

## PREPARATION, CHARACTERIZATION AND REACTIVITY OF $\text{Cp}_2\text{M}(\text{PMe}_3)_2$ COMPLEXES (M = Ti, Zr): THE MOLECULAR STRUCTURE OF $\text{Cp}_2\text{Zr}(\text{PMe}_3)_2$

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### Summary

The reduction of  $\text{Cp}_2\text{MCl}_2$  (M = Ti, Zr) with magnesium in THF in the presence of  $\text{PMe}_3$  affords the complexes  $\text{Cp}_2\text{M}(\text{PMe}_3)_2$  in high yields. These compounds lose one or both  $\text{PMe}_3$  ligands under very mild conditions.  $\text{Cp}_2\text{Ti}(\text{PMe}_3)_2$  reacts readily with  $\text{CH}_3\text{I}$ ,  $\text{CH}_3\text{C}(\text{O})\text{Cl}$ ,  $\text{PhSSPh}$ ,  $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ ,  $\text{CO}$ ,  $\text{RCN}$  (R = Me, t-Bu) or  $(\text{RN})_2\text{S}$  (R = t-Bu,  $\text{Me}_3\text{Si}$ ) to give the corresponding titanocene products. The structure of  $\text{Cp}_2\text{Zr}(\text{PMe}_3)_2$  has been determined by X-ray diffraction; the structural parameters are similar to those of the titanium analog  $\text{Cp}_2\text{Ti}(\text{PMe}_3)_2$  except that the Zr-P and Zr-C distances are longer.

### Introduction

Monomeric Group 4 metallocenes are unstable, although a large number of derivatives are known [1,2]. Several routes to these compounds have been developed, the best-known being reactions of the respective metallocene dicarbonyls [3]. Other methods include the reduction of metallocene dichlorides in the presence of potential ligands [4,5], reaction of the polymeric hydride  $[\text{Cp}_2\text{TiH}]_x$  with  $\text{H}_2$  [6], and the photo-induced dealkylation or dearylation of metallocene dialkyls and diaryls [7-9]. However, all these methods require rather drastic chemical, thermal, or photochemical conditions, and their scope and selectivity are therefore limited.

The above limitations have been overcome by the use of the Group 4 metallocene bis(trimethylphosphine) complexes  $\text{Cp}_2\text{Ti}(\text{PMe}_3)_2$  (**1**) and  $\text{Cp}_2\text{Zr}(\text{PMe}_3)_2$  (**2**) as readily available sources for the corresponding metallocenes [10,11]. In this paper,

we present details concerning the preparation, characterization and reactivity of these complexes, as well as results of an X-ray structural investigation of the zirconium compound **2**.

## Results and discussion

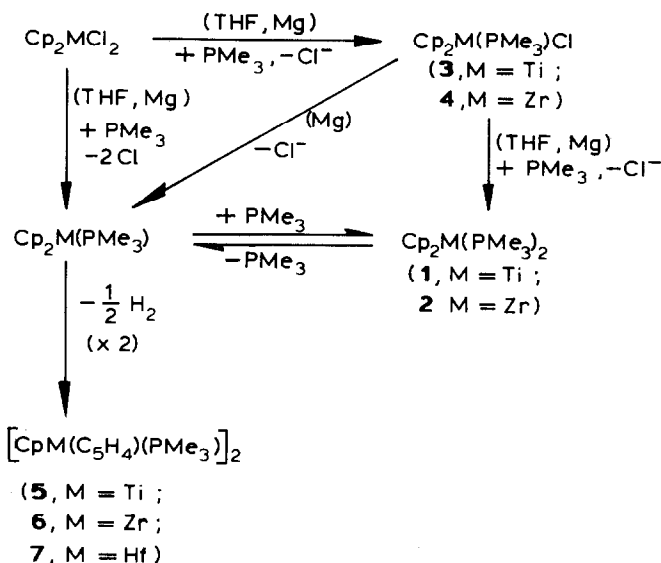
### Preparation

Reduction of  $\text{Cp}_2\text{TiCl}_2$  and  $\text{Cp}_2\text{ZrCl}_2$  by magnesium in THF solution in the presence of excess  $\text{PMe}_3$  affords **1** and **2** in yields of 100 and 55%, respectively (Scheme 1).

The mixed chloro-trimethylphosphine complexes  $\text{Cp}_2\text{M}(\text{PMe}_3)\text{Cl}$  (**3**,  $\text{M} = \text{Ti}$ ; **4**,  $\text{M} = \text{Zr}$ ) have been postulated as intermediates in these reductions, and **3** has been isolated and fully characterized [12]. In the synthesis of **2**, a binuclear compound (**6**) containing bridging  $\eta^1 : \eta^5\text{-C}_5\text{H}_4$  ligands is also isolated in relatively high yield (45%), even when an excess of  $\text{PMe}_3$  is present. This product, and its titanium (**5**) and hafnium (**7**) analogs are directly obtained in high yields from reductions of the respective metallocene dichlorides in the presence of only one equivalent of  $\text{PMe}_3$  [13]. The tendency to form binuclear complexes in reductive phosphinations thus increases on going down the series, and is dominant in the reaction of  $\text{Cp}_2\text{HfCl}_2$ , which leads almost exclusively to **7** rather than to the monomeric product  $\text{Cp}_2\text{Hf}(\text{PMe}_3)_2$ .

### Characterization

Compounds **1** and **2** have been fully characterized by elemental analysis, mass spectrometry, and by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectrometry. Thus, the  $^1\text{H}$  NMR spectrum of **1** in toluene- $d_8$  solution at  $-20^\circ\text{C}$  exhibits a triplet ( $J(\text{P-H})$  2.2 Hz) at



SCHEME 1

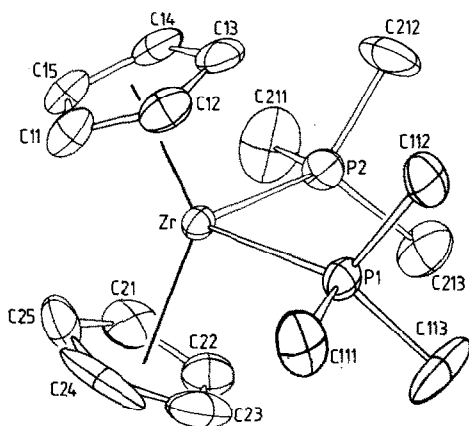


Fig. 1. Molecular structure of **2**.

$\delta$  4.5 for the Cp protons and a virtual triplet ( $J(\text{P-H})$  2.0 Hz) at  $\delta$  0.83 for the  $\text{PMe}_3$  protons. Upon warming the solution to 20°C, two new signals assigned to the 16-electron complex  $\text{Cp}_2\text{Ti}(\text{PMe}_3)$  emerge at  $\delta$  5.18 (d,  $J(\text{P-H})$  2.0 Hz) for the Cp protons and at  $\delta$  1.34 ( $J(\text{P-H})$  2.0 Hz) for the  $\text{PMe}_3$  protons. A resonance for free  $\text{PMe}_3$  is also observed at  $\delta$  0.79. Addition of excess  $\text{PMe}_3$  causes the two signals corresponding to  $\text{Cp}_2\text{Ti}(\text{PMe}_3)$  to disappear, demonstrating that there is an equilibrium between this species and **1**. Similar observations are made in the  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra of **1**. Phosphine dissociation from these complexes must therefore be very facile in solution, and probably accounts for their high reactivities toward other ligands.

The  $^1\text{H}$  NMR spectrum of **2** is analogous to that of **1**, except that at room temperature no resonance can be attributed to a 16-electron species [ $\text{Cp}_2\text{Zr}(\text{PMe}_3)$ ]. Instead, signals arise for the dinuclear species **6** [13].

The structure of **2** has been confirmed by an X-ray diffraction study, and the molecular structure is shown in Fig. 1. Bond distances and angles are given in Table 1.

The molecule **2** possesses a pseudotetrahedral coordination sphere that is typical for  $\text{Cp}_2\text{MXY}$  complexes ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ ;  $\text{X}, \text{Y} =$  neutral or uninegative ligand). This structure is analogous to the known structure of **1** [10], except that the  $\text{Zr-P}$  and  $\text{Zr-Z}$  distances ( $\text{Z} =$  centroid of the 5-membered ring) are respectively ca. 0.11 and 0.12 Å longer:

M =	$d(\text{M-P})$ (Å)	$d(\text{M-Z})$ (Å)	$\angle(\text{Z-M-Z})$ (°)	$\angle(\text{P-M-P})$ (°)
Ti ( <b>1</b> ) [10]	2.53	2.06	133.8	92.2
Zr ( <b>2</b> )	2.64	2.18	136.6	93.9

The Cp rings are planar (deviations of all C atoms  $< 0.01$  Å from the best plane), and are symmetrically positioned over the Zr atom. The normal angle of 134.4° is only slightly different from the angle  $\text{Z-Zr-Z}$  (136.6°).

### Reactivity

The most intriguing feature of compounds **1** and **2** is the facile loss of either one

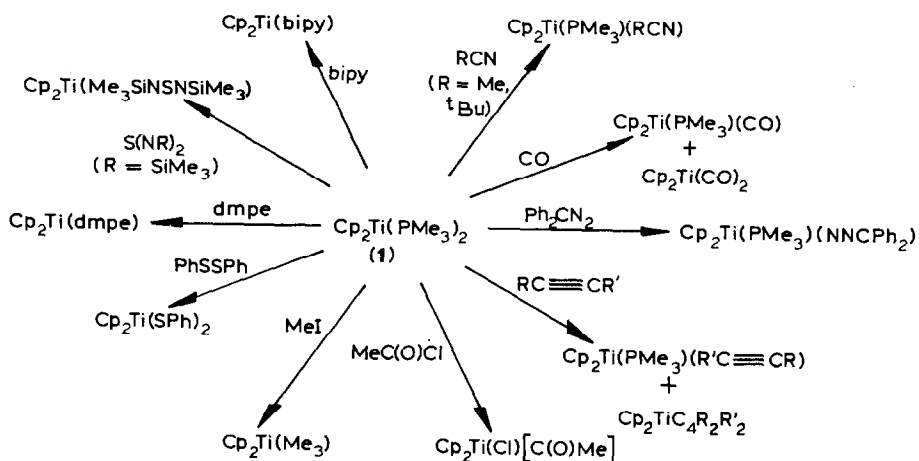
TABLE 1  
 BOND DISTANCES (Å) AND ANGLES (°) IN Cp<sub>2</sub>Zr(PMe<sub>3</sub>)<sub>2</sub> (**2**)<sup>a</sup>

Zr–P(1)	2.650(2)	P(1)–Zr–P(2)	93.9(1)
Zr–P(2)	2.638(2)	Z(1)–Zr–Z(2)	136.6(4)
		Z(1)–Zr–P(1)	104.8(2)
P(1)–C(111)	1.874(10)	Z(1)–Zr–P(2)	106.6(2)
P(1)–C(112)	1.844(9)	Z(2)–Zr–P(1)	104.1(4)
P(1)–C(113)	1.836(8)	Z(2)–Zr–P(2)	103.0(3)
P(2)–C(211)	1.877(12)	C(111)–P(1)–C(112)	98.0(4)
P(2)–C(212)	1.839(10)	C(112)–P(1)–C(113)	99.4(5)
P(2)–C(213)	1.870(10)	C(111)–P(1)–C(113)	99.2(5)
Zr–C(11)	2.500(8)	Zr–P(1)–C(111)	116.8(3)
Zr–C(12)	2.481(8)	Zr–P(1)–C(112)	118.2(3)
Zr–C(13)	2.466(9)	Zr–P(1)–C(113)	121.0(3)
Zr–C(14)	2.473(9)		
Zr–C(15)	2.498(7)	C(211)–P(2)–C(212)	98.7(6)
		C(212)–P(2)–C(213)	99.1(5)
Zr–C(21)	2.466(9)	C(211)–P(2)–C(213)	99.2(5)
Zr–C(22)	2.528(12)	Zr–P(2)–C(211)	116.6(4)
Zr–C(23)	2.531(14)	Zr–P(2)–C(212)	118.0(4)
Zr–C(24)	2.473(10)	Zr–P(2)–C(213)	121.1(4)
Zr–C(25)	2.445(12)		
Zr–Z(1)	2.172(8)		
Zr–Z(2)	2.192(12)		
C(11)–C(12)	1.399(11)		
C(12)–C(13)	1.411(13)		
C(13)–C(14)	1.458(12)		
C(14)–C(15)	1.410(12)		
C(15)–C(11)	1.406(13)		
C(21)–C(22)	1.330(17)		
C(22)–C(23)	1.307(18)		
C(23)–C(24)	1.459(23)		
C(24)–C(25)	1.472(22)		
C(25)–C(21)	1.361(15)		

<sup>a</sup> Z(1), Z(2): centres of C(11) and C(21) containing Cp rings.

or both PMe<sub>3</sub> ligands under very mild conditions in the presence of reactive substrates. A selection of reactions of **1** is shown in Scheme 2.

Compound **1** reacts readily with carbon monoxide initially to form Cp<sub>2</sub>Ti(PMe<sub>3</sub>)(CO) [12,14] and subsequently Cp<sub>2</sub>Ti(CO)<sub>2</sub> [15,16]. A reaction between **1** and diphenyldiazomethane leads to loss of one PMe<sub>3</sub> ligand and formation of a product containing a monodentate diazoalkane ligand end-on coordinated through nitrogen [17]. With C<sub>2</sub>H<sub>2</sub> the acetylene complex Cp<sub>2</sub>Ti(PMe<sub>3</sub>)(C<sub>2</sub>H<sub>2</sub>), the titanacyclopentadiene Cp<sub>2</sub>TiC<sub>4</sub>H<sub>4</sub>, and *trans*-polyacetylene are formed. Substituted acetylenes yield the analogous complexes, although no polyacetylenes are produced [18]. The oxidative addition product Cp<sub>2</sub>Ti(Cl)[C(O)CH<sub>3</sub>] [19] is obtained when **1** is treated with acetyl chloride. An analogous reaction is observed between **1** and iodomethane, forming Cp<sub>2</sub>Ti(Me)I [20]. In the reaction of diphenyl disulfide and **1**, the sulfur–sulfur bond is cleaved to give Cp<sub>2</sub>Ti(SPh)<sub>2</sub> [21]. Both PMe<sub>3</sub> ligands of **1** are displaced



SCHEME 2

readily by the chelating ligand 1,2-bis(dimethylphosphino)ethane (dmpe) to afford  $\text{Cp}_2\text{Ti}(\text{dmpe})$  [22].

Bis(trimethylsilyl) sulfur diimide,  $\text{S}(\text{NSiMe}_3)_2$ , reacts with 1 to give  $\text{Cp}_2\text{Ti}(\text{Me}_3\text{SiNSNSiMe}_3)$ . A reaction between 1 and 2,2'-bipyridine (bipy) affords the known substitution product  $\text{Cp}_2\text{Ti}(\text{bipy})$  [23,24]. Compound 1 reacts with nitriles to give mono- or disubstitution products; thus, reactions with one equivalent of either acetonitrile or pivalonitrile give the complexes  $\text{Cp}_2\text{Ti}(\text{PMe}_3)(\text{NCR})$  ( $\text{R} = \text{Me, t-Bu}$ ), whereas phthalodinitrile yields  $\text{Cp}_2\text{Ti}[(\text{NC})_2\text{C}_6\text{H}_4]$ .

## Experimental

**General data.** All operations were performed under argon by use of Schlenk techniques. Pentane, toluene and THF were dried over Na/K alloy and freshly distilled before use.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at 90 and 22.5 MHz on a Fourier transform JEOL FX 90 Q spectrometer and are reported in  $\delta$  values downfield from  $\text{SiMe}_4$ . The residual methyl proton resonance of toluene occurring at 2.09 ppm was used as internal standard in the  $^1\text{H}$  spectra, and the internal standard for  $^{13}\text{C}$  spectra was the methyl resonance of toluene at 20.4 ppm.

IR spectra were obtained in KBr using a Perkin-Elmer 297 spectrometer. Electron-impact mass spectra were recorded on a Varian CH7 mass spectrometer at 70 eV; the data are based on the isotopes  $^{48}\text{Ti}$  and  $^{90}\text{Zr}$ , respectively. Elemental analyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts.

### Synthesis of bis( $\eta^5$ -cyclopentadienyl)bis(trimethylphosphine)zirconium (2)

A mixture of  $\text{Cp}_2\text{ZrCl}_2$  (5.0 g, 17 mmol), magnesium turnings (2.1 g, 86.4 mmol), THF (ca. 200 ml) and  $\text{PMe}_3$  (8.0 ml, 84 mmol) was stirred at room temperature in a water bath. The mixture darkened immediately, becoming yellow-green in 1 min. After 5 min it was deep amber, and in 30 min deep red. After 20 h the solvent was

removed in vacuo from the deep red solution. The residue was extracted with pentane, the pentane solution was filtered and the solution was concentrated in vacuo. A pentane-insoluble red powder was removed in this filtration and identified by  $^1\text{H}$  NMR to be identical to the  $\eta^1 : \eta^5\text{-C}_5\text{H}_4$ -bridged dimer **6** [13]. After storage of the pentane solution at  $-20^\circ\text{C}$ ,  $\text{Cp}_2\text{Zr}(\text{PMe}_3)_2$  was obtained as red-brown crystals (3.47 g, 55% yield).  $^1\text{H}$  NMR (toluene- $d_8$ ,  $-20^\circ\text{C}$ , ppm) 4.75 (t, 10H, Cp,  $^3J(\text{P,H})$  2.0 Hz), 0.96 (vt, 18H,  $\text{PMe}_3$ ,  $^2J(\text{P,H})$  4.9 Hz).  $^{13}\text{C}$  NMR (toluene- $d_8$ ,  $-20^\circ\text{C}$ , ppm) 89.8 (Cp), 25.2 (m,  $\text{PMe}_3$ ).  $^{31}\text{P}$  NMR (toluene- $d_8$ ,  $-20^\circ\text{C}$ , ppm) 24.0. Mass spectrum  $m/e$  372 ( $M^+$ ), 296 ( $M^+ - \text{PMe}_3$ ), 220 ( $\text{Cp}_2\text{Zr}^+$ ), 76 ( $\text{PMe}_3^+$ ), 61 ( $\text{PMe}_2^+$ ). Anal. Found: C, 50.94; H, 7.22.  $\text{C}_{16}\text{H}_{28}\text{P}_2\text{Zr}$  calc: C, 51.44; H, 7.56%.

*Synthesis of bis( $\eta^5$ -cyclopentadienyl)bis(trimethylphosphine)titanium (I)*

A procedure analogous to that given above for **2** was followed [10].  $^1\text{H}$  NMR (toluene- $d_8$ ,  $-20^\circ\text{C}$ , ppm) 4.51 (t, 10H, Cp,  $^3J(\text{P,H})$  2.2 Hz), 0.83 (vt, 18H,  $\text{PMe}_3$ ,  $^2J(\text{P,H})$  2.0 Hz).  $^{13}\text{C}$  NMR (toluene- $d_8$ ,  $-20^\circ\text{C}$ , ppm) 91.2 (Cp), 23.6 (br, m,  $\text{PMe}_3$ ).  $^{31}\text{P}$  NMR (toluene- $d_8$ ,  $-20^\circ\text{C}$ ) 45.2 (br). Mass spectrum  $m/e$  330 ( $M^+$ ), 253 ( $M^+ - \text{PMe}_3\text{H}$ ), 178 ( $\text{Cp}_2\text{Ti}^+$ ), 113 ( $\text{CpTi}^+$ ), 76 ( $\text{PMe}_3^+$ ), 61 ( $\text{PMe}_2^+$ ). Anal. Found: C, 57.91; H, 8.53.  $\text{C}_{16}\text{H}_{28}\text{P}_2\text{Ti}$  calc: C, 58.19; H, 8.55%.

*Reaction of bis( $\eta^5$ -cyclopentadienyl)bis(trimethylphosphine)titanium with 2,2'-bipyridine*

$\text{Cp}_2\text{Ti}(\text{PMe}_3)_2$  (510 mg, 1.54 mmol) was dissolved in 40 ml of pentane and the solution was cooled to  $-78^\circ\text{C}$ , 2,2'-bipyridine (241 mg, 1.54 mmol) was added and the solution was allowed to slowly warm to room temperature. The mixture gradually became green-black as it warmed. The solvent was removed in vacuo. The residue was extracted with pentane, filtered and the solution concentrated in vacuo. Storage at  $-20^\circ\text{C}$  resulted in the formation of green-black needles (510 mg, 99%). Mass spectrum  $m/e$  334 ( $M^+$ , 74%), 269 ( $M^+ - \text{Cp}$ , 10%), 178 ( $\text{Cp}_2\text{Ti}^+$ , 100%), 156 (bipyridine $^+$ ). Anal. Found: C, 71.55; H, 5.41; N, 7.78.  $\text{C}_{20}\text{H}_{18}\text{N}_2\text{Ti}$  calc: C, 71.86; H, 5.43; N, 8.38%.

*Reaction of bis( $\eta^5$ -cyclopentadienyl)bis(trimethylphosphine)titanium with phthalodinitrile*

$\text{Cp}_2\text{Ti}(\text{PMe}_3)_2$  (520 mg, 1.57 mmol) in 50 ml THF was cooled to  $-78^\circ\text{C}$  and phthalodinitrile (98%, 205 mg, 1.57 mmol) was added. The solution turned black upon addition. It was allowed to warm to room temperature and thereby gradually turned deep violet. After 1 h the solvent was removed in vacuo, depositing a black-violet crystalline solid which was washed with pentane and dried. It was then extracted with methylene chloride, filtered, concentrated in vacuo and cooled at  $-78^\circ\text{C}$ . No crystallization occurred, so the solvent was removed and a mass spectrum was obtained:  $\text{C}_{18}\text{H}_{14}\text{N}_2\text{Ti}$   $m/e$  301 ( $M^+ - 5\text{H}$ ), 290 ( $M^+ - \text{NH}_2$ ), 194 ( $M^+ - \text{C}_5\text{H}_4\text{Ti}$ ), 128 ( $\text{C}_8\text{H}_4\text{N}_2^+$ ). IR (KBr)  $\nu(\text{CN})$  2237  $\text{cm}^{-1}$ .

*Reaction of bis( $\eta^5$ -cyclopentadienyl)bis(trimethylphosphine)titanium with pivalonitrile*

A solution of  $\text{Cp}_2\text{Ti}(\text{PMe}_3)_2$  (410 mg, 1.24 mmol) in 75 ml THF was cooled to  $-78^\circ\text{C}$  and pivalonitrile (0.14 ml, 1.3 mmol) was added dropwise. Upon slow warming to room temperature the solution became black. The solvent was removed in vacuo and the residue was washed with pentane, yielding 400 mg of crude

product. The product was redissolved in toluene, filtered, and the filtrate was concentrated and cooled. Repeated attempts of crystallization failed. Mass spectrum  $m/e$  261 ( $M^+ - \text{PMe}_3$ ), 178 ( $\text{Cp}_2\text{Ti}^+$ ), 113 ( $\text{CpTi}^+$ ).  $^1\text{H}$  NMR (toluene- $d_8$ ,  $30^\circ\text{C}$ , ppm) 5.41 (broad d, 10H, Cp), 0.90 (br,  $\text{PMe}_3$ ), 0.77 (s, 9H t-butyl).

*Reaction of bis( $\eta^5$ -cyclopentadienyl)bis(trimethylphosphine)titanium with acetonitrile*

$\text{Cp}_2\text{Ti}(\text{PMe}_3)_2$  (390 mg, 1.18 mmol) was dissolved in ca. 20 ml pentane and cooled to  $-78^\circ\text{C}$ . Acetonitrile (0.06 ml, 1 mmol) was added and the stirred solution was allowed to warm slowly to room temperature. On warming, a chocolate-brown precipitate gradually formed. After 4 h the solvent was removed in vacuo, yielding 340 mg (98%) of  $\text{Cp}_2\text{Ti}(\text{PMe}_3)(\text{CH}_3\text{CN})$ .  $^1\text{H}$  NMR (toluene- $d_8$ ,  $-20^\circ\text{C}$ , ppm) 4.82 (br, 10H, Cp), 2.43 (br, 3H, MeCN), 0.81 (br,  $\text{PMe}_3$ ).

*Reaction of bis( $\eta^5$ -cyclopentadienyl)bis(trimethylphosphine)titanium with carbon monoxide*

A solution of  $\text{Cp}_2\text{Ti}(\text{PMe}_3)_2$  (100 mg, 0.3 mmol) in 10 ml pentane was treated with CO, which was admitted as a gentle stream via a pipet. After 5 min an IR spectrum of the solution exhibited  $\nu(\text{CO})$  absorptions indicating a ca. 50/50 mixture of  $\text{Cp}_2\text{Ti}(\text{PMe}_3)(\text{CO})$  and  $\text{Cp}_2\text{Ti}(\text{CO})_2$ . After 10 min, conversion to the dicarbonyl [16] was complete.

*Reaction of bis( $\eta^5$ -cyclopentadienyl)bis(trimethylphosphine)zirconium with carbon monoxide*

A sample of  $\text{Cp}_2\text{Zr}(\text{PMe}_3)_2$  (20 mg, 54  $\mu\text{mol}$ ) in 20 ml pentane was stirred under an atmosphere of CO for 0.5 h. An IR spectrum of this pentane solution indicated the formation of a mixture of  $\text{Cp}_2\text{Zr}(\text{PMe}_3)(\text{CO})$  and  $\text{Cp}_2\text{Zr}(\text{CO})_2$ . After an additional 0.5 h treatment with CO, the amber solution was passed through a plug of 5% deactivated alumina and the solvent removed.  $\text{Cp}_2\text{Zr}(\text{CO})_2$  [16] was obtained as black needles (14 mg, 94%).

*Reaction of bis( $\eta^5$ -cyclopentadienyl)bis(trimethylphosphine)titanium with bis(trimethylsilyl) sulfur diimide*

Bis(trimethylsilyl) sulfur diimide (0.54 ml, 2.3 mmol) was added dropwise via pipet to a solution of  $\text{Cp}_2\text{Ti}(\text{PMe}_3)_2$  (690 mg, 2.09 mmol) in 30 ml of pentane at  $20^\circ\text{C}$ . The solution immediately turned violet. After 4.5 h the solvent was removed in vacuo, depositing a violet crystalline solid (0.86 mg, 97%). A  $^1\text{H}$  NMR spectrum indicated the formation of  $\text{Cp}_2\text{Ti}(\text{Me}_3\text{SiNSNSiMe}_3)$ .  $^1\text{H}$  NMR (benzene- $d_6$ ,  $30^\circ\text{C}$ , ppm) 5.03 (s, 10H, Cp),  $-0.33$  (s, 18H,  $\text{SiMe}_3$ ). Repeated attempts at crystallization were unsuccessful.

*Reaction of bis( $\eta^5$ -cyclopentadienyl)bis(trimethylphosphine)titanium with bis(dimethylphosphino)ethane (dmpe)*

A solution of  $\text{Cp}_2\text{Ti}(\text{PMe}_3)_2$  (320 mg, 0.97 mmol) in 50 ml pentane was treated with dmpe (0.18 ml, 0.98 mmol) at room temperature. The solution was stirred for 3 h, during which time a crystalline brown solid was deposited. The solvent was then removed in vacuo and the residue was extracted with toluene. After filtration, concentration and addition of a layer of pentane, the mixture was stored at  $-20^\circ\text{C}$ . The supernatant solution was later decanted from orange-brown crystals of

$\text{Cp}_2\text{Ti}(\text{dmpe})$  (222 mg, 70%). The  $^1\text{H}$  NMR spectrum was identical to that reported in the literature [22] ( $^1J(\text{P},\text{C})$  18 Hz,  $\text{PMe}_3$ ).

*Reaction of bis( $\eta^5$ -cyclopentadienyl)bis(trimethylphosphine)titanium with iodomethane*

Iodomethane (0.033 ml, 0.53 mmol) was added dropwise to a solution of  $\text{Cp}_2\text{Ti}(\text{PMe}_3)_2$  (176 mg, 0.533 mmol) in ca. 15 ml pentane at room temperature. A beige-green, flocculent solid precipitated instantly. After 30 min the solvent was removed in vacuo, yielding 168 mg (99%) of  $\text{Cp}_2\text{Ti}(\text{CH}_3)(\text{I})$  [20].

*Reaction of bis( $\eta^5$ -cyclopentadienyl)bis(trimethylphosphine)titanium with acetyl chloride*

A solution of  $\text{Cp}_2\text{Ti}(\text{PMe}_3)_2$  [151 mg, 0.46 mmol] in 10 ml toluene was treated with acetyl chloride (0.16 ml, 2.3 mmol) at room temperature. A precipitate formed immediately. After 1 h the solvent was removed in vacuo, yielding  $\text{Cp}_2\text{Ti}[\text{C}(\text{O})\text{Me}](\text{Cl})$  (118 mg, 100%) as an orange solid [19].

*Reaction of bis( $\eta^5$ -cyclopentadienyl)bis(trimethylphosphine)titanium with diphenyldisulfide*

Diphenyldisulfide (67 mg, 0.30 mmol) was added to a solution of  $\text{Cp}_2\text{Ti}(\text{PMe}_3)_2$ , (99 mg, 0.30 mmol) in 10 ml toluene in a Schlenk tube. The solution immediately turned purple. After 0.5 h, the solvent was removed in vacuo to leave  $\text{Cp}_2\text{Ti}(\text{SPh})_2$  (118 mg, 99%) [21].

*X-Ray structure*

Crystal data:  $\text{C}_{16}\text{H}_{28}\text{P}_2\text{Zr}$ ,  $M = 373.56$ ,  $P2_1/c$ ,  $a$  14.518(4),  $b$  8.544(2),  $c$  15.184(3) Å,  $\beta$  97.62(3)°;  $D_{\text{calc}}$  1.329 g cm $^{-3}$  for  $Z = 4$ . X-ray data were taken at 20°C with a Philips PW1100-single crystal diffractometer (graphite monochroma-

TABLE 2  
ATOMIC COORDINATES FOR  $\text{Cp}_2\text{Zr}(\text{PMe}_3)_2$  (2)

Atom	$x$	$y$	$z$	$U_{\text{eq}}$
Zr	0.2908(1)	0.4066(1)	0.1921(1)	0.037(1)
P(1)	0.2891(1)	0.5892(2)	0.0509(1)	0.050(1)
C(111)	0.3952(6)	0.7114(12)	0.0445(6)	0.097(11)
C(112)	0.2019(6)	0.7472(9)	0.0344(5)	0.080(9)
C(113)	0.2745(10)	0.5067(11)	-0.0618(4)	0.115(16)
P(2)	0.1299(1)	0.2747(2)	0.1341(1)	0.058(1)
C(211)	0.0974(8)	0.09784(13)	0.1962(8)	0.131(16)
C(212)	0.0236(6)	0.2904(14)	0.1377(8)	0.122(15)
C(11)	0.3476(6)	0.5774(9)	0.3217(4)	0.069(8)
C(12)	0.2939(6)	0.6716(9)	0.2593(5)	0.068(8)
C(13)	0.2010(6)	0.6187(9)	0.2506(4)	0.069(9)
C(14)	0.1978(6)	0.4853(11)	0.3099(4)	0.072(9)
C(15)	0.2891(6)	0.4651(10)	0.3531(4)	0.068(9)
C(21)	0.3465(8)	0.1337(9)	0.2040(7)	0.088(12)
C(22)	0.3424(8)	0.1633(13)	0.1176(7)	0.094(12)
C(23)	0.4018(9)	0.2713(14)	0.1017(8)	0.100(14)
C(24)	0.4529(6)	0.3225(12)	0.1860(15)	0.143(24)
C(25)	0.4132(8)	0.2236(15)	0.2509(6)	0.098(12)



tor, Mo- $K_{\alpha}$ -irradiation,  $\lambda$  0.71069 Å, crystal dimensions: 0.5, 0.3, 0.3 mm);  $\theta/2\theta$ -operation;  $\theta(\max)$  25°; Lp correction. No absorption correction ( $\mu$  6.6 cm<sup>-1</sup>); 2757 reflections of a total of 3282 independent reflections with  $|F_0| \geq 2\sigma(F_0)$  were used for the subsequent calculations. Structure determination by means of heavy-atom method. The non-hydrogen atoms were refined with anisotropic temperature factors. Most of the H atoms could be located in a  $\Delta F$  syntheses. The H atoms were ignored in the calculations. Final values for  $R$  and  $R_w(F)$ : 0.064 and 0.065; maximum residual electron density in a final  $\Delta F$  synthesis: 0.56 e/Å<sup>3</sup>. The SHELX-76 system of programs was used [25]. The complex form factors for neutral atoms were taken from refs. [26 and 27]. Atomic coordinates are listed in Table 2; the  $U_{eq}$  values were calculated by means of the formula  $U_{eq} = 1/3 \sum_{ij} a_i^* b_j^* a_i \cdot a_j$  from the  $U_{ij}$  values. Further details of the crystal structure determination can be requested from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen, by giving the code number CSD 52011, the names of the authors of this paper, and the reference.

## References

- 1 G.P. Pez and J.N. Armor, *Adv. Organomet. Chem.*, 19 (1981) 1.
- 2 M. Bottrill, P.D. Gavens and J. McMeeking in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, Vol. 3, Pergamon Press, Oxford, 1982, p. 281.
- 3 D.T. Sikora, D.W. Macomber and M.D. Rausch, *Adv. Organomet. Chem.*, 25 (1986) 317.
- 4 G.W. Watt, L.S. Baye and F.O. Drummond, Jr., *J. Am. Chem. Soc.*, 88 (1966) 1138.
- 5 J.-J. Salzmänn and P. Mosimann, *Helv. Chim. Acta*, 50 (1967) 1831.
- 6 J.E. Bercaw, R.H. Marvich, L.G. Bell and H.H. Brintzinger, *J. Am. Chem. Soc.*, 94 (1972) 1219.
- 7 H. Alt and M.D. Rausch, *J. Am. Chem. Soc.*, 96 (1974) 5936.
- 8 M.D. Rausch, W.H. Boon and H.G. Alt, *J. Organomet. Chem.*, 141 (1977) 299.
- 9 M.D. Rausch, W.H. Boon and E.A. Mintz, *J. Organomet. Chem.*, 160 (1978) 81.
- 10 L.B. Kool, M.D. Rausch, H.G. Alt, M. Herberhold, U. Thewalt and B. Wolf, *Angew. Chem.*, 97 (1985) 425; *Angew. Chem. Int. Ed. Engl.*, 24 (1985) 394.
- 11 L.B. Kool, M.D. Rausch, H.G. Alt, M. Herberhold, Twelfth International Conference on Organometallic Chemistry, Vienna, Austria, Sept. 8–13, 1985; Abstract 185.
- 12 L.B. Kool, M.D. Rausch, H.G. Alt, M. Herberhold, B. Wolf and U. Thewalt, *J. Organomet. Chem.*, 297 (1986) 159.
- 13 L.B. Kool, M.D. Rausch, H.G. Alt, M. Herberhold, U. Thewalt and B. Honold, *J. Organomet. Chem.*, 310 (1986) 27.
- 14 B. Demerseman, G. Bouquet and M. Bigorgne, *J. Organomet. Chem.*, 93 (1975) 199; 132 (1977) 223.
- 15 J.G. Murray, *J. Am. Chem. Soc.*, 81 (1959) 752; 83 (1961) 1287.
- 16 D.J. Sikora, K.J. Moriarty and M.D. Rausch, *Inorg. Synth.*, 24 (1986) 147.
- 17 L.B. Kool, M.D. Rausch, H.G. Alt, M. Herberhold, A.F. Hill, U. Thewalt and B. Wolf, *J. Chem. Soc., Chem. Commun.*, (1986) 408.
- 18 H.G. Alt, H.E. Engelhardt, M.D. Rausch and L.B. Kool, *J. Am. Chem. Soc.*, 107 (1985) 3717; *idem*, *J. Organomet. Chem.*, in press.
- 19 G. Fachinetti, C. Floriani and H. Stoeckli-Evans, *J. Chem. Soc., Dalton Trans.*, (1977) 2297.
- 20 H.C. Beachell and S.A. Butter, *Inorg. Chem.*, 4 (1965) 1133.
- 21 G. Fachinetti and C. Floriani, *J. Chem. Soc., Dalton Trans.*, (1974) 2433.
- 22 G.S. Girolami, G. Wilkinson, M. Thornton-Pett and M.B. Hursthouse, *J. Chem. Soc. Dalton Trans.*, (1984) 2347.
- 23 E.O. Fischer and R. Amtmann, *J. Organomet. Chem.*, 9 (1967) P15.
- 24 F. Calderazzo, J.J. Salzmänn and P. Mosimann, *Inorg. Chim. Acta*, 1 (1967) 65.
- 25 G.M. Sheldrick, Göttingen, unpublished.
- 26 D.T. Cromer and J.B. Mann, *Acta Cryst.*, A24 (1968) 321.
- 27 D.T. Cromer and D. Liberman, *J. Chem. Phys.*, 53 (1970) 1891.