

## TITANOCENE AND ZIRCONOCENE DICHLORIDE DERIVATIVES WITH HYDROXYLIC REAGENTS

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### Summary

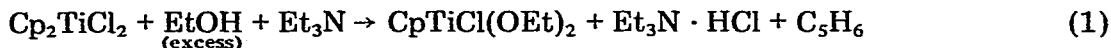
The reaction of  $\text{Cp}_2\text{TiCl}_2$  ( $\text{Cp} = \text{C}_5\text{H}_5$ ) with ethanol in the presence of  $\text{Et}_3\text{N}$  in acetonitrile yields the derivatives  $\text{CpTiCl}(\text{OEt})_2$  or  $\text{CpTiCl}_2(\text{OEt})$ . Similar reactions of  $\text{Cp}_2\text{MCl}_2$  ( $\text{M} = \text{Ti}$  or  $\text{Zr}$ ) with glycols ( $\text{GH}_2 = 1,2$ -propanediol, 2,3-butanediol, pinacol or hexylene glycol) or fluoro- $\beta$ -diketones ( $\text{KeH} = \text{hexafluoroacetylacetone}(\text{hfa}), \text{benzoyltrifluoroacetone}(\text{bta})$  or 2-thenoyltrifluoroacetone ( $\text{tta}$ )) gave  $\text{CpMCl}(\text{G})$  or  $\text{CpMCl}(\text{Ke})_2$ .

### Introduction

The reactions of  $\text{Cp}_2\text{MCl}_2$  ( $\text{M} = \text{Ti}$  or  $\text{Zr}$ ) with thiols yield products of formula  $\text{Cp}_2\text{M}(\text{SR})_2$  ( $\text{M} = \text{Ti}$  [1–4] or  $\text{Zr}$  [5,6]) in which both the chlorine atoms are replaced by  $-\text{SR}$  group. In contrast, the reactions of  $\text{Cp}_2\text{TiCl}_2$  with ethanol under reflux has been reported by Nesmeyanov et al. to be more complex, leading to formation of  $\text{CpTiCl}(\text{OEt})_2$  [7]. It thus seemed of interest to re-examine the reactions of  $\text{Cp}_2\text{TiCl}_2$  with ethanol, and to extend the study to reactions with other hydroxylic species viz: glycols and fluoro- $\beta$ -diketones.

### Results and discussion

Treatment of  $\text{Cp}_2\text{TiCl}_2$  at room temperature with an excess of ethanol in acetonitrile in presence of  $\text{Et}_3\text{N}$  yielded  $\text{CpTiCl}(\text{OEt})_2$  (eq. 1).

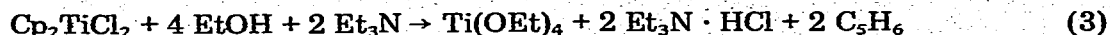


When only one mol of ethanol was used in the presence or absence of  $\text{Et}_3\text{N}$ , replacement of the cyclopentadienyl group rather than chlorine occurs, with formation of  $\text{CpTiCl}_2(\text{OEt})$ : (eq. 2).



If the reaction of  $\text{Cp}_2\text{TiCl}_2$  with an excess of ethanol in presence of  $\text{Et}_3\text{N}$  is

carried out under reflux, titanium tetraethoxide is formed almost quantitatively according to eq. 3.



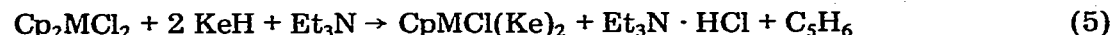
The replacement of one chlorine and one Cp group was also observed in the reactions of  $\text{Cp}_2\text{MCl}_2$  with glycols and fluoro- $\beta$ -diketones. (Frazer et al. [8] have already observed this behaviour in the reactions of  $\text{Cp}_2\text{MCl}_2$  with  $\beta$ -diketones.) The reactions of  $\text{Cp}_2\text{MCl}_2$  with glycols in the molar ratio 1 : 1 in acetonitrile in presence of  $\text{Et}_3\text{N}$  were carried out at the room temperature;



(i)

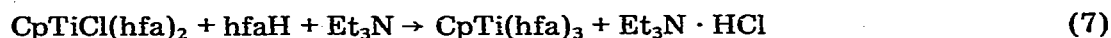
where M = Ti or Zr;  $\text{GH}_2$  = 1,2-propanediol, 2,3-butanediol, pinacol or hexylene glycol. The products I (with  $\text{GH}_2$  = pinacol and hexylene glycol) have also been obtained by treatment of  $\text{CpTiCl}_3$  with glycol in acetonitrile in presence of  $\text{Et}_3\text{N}$ .

Similar reactions at room temperature with fluoro- $\beta$ -diketones gave monomeric, dark red compounds of general formula,  $\text{CpMCl}(\text{Ke})_2$  (eq. 5),



(ii)

where M = Ti or Zr: KeH = hfa, bta or tta. These products reacted further with an excess of glycol or hexafluoroacetylacetone under reflux to give the products  $\text{Ti}(\text{G})_2$  and  $\text{CpTi}(\text{hfa})_3$  as in eq. 6 and 7.



The failure of  $\text{CpTi}(\text{hfa})_3$  to react with excess hexafluoroacetylacetone is probably due to steric hinderance. In the case of glycol, the chelating effect would facilitate removal of the remaining Cp or Cl ligand attached to titanium in the intermediate product  $\text{XTi}(\text{G})(\text{GH})$ .

## Experimental

Moisture was carefully excluded in all the experiments. Benzene, acetonitrile and petroleum ether were dried by standard methods [9]. 1,2-Propanediol (b.p. 188.9°C), 2,3-butanediol (b.p. 182°C), pinacol (b.p. 172°C), and hexylene glycol (b.p. 195°C) were distilled before use. Hexafluoroacetylacetone (b.p. 63°C) and benzoyltrifluoroacetone (b.p. 224°C) were distilled before use. 2-Thenoyltrifluoroacetone (m.p. 42°C) was used as supplied. Triethylamine (b.p. 89.4°C) was dried over KOH.  $\text{Cp}_2\text{TiCl}_2$ ,  $\text{Cp}_2\text{ZrCl}_2$  and  $\text{CpTiCl}_3$  (all Alfa-Inorganics) were also used as supplied. Titanium and zirconium were estimated as their oxides and chlorine was estimated gravimetrically as silver chloride. Molecular weights were determined osmometrically. IR were recorded on a Perkin-Elmer 337 with KBr plates.

**1 Reaction of  $Cp_2TiCl_2$  with ethanol at room temperature in the molar ratio 1 : 1 in acetonitrile in presence of  $Et_3N$  (or absence of  $Et_3N$ )**

To  $Cp_2TiCl_2$  (2.00 g) was added ~70 ml acetonitrile and ethanol (0.38 g). The mixture was stirred for ~6 h and the acetonitrile was removed under vacuo. Extraction with benzene, followed by removal of the  $Et_3N \cdot HCl$  by filtration, evaporation of the solvent and drying of the residue at 30°C/0.1 mmHg for 2½ h yielded a yellow solid (yield, 83%). (Found: Ti, 20.99; Cl, 30.99  $CpTiCl_2(OEt)$ , calcd.: Ti, 20.89; Cl, 30.97%.)

**2 Reaction of  $Cp_2TiCl_2$  with excess ethanol at room temperature in acetonitrile in presence of  $Et_3N$**

To the  $Cp_2TiCl_2$  in ~70 ml acetonitrile was added a mixture of  $Et_3N$  and

TABLE 1

REACTIONS OF  $Cp_2TiCl_2$  AND  $Cp_2ZrCl_2$  WITH GLYCOLS (MOLAR RATIO 1 : 1 : 2)<sup>a</sup>

Reactants (g)		Nature of the product yield (%)	Analysis found (calcd.) (%)		Molecular complexity
			Ti/Zr	Cl	
$Cp_2TiCl_2$ 1.42	Hexylene glycol 0.681	Brown solid $CpTi(Hexy.gly.)Cl$ 88	17.81 (18.10)	13.35 (13.42)	1.00
$CpTiCl_3$ 2.58	Hexylene glycol 1.41	Brown solid $CpTi(Hexy.gly.)Cl$ 90	17.91 (18.10)	13.36 (13.42)	0.99
$Cp_2TiCl_2$ 1.62	Pinacol 0.779	Reddish brown solid $CpTi(Pinacol)Cl$ 88	18.08 (18.10)	13.40 (13.42)	0.98
$CpTiCl_3$ 2.01	Pinacol 1.08	Reddish brown solid $CpTi(Pinacol)Cl$ 87	18.10 (18.10)	13.39 (13.42)	1.00
$Cp_2ZrCl_2$ 2.40	Pinacol 0.852	Yellow solid $CpZr(Pinacol)Cl$ 90	30.10 (29.63)	11.42 (11.53)	0.99
$Cp_2ZrCl_2$ 2.00	Hexylene glycol 0.812	Yellow solid $CpZr(Hexy.gly.)Cl$ 91	29.99 (29.63)	11.45 (11.53)	1.05
$Cp_2TiCl_2$ 2.60	1,2-Propanediol 0.797	Light brown solid $CpTi(Prop.1,2-diol)Cl$ 78	21.54 (21.53)	16.00 (15.96)	0.98
$Cp_2TiCl_2$ 1.49	2,3-Butanediol 0.539	Light yellow solid $CpTi(Buta.2,3-diol)Cl$ 76	20.18 (20.26)	14.99 (15.02)	0.96
$Cp_2ZrCl_2$ 2.00	1,2-Propanediol 0.521	Light brown solid $CpZr(Prop.1,2-diol)Cl$ 79	34.53 (34.33)	13.40 (13.34)	0.98
$Cp_2ZrCl_2$ 2.54	2,3-Butanediol 0.784	Light yellow solid $CpZr(Buta.2,3-diol)Cl$ 82	32.93 (32.60)	12.72 (12.67)	0.99

<sup>a</sup> Reaction conditions: all mixtures were stirred for 6 h.

TABLE 2  
 REACTIONS OF  $\text{Cp}_2\text{TiCl}_2$  AND  $\text{Cp}_2\text{ZrCl}_2$  WITH FLUORO- $\beta$ -DIKETONES (MOLAR RATIO 1 : 2 : 2)<sup>a</sup>

Reactants (g)	Nature of the product yield (%)	Analysis found (calcd.) (%)		Molecular complexity	
		Ti/Zr	Cl		
$\text{Cp}_2\text{TiCl}_2$ 1.49	Hexafluoro- acetylacetone 2.49	Dark red solid $\text{CpTi(hfa)}_2\text{Cl}$ 78	8.52 (8.53)	6.28 (6.32)	1.00
$\text{Cp}_2\text{TiCl}_2$ 1.16	Benzoyltri- fluoroacetone 1.94	Dark red solid $\text{CpTi(bta)}_2\text{Cl}$ 72	8.32 (8.32)	6.02 (6.17)	1.00
$\text{Cp}_2\text{TiCl}_2$ 1.39	2-Thenoyltri- fluoroacetone 2.52	Dark red solid $\text{CpTi(tta)}_2\text{Cl}$ 75	8.16 (7.98)	5.78 (5.92)	0.99
$\text{Cp}_2\text{ZrCl}_2$ 1.18	Hexafluoro- acetylacetone 1.68	Dark red solid $\text{CpZr(hfa)}_2\text{Cl}$ 76	15.4 (15.1)	5.80 (5.87)	1.01
$\text{Cp}_2\text{ZrCl}_2$ 2.23	Benzoyltri- fluoroacetone 3.32	Dark red solid $\text{CpZr(bta)}_2\text{Cl}$ 82	15.1 (14.7)	5.71 (5.73)	1.00
$\text{Cp}_2\text{ZrCl}_2$ 1.20	2-Thenoyltri- fluoroacetone 2.02	Dark red solid $\text{CpZr(tta)}_2\text{Cl}$ 80	14.8 (14.4)	5.58 (5.61)	1.00

<sup>a</sup> Reaction conditions: all mixtures were stirred for 4 h.

TABLE 3  
 REACTIONS UNDER REFLUXING CONDITIONS<sup>a</sup>

Reactants (g)	Molar ratio	Nature of the product yield (%)	Analysis found (calcd.) Ti (%)
$\text{Cp}_2\text{TiCl}_2$ 2.54	EtOH (excess) 2.93	1 : 6 : 2 Colourless liquid $\text{Ti(OEt)}_4$ 95	21.00 (20.99)
$\text{CpTiCl}$ (Pinacol) 2.75	Pinacol (excess) 2.65	1 : 2 : 2 White solid $\text{Ti(Pinacol)}_2$ 60	16.99 (17.09)
$\text{CpTiCl}$ (Hexylene glycol) 2.50	Hexylene glycol (excess) 2.39	1 : 2 : 2 White solid $\text{Ti(Hexy.gly.)}_2$ 62	16.95 (17.09)
$\text{CpTiCl(hfa)}_2$ 2.63	Hexafluoro- acetylacetone (excess) 4.05	1 : 4 : 2 Reddish brown solid $\text{CpTi(hfa)}_3$ 75	6.45 (6.54)

<sup>a</sup> Reaction conditions: all mixtures were refluxed for 4 h.

ethanol (excess). Subsequent procedure as above gave a light brown solid (yield, 85%). (Found: Ti, 21.00; Cl, 14.82  $\text{CpTiCl}(\text{OEt})_2$ , calcd.: Ti, 20.08; Cl, 14.88%.)

**3 Reactions of  $\text{Cp}_2\text{MCl}_2$  with glycols or fluoro- $\beta$ -diketones at room temperature in acetonitrile in presence of  $\text{Et}_3\text{N}$**

These were carried out as for reaction 1 above. The products were crystallized from petroleum ether (60–80°C) (see Tables 1 and 2).

**4 Reaction of  $\text{Cp}_2\text{TiCl}_2$  or  $\text{CpTiCl}(\text{G})$  or  $\text{CpTiCl}(\text{hfa})_2$  with excess hydroxylic species in presence of  $\text{Et}_3\text{N}$**

The appropriate titanocene compound was dissolved in 60 ml benzene and an excess of the alcohol or diketone was added. The mixture was refluxed for 4 h. Filtration and removal of the solvent under reduced pressure yielded the compounds indicated in Table 3.

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