

## REACTIONS OF DICYCLOPENTADIENYL TITANIUM(III) COMPOUNDS WITH CARBON MONOXIDE \*

E.J.M. DE BOER, L.C. TEN CATE, A.G.J. STARING, and J.H. TEUBEN \*

*Laboratorium voor Anorganische Chemie, Rijksuniversiteit Groningen, Nijenborgh 16, 9747 AG Groningen (The Netherlands)*

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### Summary

Reactions of  $\text{Cp}_2\text{TiR}$  ( $\text{R} = \text{Cl}, \text{C}_6\text{F}_5, \text{C}_6\text{H}_5, o\text{-CH}_3\text{C}_6\text{H}_4$ ) with CO give two types of products: terminally coordinated adducts,  $\text{Cp}_2\text{Ti}(\text{R})\text{CO}$ , and insertion products,  $\text{Cp}_2\text{TiCOR}$ , i.e. acyl compounds. The acyl ligand is  $\eta^2$ -coordinated at the titanium atom. The preparations and properties of the compounds are described.

### Introduction

Being of great industrial importance, the carbonylation of hydrocarbons and other substrates in the presence of transition metal complexes has been extensively studied. However, until recently little was known about the carbonyl chemistry of early transition metals [1–4]. The complexes previously studied were mainly compounds of tetravalent titanium, zirconium or hafnium and we now report reactions of some compounds of trivalent titanium,  $\text{Cp}_2\text{TiR}$  ( $\text{R} = \text{Cl}, \text{C}_6\text{F}_5, \text{C}_6\text{H}_5, o\text{-CH}_3\text{C}_6\text{H}_4$ ).

### Results and discussion

Reaction of CO with  $\text{Cp}_2\text{TiR}$  gives two types of products, depending on the nature of R. If R is strongly electron-withdrawing ( $\text{R} = \text{Cl}, \text{C}_6\text{F}_5$ ), adducts  $\text{Cp}_2\text{Ti}(\text{R})\text{CO}$  are formed, but for more electron-donating groups R ( $\text{R} = \text{C}_6\text{H}_5, o\text{-CH}_3\text{C}_6\text{H}_4$ ) insertion of CO into the Ti–R bond occurs and acyl compounds,  $\text{Cp}_2\text{TiCOR}$ , are formed.

#### *Adducts $\text{Cp}_2\text{Ti}(\text{R})\text{CO}$*

For  $\text{R} = \text{C}_6\text{F}_5$  the adduct  $\text{Cp}_2\text{Ti}(\text{C}_6\text{F}_5)\text{CO}$  is formed. Admission of CO to a saturated solution of  $\text{Cp}_2\text{TiC}_6\text{F}_5$  in toluene results in the up-take of 1 mol of CO and brown-green needles of analytically pure  $\text{Cp}_2\text{Ti}(\text{C}_6\text{F}_5)\text{CO}$  separate (Ta-

\* Dedicated to Professor Joseph Chatt on the occasion of his 65th birthday.

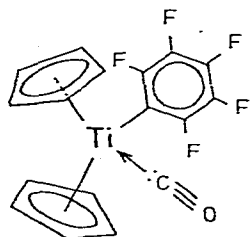


Fig. 1. Structure of  $\text{Cp}_2\text{Ti}(\text{C}_6\text{F}_5)\text{CO}$ .

ble 1). The compound dissociates in solution in vacuo to give  $\text{Cp}_2\text{TiC}_6\text{F}_5$  and CO. The decomposition temperature of the solid compound is  $140^\circ\text{C}$  (by DTA), but slow decomposition occurs even at room temperature (under  $\text{N}_2$  or Ar); in this case,  $\text{Cp}_2\text{Ti}(\text{CO})_2$  (identified by IR) is one of the products.

*Spectroscopic properties.* The spectroscopic properties of the adduct  $\text{Cp}_2\text{Ti}(\text{C}_6\text{F}_5)\text{CO}$  are in agreement with the structure shown in Fig. 1.

The IR spectrum (see Fig. 4) shows, in addition to the absorptions characteristics of  $\eta^5\text{-C}_5\text{H}_5$  and  $\text{C}_6\text{F}_5$ , a  $\nu(\text{CO})$  band at  $2060\text{ cm}^{-1}$ , which indicates a terminal CO ligand. This represents a shift of  $35\text{--}180\text{ cm}^{-1}$  to higher wavenumbers compared to  $\text{Cp}_2\text{Ti}(\text{CO})_2$  [5] and  $\text{Cp}_2\text{Ti}(\text{CO})\text{-}\eta^2\text{-C}_6\text{H}_5\text{CCC}_6\text{H}_5$  [6]. This is not unexpected, since in the latter complexes the metal has two electrons available for back donation whereas in  $\text{Cp}_2\text{Ti}(\text{C}_6\text{F}_5)\text{CO}$  it has only one. Furthermore, the increase of the formal charge at the titanium in the latter adduct stabilizes and contracts the titanium orbitals, resulting in less efficient overlap for back donation.

Compared to another, though less well characterized carbonyl compound of tervalent titanium, viz.  $\text{TiCl}_3(\text{CO})(\text{P}(\text{C}_2\text{H}_5)_3)_2$  [7], the  $\nu(\text{CO})$  frequency in  $\text{Cp}_2\text{-}$

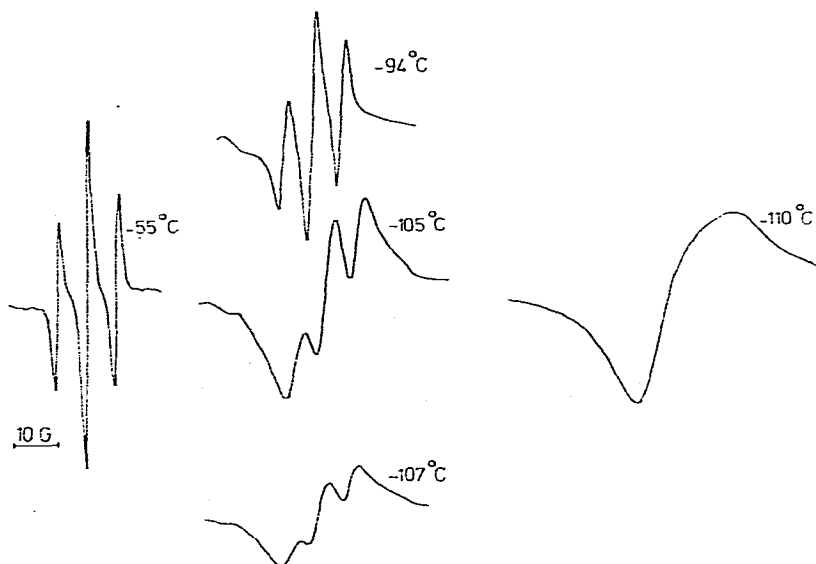


Fig. 2. EPR spectra of  $\text{Cp}_2\text{Ti}(\text{C}_6\text{F}_5)\text{CO}$  at several temperatures.

$\text{Ti}(\text{C}_6\text{F}_5)\text{CO}$  is considerably increased ( $\Delta\nu(\text{CO}) +185 \text{ cm}^{-1}$ ) but this may be due to ligand effects.

The EPR spectrum of the adduct  $\text{Cp}_2\text{Ti}(\text{C}_6\text{F}_5)\text{CO}$  in benzene/toluene (1/4) is strongly temperature dependent. Spectra at several temperatures are shown in Fig. 2.

At  $-55^\circ\text{C}$  a well-resolved triplet (1/2/1) is observed ( $g = 1.994$ ) while on further cooling the signal changes into a singlet at  $-110^\circ\text{C}$ . The explanation for this may be as follows: According to the Lauher and Hoffmann model for bent  $\text{Cp}_2\text{M}$  systems [8], the odd electron in the adduct occupies the orbital directed along the Y-axis ( $1a_1$  in  $C_{2v}$  symmetry) (Fig. 3). Interaction with two equivalent fluorine atoms ( $I = \frac{1}{2}$ ) will result in a 1/2/1 hyperfine splitting. Most likely this proceeds via a through-space mechanism involving the *ortho*-fluorine atoms as shown in Fig. 3. A through-bond interaction is less likely because in  $\text{Cp}_2\text{TiC}_6\text{F}_5$  no fluorine interaction is observed [9], and also no interactions with *meta*- or *para*-fluorine atoms are present in the adduct.

The temperature dependence of the EPR spectra indicates that the equivalence of the two *ortho*-fluorines is due to a dynamic and not a static effect. The equivalence of the two *ortho*-fluorines at  $-55^\circ\text{C}$  could arise from a fast (on EPR time scale) rotation of the  $\text{C}_6\text{F}_5$  ring around the Ti—C bond [17]. The observation of a singlet (and not a doublet) signal at low temperatures may indicate that in the equilibrium position neither fluorine interacts with the  $1a_1$  orbital. Probably, this means that the  $\text{C}_6\text{F}_5$  ring plane is inclined from the  $yz$  plane.

$\text{Cp}_2\text{TiCl}$  does not react with CO, probably, because the monochloride is stabilized by the formation of the dimer,  $(\text{Cp}_2\text{TiCl})_2$ . This view is supported by the reaction of CO with  $(\text{C}_5\text{Me}_5)_2\text{TiCl}$  ( $\text{C}_5\text{Me}_5 \equiv$  pentamethylcyclopentadienyl), which does not dimerize owing to the bulkiness of the  $\text{C}_5\text{Me}_5$  ligands (see Experimental).

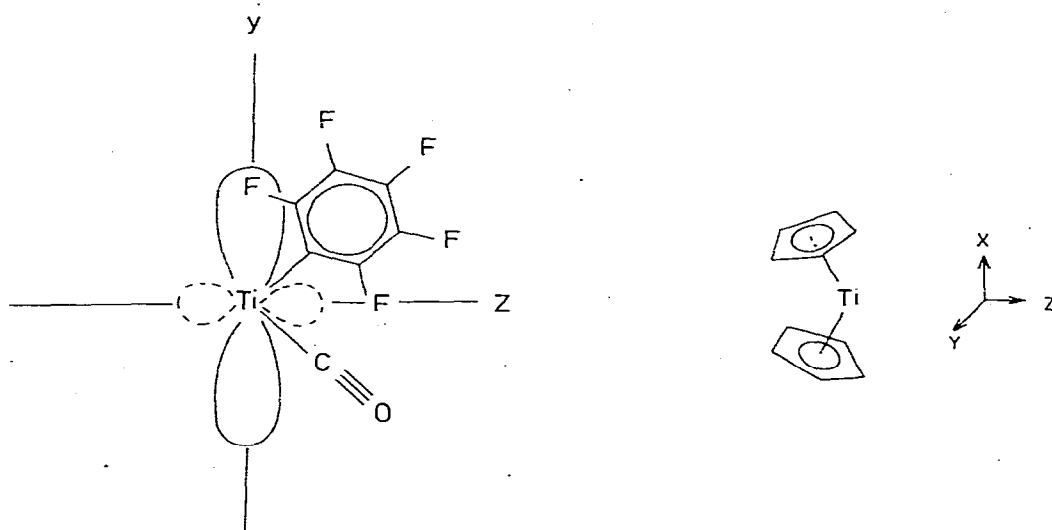
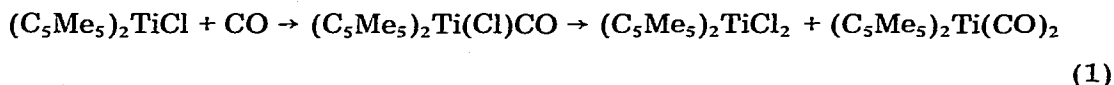


Fig. 3. Through-space interaction. The coordinate system used is shown on the right-hand side.

Monomeric  $(C_5Me_5)_2TiCl$  does react with CO giving the adduct  $(C_5Me_5)_2Ti(Cl)CO$ . This compound is unstable at room temperature and disproportionates slowly according to equation 1. The reaction can be followed by IR and EPR spectroscopy. The IR spectrum of the adduct shows the  $\nu(CO)$  band at 2000



$cm^{-1}$  (comparable to the  $\nu(CO)$  band in  $Cp_2Ti(C_6F_5)CO$ ). The intensity of this band slowly decreases, while at the same time two new bands appear at 1930 and 1850  $cm^{-1}$ , and these are ascribed to  $(C_5Me_5)_2Ti(CO)_2$ .

The EPR spectrum of  $(C_5Me_5)_2TiCl$  in toluene shows a singlet with  $g = 1.956$ . On admission of CO, the singlet is shifted to  $g = 1.968$ ; after 16 h the EPR signal has completely disappeared.

Probably, the thermal decomposition of  $Cp_2Ti(C_6F_5)CO$  is analogous to the disproportionation of  $(C_5Me_5)_2Ti(Cl)CO$ . Surprisingly,  $Cp_2Ti(C_6F_5)CO$  does not show an alternative, more common rearrangement, namely insertion of the CO molecule into the Ti-R bond with formation of an acyl compound. Such a

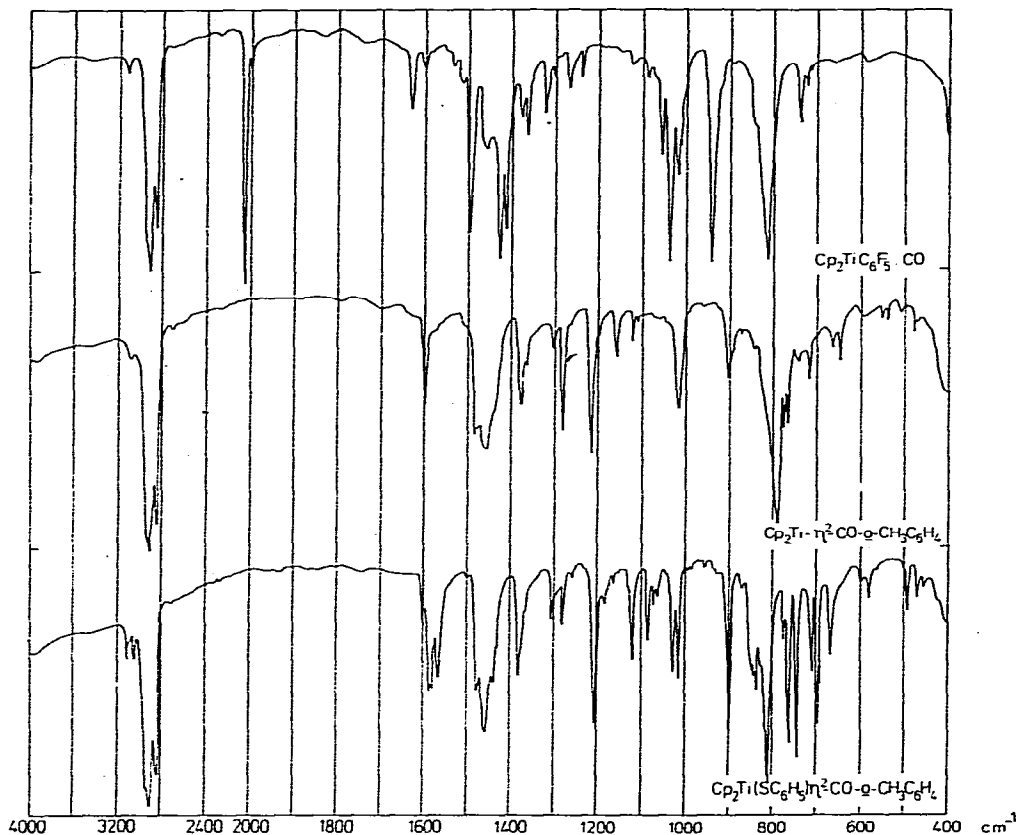


Fig. 4. IR spectra of  $Cp_2Ti(C_6F_5)CO$ ,  $Cp_2Ti-\eta^2-CO-o-CH_3C_6H_4$  (I), and  $Cp_2Ti(SC_6H_5)\eta^2-CO-o-CH_3C_6H_4$  (III).

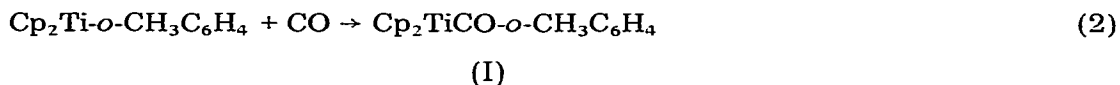
TABLE 1  
ANALYTICAL DATA (found (calc.) (%))

	Ti	C	H
$\text{Cp}_2\text{Ti}(\text{C}_6\text{F}_5)\text{CO}$	12.94 (12.84)	55.04 (54.69)	2.80 (2.68)
$\text{Cp}_2\text{TiCO-}o\text{-CH}_3\text{C}_6\text{H}_4$ (I)	16.12 (16.13)	71.83 (72.72)	5.87 (5.72)
$\text{Cp}_2\text{Ti}(\text{SC}_6\text{H}_5)\text{CO-}o\text{-CH}_3\text{C}_6\text{H}_4$ (III)	11.96 (11.80)	71.00 (70.94)	5.58 (5.42)

rearrangement does occur in the reactions of  $\text{Cp}_2\text{TiR}$  with  $\text{R} = o\text{-CH}_3\text{C}_6\text{H}_4$  and  $\text{C}_6\text{H}_5$ .

#### Acyl compounds $\text{Cp}_2\text{TiCOR}$

The reaction of  $\text{Cp}_2\text{Ti-}o\text{-CH}_3\text{C}_6\text{H}_4$  with CO in hexane proceeds according to equation 2. The formation of the acyl compound probably proceeds via initial



coordination of the CO molecule, i.e. via  $\text{Cp}_2\text{Ti}(\text{C}_6\text{F}_5)\text{CO}$ , but we could not isolate this adduct.

The green-brown compound I is very air-sensitive and well soluble in hexane, ether, and toluene. The elemental analyses are in accordance with I (see Table 1). The compound is monomeric in solution and contains one unpaired electron per titanium atom. The decomposition temperature is fairly high for a compound of type  $\text{Cp}_2\text{TiR}$  (Table 2); this is ascribed to the  $\eta^2$ -coordination of the acyl ligand at the titanium atom (see Fig. 5), derived from the physical and spectroscopic properties of I.

*Chemical properties.* Compound I does not react with  $\text{N}_2$  or CO in hexane. With HCl in ether and with  $\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5$ , I reacts according to eq. 3 and 4, respectively:

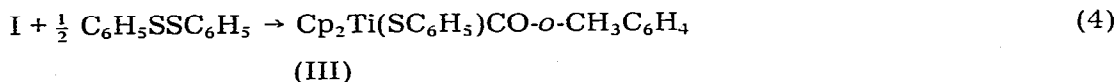


TABLE 2  
 $\text{Cp}_2\text{Ti-}\eta^2\text{-CO-}o\text{-CH}_3\text{C}_6\text{H}_4$  (I); SOME PHYSICAL PROPERTIES

Molecular weight <sup>a</sup> :	found 278, calcd. 297
Magnetic moment <sup>b</sup> :	$\mu_{\text{eff}} 1.85 \mu_{\beta}$
EPR <sup>c</sup> :	singlet, $g 1.975$
Decomposition temperature <sup>d</sup> :	$103^\circ\text{C}$

<sup>a</sup>Cryoscopy in benzene. <sup>b</sup>( $\mu_{\text{eff}}$ )<sub>calc.</sub>  $1.73 \mu_{\beta}$ . <sup>c</sup>In hexane. <sup>d</sup>by DTA.

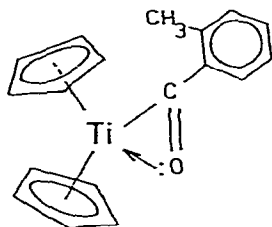


Fig. 5. Structure of  $\text{Cp}_2\text{Ti}-\eta^2\text{-CO}-o\text{-CH}_3\text{C}_6\text{H}_4$  (I).

**Spectroscopic properties.** The IR spectra of I (Fig. 4), II, and III (Fig. 4) show the characteristic absorptions of  $\eta^5\text{-C}_5\text{H}_5$  and the acyl groups. The  $\nu(\text{CO})$  band in II and III is observed at  $1570\text{--}1580\text{ cm}^{-1}$ , indicating  $\eta^2$ -coordination of the acyl ligand in these compounds [10]. In I we expect  $\nu(\text{CO})$  at even lower wavenumbers [11], and so we tentatively assign the low-intensity band at  $1470\text{ cm}^{-1}$  to this vibration.

The  $^{13}\text{C}$  NMR spectrum of III ( $\text{CDCl}_3/\text{TMS}$ ,  $-20^\circ\text{C}$ ) exhibits the resonance of the acyl carbon atom at 286.5 ppm, a rather low value but again in accordance with  $\eta^2$ -coordination of the acyl ligand [11,12].

The  $\eta^2$ -coordination of the acyl ligand as demonstrated, makes I a 17-electron species. This explains the inertness of I to two-electron donor molecules such as  $\text{N}_2$  and  $\text{CO}$ . Also the relatively high thermal stability of I can now be understood since the vacant, low-energy metal orbital involved in the thermal decomposition of compounds  $\text{Cp}_2\text{TiR}$  with  $\text{R} = \text{alkyl, aryl}$  [13], is now used for coordination of the acyl oxygen atom. However, a vacant metal orbital can again be created if the titanium oxygen bond is loosened e.g. by coordination of the acyl oxygen to another Lewis acid. Indeed, addition of an excess of  $\text{Me}_3\text{Al}$  (in hexane) to I under  $\text{CO}$  gives a rapid reaction in which about two moles of  $\text{CO}$  are absorbed. One of the reaction products is  $\text{Cp}_2\text{Ti}(\text{CO})_2$  (eq. 5).



Characterization of the organic products formed, for example  $o\text{-CH}_3\text{C}_6\text{H}_4\text{C}(=\text{O})\text{-}o\text{-CH}_3\text{C}_6\text{H}_4$  [14,15] was unsuccessful.

Attempts were made to reduce the acyl ligand of I by reaction with  $\text{H}_2$ , but neither I nor I in combination with excess  $\text{Me}_3\text{Al}$  showed any reaction.

The reaction of  $\text{Cp}_2\text{TiC}_6\text{H}_5$  with  $\text{CO}$  is more complicated than the reaction of  $\text{Cp}_2\text{Ti-}o\text{-CH}_3\text{C}_6\text{H}_4$ .  $\text{Cp}_2\text{TiC}_6\text{H}_5$  reacts very rapidly with  $\text{CO}$  at  $0^\circ\text{C}$  and about 2 mol of  $\text{CO}$  are consumed. After evaporating the solvents and reaction of the product with  $\text{HCl}$  in ether, several organic products are present e.g.  $\text{C}_6\text{H}_5\text{C}(=\text{O})\text{C}(=\text{O})\text{C}_6\text{H}_5$  (5–7%) (GLC–MS). These results indicate that in the reaction of  $\text{Cp}_2\text{TiC}_6\text{H}_5$  with  $\text{CO}$  insertion of  $\text{CO}$  into the  $\text{Ti-C}_6\text{H}_5$  bond again occurs. A detailed study of the reaction is in progress.

## Experimental

### General remarks

All experiments were performed in an inert atmosphere ( $\text{N}_2$  or  $\text{Ar}$ ). Com-

pounds  $\text{Cp}_2\text{TiR}$  were prepared as described previously [9], CO was purchased from Matheson. Elemental analyses were performed at the Microanalytical Department of this University under supervision of Mr. A.F. Hamminga.  $^{13}\text{C}$  NMR spectra were recorded on a Varian XL-100 spectrometry by Drs. O. Piepers of the Organic Department of this University. IR spectra of Nujol mulls were recorded on a JASCO-IRA-2 spectrophotometer. EPR spectra were recorded on a Varian E4x-band EPR spectrophotometer. GLC analyses were carried out using a Packard 428 or a Hewlett-Packard 7620 chromatograph.

### CO adducts

#### *Preparation of $\text{Cp}_2\text{Ti}(\text{C}_6\text{F}_5)\text{CO}$*

A solution of 545 mg (1.6 mmol) of  $\text{Cp}_2\text{TiC}_6\text{F}_5$  in 20 ml of toluene was connected to a gas burette filled with CO. The take-up of CO started immediately and stopped after 35.6 ml (1.5 mmol). Upon slowly cooling to  $-30^\circ\text{C}$  the adduct crystallized as green-brown needles. The crystals were isolated, washed with pentane, dried in vacuo ( $-10^\circ\text{C}$ ) and sealed in ampoules. Yield 340 mg (0.9 mmol, 60%).

#### *Reaction of $(\text{C}_5\text{Me}_5)_2\text{TiCl}$ with CO*

*Preparation of  $(\text{C}_5\text{Me}_5)_2\text{TiCl}$ .* 1.93 g (5.07 mmol) of  $\text{TiCl}_3 \cdot 3 \text{ THF}$  was refluxed with 1.48 g (10.4 mmol) of  $\text{C}_5\text{Me}_5\text{Li}$  [16] during 24 h. Subsequently, THF was evaporated and  $(\text{C}_5\text{Me}_5)_2\text{TiCl}$  was obtained from the residue by sublimation ( $140^\circ\text{C}/0.01 \text{ mmHg}$ ). Yield 0.92 g (50%). Analysis: Found: Cl, 10.06; Ti, 13.62.  $\text{C}_{20}\text{H}_{30}\text{ClTi}$  calcd.: Cl, 10.02; Ti, 13.54%. IR: 2900s, 1485m, 1455m, 1375s, 1020m, 435s  $\text{cm}^{-1}$  (sublimed on KBr discs). EPR:  $g = 1.956$  (in toluene). Magn. mom.:  $\mu_{\text{eff}} = 1.72 \mu_{\beta}$ . Mol. weight: 360 (calcd.: 353.5).

*Reaction with CO.* To a solution of  $(\text{C}_5\text{Me}_5)_2\text{TiCl}$  in hexane, CO was added at room temperature. After 5 min the solution was filtered and cooled to  $-78^\circ\text{C}$ . The IR spectrum of the brown precipitate showed, in addition to CO absorptions of  $(\text{C}_5\text{Me}_5)_2\text{Ti}(\text{CO})_2$ , an  $\nu(\text{CO})$  band at  $2000 \text{ cm}^{-1}$ . Additional stirring of the mixture under CO resulted in a precipitate of  $(\text{C}_5\text{Me}_5)_2\text{TiCl}_2$  and a yellow-brown solution, which on cooling gave  $(\text{C}_5\text{Me}_5)_2\text{Ti}(\text{CO})_2$ . The products were obtained in nearly equimolar amounts.

#### *Preparation of $\text{Cp}_2\text{Ti-}\eta^2\text{CO-o-CH}_3\text{C}_6\text{H}_4$ (I)*

To a solution of 400 mg (1.5 mmol) of  $\text{Cp}_2\text{Ti-o-CH}_3\text{C}_6\text{H}_4$  in 25 ml of hexane, CO was added at  $0^\circ\text{C}$ . The amount of CO absorbed was 32.0 ml (1.3 mmol). After stirring for one additional hour, during which no more CO was absorbed, the mixture was warmed to room temperature and filtered. Upon cooling the solution to  $-90^\circ\text{C}$ , I separated as brown-green crystals. After decanting off the mother liquor the product was washed with hexane at  $-40^\circ\text{C}$ , dried in vacuo at  $0^\circ\text{C}$ , and stored in ampoules. Yield 320 mg (1.3 mmol, 70%).

#### *Reaction with HCl in diethyl ether*

To a suspension of 0.76 g (2.5 mmol) of I in 5 ml of diethyl ether an excess of HCl in diethyl ether was added at  $-78^\circ\text{C}$ . The mixture rapidly turned red-pink and  $\text{H}_2$  was evolved (GLC). After warming to room temperature and addi-

tional stirring for 4 h, the volatiles were condensed at  $-196^{\circ}\text{C}$ . After washing with n-pentane the residue was isolated. Yield 0.70 g of yellow-pink material consisting of  $\text{Cp}_2\text{Ti}(\text{Cl})\text{-}\eta^2\text{-CO-o-CH}_3\text{C}_6\text{H}_4$  (II) (40%) and  $\text{Cp}_2\text{TiCl}_2$  (60%).  $\text{Cp}_2\text{TiCl}_2$  was removed from the product by washing with acetone.

*Preparation of  $\text{Cp}_2\text{Ti}(\text{SC}_6\text{H}_5)\text{-}\eta^2\text{-CO-o-CH}_3\text{C}_6\text{H}_4$  (III)*

To a solution of 400 mg (1.3 mmol) of I in 20 ml of toluene, 140 mg (0.65 mmol) of  $\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5$  was added slowly at  $0^{\circ}\text{C}$ . The resulting red solution was cooled to  $-90^{\circ}\text{C}$ ; III crystallized as orange needles. After decanting the mother liquor and washing with pentane, the compound was dried in vacuo and isolated in ampoules. Yield 210 mg (0.5 mmol, 40%).

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