Me,6H) 7.30–7.60(br,Ph,8H)
7	$Cp_2Ti(Cl)SnPh_3$	6.28(s,Cp,10H), 7.36(m,Ph,15H)
8	$Cp_2Ti(Cl)Sn(PhMe\text{-}p)_3$	6.23(s,Cp,10H), 2.34(s,Me,9H) 7.04–7.48(br,Ph,12H)
10	$Cp_2Ti(Cl)Sn(PhOMe\text{-}p)_3$	6.24(s,Cp,10H), 3.80(s,Me,9H) 6.84–7.36(br,Ph,12H)
11	$Cp_2Ti(Cl)Sn(Ph\text{-}Me)_3$	6.24(s,Cp,10H), 2.32(s,Me,9H) 7.18(br,Ph,12H)
12	$Cp_2Ti(I)SnPh_3$	6.40(s,Cp,10H), 7.30(s,Ph,15H)
13	$(MeCp)_2Ti(Cl)SnPh_3$	4.94–5.70(q,Cp,4H), 6.54–7.00(q,Cp,4H) 1.92(s,Me,6H), 7.26(m,Ph,15H)
14	$(MeCp)_2Ti(Cl)Sn(PhMe\text{-}p)_3$	4.94–5.76(q,Cp,4H), 6.54–7.24(q,Cp,4H) 2.26(s,PhMe,9H), 1.92(s,Cp – Me,6H), 7.24(m,Ph,12H)
15	$(MeCp)_2Ti(Cl)Sn(PhMe\text{-}m)_3$	5.16–5.66(q,Cp,4H), 7.28–7.64(q,Cp,4H) 2.26(s,PhMe,9H), 1.96(s,Cp – Me,6H), 7.24(m,Ph,12H)
16	$(MeCp)_2Ti(Cl)Sn(PhOMe\text{-}p)_3$	4.92–5.70(q,Cp,4H), 6.60–7.04(q,Cp,4H) 3.80(s,PhOMe,9H), 1.92(s,CpMe,6H), 7.20(s,Ph,12H)
17	$(MeCp)_2Ti(Cl)Sn(PhCl\text{-}m)_3$	4.94–5.78(q,Cp,4H), 6.50–6.92(q,Cp,4H) 1.92(s,Me,6H), 7.17(m,Ph,12H)
18	$(MeCp)Ti(Br)SnPh_3$	4.54–5.60(q,Cp,4H), 6.74–6.92(q,Cp,4H) 1.92(s,Me,6H), 7.24(m,Ph,15H)
19	$(MeCp)_2Ti(I)SnPh_3$	4.54–5.60(q,Cp,4H), 7.14–7.34(q,Cp,4H) 7.38(m,Ph,15H)

More information was obtained by use of ^{119}Sn NMR spectroscopy. There are large numerical differences among different organo-tin compounds (see Table 4).

TABLE 4 δ ^{119}Sn Values of Compounds Containing M–Sn Bonds

Compound	δ	*Compounds*	δ
$Cp_2Mo(Cl)SnMe_3$	90.0[2]	$Cp_2Ti(I)SnPh_3$	129.29
$Cp_2Mo(H)SnMe_3$	123.0[2]	$Cp_2Ti(Br)SnPh_2Br$	161.35
$Cp_2Ta(H)_2SnMe_3$	53.0[2]	$Cp_2Ti(Br)SnPh_3$	75.57
$Cp_2Ti(Cl)SnPh_2Cl$	125.2	$(MeCp)_2Ti(Cl)SnPh_3$	40.38
$Cp_2Ti(Cl)SnPh_3$	48.5	$(MeCp)_2Ti(I)SnPh_3$	123.93
$Me_3PbSnMe_3$	− 57.0[2]	$Cp_2Ti(NCO)SnPh_3$	30.37
$(CO)_5ReSnMe_3$	− 89.0[2]	$(MeCp)Ti(NCO)SnPh_3$	22.58
Ph_3SnCl	− 44.8	Ph_3SnI	− 113.38

disproportionation reaction between Ph_4Sn and SnX_4 in the appropriate ratio, was satisfactory [4].

Triphenyltin iodide was prepared by another method [5], iodine in chloroform being stirred with Ph_4Sn; Ph_3SnI crystallized from the reaction mixture after filtration. The Ph_2SnBr_2 was also prepared by the direct bromination of Ph_4Sn [6].

The Reaction of $Cp_2Ti(CO)_2$ with an Aryltin Halide

As an example of the reaction, the substrate, $Cp_2Ti(CO)_2$ 1.3 g (5.5 mmol), dissolved in 25 mL of toluene, was stirred with 2.1 g (6.1 mmol) of Ph_2SnCl_2 under argon protection at 15–20°C. After 5 hours, the solution became green, and a precipitate settled out. When no more precipitate formed, the solid was collected and dissolved in benzene. After the solvent had been evaporated, a green solid that remained was washed with benzene, then with ligroin. The product was dried in a vacuum to yield 1.8 g of $Cp_2Ti(Cl)SnPh_2Cl$, m.p. 138–40° (d).

The Reaction of $Cp_2Ti(CO)_2$ with Ph_3SnCl

Equimolar amounts of $Cp_2Ti(CO)_2$ and the tertiary tin halide were allowed to react. The solvent used was toluene, as before. After the reaction had ceased, the separation of the product $Cp_2Ti(Cl)SnPh_3$ was effected by filtration. The yield was 88%, m.p. 183–185°C (d). The original solution from the reaction mixture was concentrated and passed through an Al_2O_3 column, to give a white crystalline by-product. It was proved to be $Ph_3Sn\text{–}SnPh_3$, m.p. 234–236, yield 9.2%.

The Reaction of $Cp_2Ti(CO)_2$ with $PhSnCl_3$

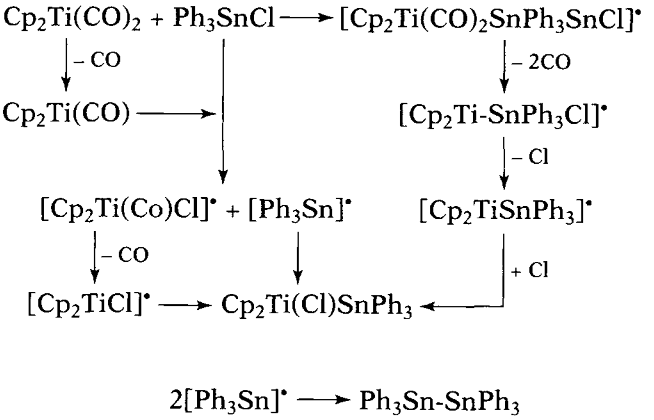
The organotin trihalides reacted with the substrate very vigorously. In toluene solution, when they were mixed, CO was evolved immediately. A red precipitate could be perceived at the bottom of the reaction flask and then metallic tin. The Sn was separated mechanically, and the red crystalline substance was collected and proved to be Cp_2TiCl_2. When $PhSnCl_3$ was used in excess, no metallic tin precipitated. Instead, Ph_2SnCl_2 and Cp_2TiCl_2 could be separated in equal molar amounts, $SnCl_2$ being left in the solution.

DISCUSSION

On the basis of the information furnished by the ESR signals, all the aryltin halides reacted with

TABLE 5 The Rate of CO Evolution in mL in the Reaction in the Presence of Added Hydroquinone as against That without the Radical Inhibitor Present

Time in Hours	*0.5*	*1*	*2*	*4*	*5.5*	*7*	*17*	*24*	*26*	*28*	*34*
No hydroquinone	5	10	21	43	55	65	100	115	122	132	150
Adding 0.12 g HQ	4	8	15	28	42	52	80	87	100	112	135



SCHEME 1

$Cp_2Ti(CO)_2$ by a free-radical path. If a radical inhibitor such as hydroquinone was added, the rate of the reaction was retarded, as monitored by the evolution of CO (Table 5).

The reaction was carried out by measuring the gas volume evolved. The inhibitor did not completely stop the evolution of CO, since $Cp_2Ti(CO)_2$ may itself decompose when exposed to light for a period of time. In its reaction with an aryltin halide, formation of a Ti–Sn radical was detected by the ESR spectra, the *g* value in every case being 1.975, accompanied by signals at $g = 1.994–2.044$ depending upon the types of halide involved (see Table 1). The appearance of $Ph_3Sn–SnPh_3$ unequivocally rationalized the existence of the organotin radical, which however could not be detected by ESR spectroscopy [3]. The following scheme is postulated to show a possible reaction path between $Cp_2Ti(CO)_2$ and Ph_3SnCl:

The chemical shift values of ^{119}Sn in the different compounds represent criteria of the chemical environment of the tin atom in the various compounds. The electronegativity of the metal bonding, and the electron shielding on the tin atom, affect the δ values of the ^{119}Sn. In general, the more electropositive the metal combining with the tin atom, the more this tends to give positive values. As shown in Table 4, halogen on Ti and methyl substitution on the Cp ring exert a complicated influence on the δ values. There may be steric factors involved.

The mass spectra also revealed the unstable bonding of Ti–Sn. There was only a small percentage of the molecular ion of the Ti–Sn species found. In all MS spectra, Cp_2Ti+ was the most abundant species among the rest of the organo-metallic ions. The following MS spectra of $Cp_2Ti(Cl)Sn(Ph)_3$ are obtained by the EI method; for example:

564 (M+, 1), 386 (Ph_2SnCl, 1), 351 (Ph_3Sn, 19), 309 (Ph_2SnCl, 21), 213 (Cp_2TiCl, 31), 197 (PhSn, 29), *178 (Cp_2Ti, 100)*, 155 (SnCl, 27), 154 (Ph_2, 46), 148 (CpTiCl, 52), 120 (Sn, 21), 113 (CpTi, 12), 83 (TiCl, 12), 77 (Ph, 17), 65 (Cp, 3), 51 (C_4H_3, 18), 39 (C_3H_3, 9).

The numerical values in the parentheses denote the abundance of the ions.

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