Journal of Organometallic Chemistry, 121 (1976) 199—203
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

TITANOCENE AND ZIRCONOCENE DICHLORIDE DERIVATIVES WITH HYDROXYLIC REAGENTS

P.C. BHARARA
Chemical Laboratories, University of Delhi, Delhi-110007 (India)

(Received May 25th, 1976)

Summary

The reaction of Cp_2TiCl_2 ($Cp = C_5H_5$) with ethanol in the presence of Et_3N in acetonitrile yields the derivatives $CpTiCl(OEt)_2$ or $CpTiCl_2(OEt)$. Similar reactions of Cp_2MCl_2 (M = Ti or Zr) with glycols (GH_2 = 1,2-propanediol, 2,3-butanediol, pinacol or hexylene glycol) or fluoro-β-diketones (KeH = hexafluoroacetylacetone(hfa), benzoyltrifluoroacetone (bta) or 2-thenoyltrifluoroacetone (tta)) gave CpMCl(G) or $CpMCl(Ke)_2$.

Introduction

The reactions of Cp_2MCl_2 (M = Ti or Zr) with thiols yield products of formula $Cp_2M(SR)_2$ (M = Ti [1—4] or Zr [5,6]) in which both the chlorine atoms are replaced by —SR group. In contrast, the reactions of Cp_2TiCl_2 with ethanol under reflux has been reported by Nesmeyanov et al. to be more complex, leading to formation of $CpTiCl(OEt)_2$ [7]. It thus seemed of interest to re-examine the reactions of Cp_2TiCl_2 with ethanol, and to extend the study to reactions with other hydroxylic species viz: glycols and fluoro-β-diketones.

Results and discussion

Treatment of Cp_2TiCl_2 at room temperature with an excess of ethanol in acetonitrile in presence of Et_3N yielded $CpTiCl(OEt)_2$ (eq. 1).

$$Cp_2TiCl_2 + \underset{(excess)}{EtOH} + Et_3N \rightarrow CpTiCl(OEt)_2 + Et_3N \cdot HCl + C_5H_6 \qquad (1)$$

When only one mol of ethanol was used in the presence or absence of Et_3N, replacement of the cyclopentadienyl group rather than chlorine occurs, with formation of $CpTiCl_2(OEt)$: (eq. 2).

$$Cp_2TiCl_2 + EtOH \rightarrow CpTiCl_2(OEt) + C_5H_6 \qquad (2)$$

If the reaction of Cp_2TiCl_2 with an excess of ethanol in presence of Et_3N is carried out under reflux, titanium tetraethoxide is formed almost quantitatively according to eq. 3.

$$Cp_2TiCl_2 + 4\,EtOH + 2\,Et_3N \rightarrow Ti(OEt)_4 + 2\,Et_3N \cdot HCl + 2\,C_5H_6 \qquad (3)$$

The replacement of one chlorine and one Cp group was also observed in the reactions of Cp_2MCl_2 with glycols and fluoro-β-diketones. (Frazer et al. [8] have already observed this behaviour in the reactions of Cp_2MCl_2 with β-diketones.) The reactions of Cp_2MCl_2 with glycols in the molar ratio 1 : 1 in acetonitrile in presence of Et_3N were carried out at the room temperature;

$$Cp_2MCl_2 + GH_2 + Et_3N \rightarrow \underset{(I)}{CpMCl(G)} + Et_3N \cdot HCl + C_5H_6 \qquad (4)$$

where M = Ti or Zr; GH_2 = 1,2-propanediol, 2,3-butanediol, pinacol or hexylene glycol. The products I (with GH_2 = pinacol and hexylene glycol) have also been obtained by treatment of $CpTiCl_3$ with glycol in acetonitrile in presence of Et_3N.

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

$$Cp_2MCl_2 + 2\,KeH + Et_3N \rightarrow \underset{(II)}{CpMCl(Ke)_2} + Et_3N \cdot HCl + C_5H_6 \qquad (5)$$

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 $Ti(G)_2$ and $CpTi(hfa)_3$ as in eq. 6 and 7.

$$CpTiCl(G) + GH_2 + Et_3N \rightarrow Ti(G)_2 + C_5H_6 + Et_3N \cdot HCl \qquad (6)$$

$$CpTiCl(hfa)_2 + hfaH + Et_3N \rightarrow CpTi(hfa)_3 + Et_3N \cdot HCl \qquad (7)$$

The failure of $CpTi(hfa)_3$ 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 XTi(G)(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. Cp_2TiCl_2, Cp_2ZrCl_2 and $CpTiCl_3$ (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 $2\frac{1}{2}$ 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)[a]

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 CpTiCl(Prop.1,2-diol) 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

[a] Reaction conditions: all mixtures were stirred for 6 h.

TABLE 2

REACTIONS OF Cp_2TiCl_2 AND Cp_2ZrCl_2 WITH FLUORO-β-DIKETONES (MOLAR RATIO 1 : 2 : 2)[a]

Reactants (g)		Nature of the product yield (%)	Analysis found (calcd.) (%)		Molecular complexity
			Ti/Zr	Cl	
Cp_2TiCl_2 1.49	Hexafluoroacetylacetone 2.49	Dark red solid $CpTi(hfa)_2Cl$ 78	8.52 (8.53)	6.28 (6.32)	1.00
Cp_2TiCl_2 1.16	Benzoyltrifluoroacetone 1.94	Dark red solid $CpTi(bta)_2Cl$ 72	8.32 (8.32)	6.02 (6.17)	1.00
Cp_2TiCl_2 1.39	2-Thenoyltrifluoroacetone 2.52	Dark red solid $CpTi(tta)_2Cl$ 75	8.16 (7.98)	5.78 (5.92)	0.99
Cp_2ZrCl_2 1.18	Hexafluoroacetylacetone 1.68	Dark red solid $CpZr(hfa)_2Cl$ 76	15.4 (15.1)	5.80 (5.87)	1.01
Cp_2ZrCl_2 2.23	Benzoyltrifluoroacetone 3.32	Dark red solid $CpZr(bta)_2Cl$ 82	15.1 (14.7)	5.71 (5.73)	1.00
Cp_2ZrCl_2 1.20	2-Thenoyltrifluoroacetone 2.02	Dark red solid $CpZr(tta)_2Cl$ 80	14.8 (14.4)	5.58 (5.61)	1.00

[a] Reaction conditions: all mixtures were stirred for 4 h.

TABLE 3

REACTIONS UNDER REFLUXING CONDITIONS[a]

Reactants (g)		Molar ratio	Nature of the product yield (%)	Analysis found (calcd.) Ti (%)
Cp_2TiCl_2 2.54	EtOH (excess) 2.93	1 : 6 : 2	Colourless liquid $Ti(OEt)_4$ 95	21.00 (20.99)
CpTiCl (Pinacol) 2.75	Pinacol (excess) 2.65	1 : 2 : 2	White solid $Ti(Pinacol)_2$ 60	16.99 (17.09)
CpTiCl (Hexylene glycol) 2.50	Hexylene glycol (excess) 2.39	1 : 2 : 2	White solid $Ti(Hexy.gly.)_2$ 62	16.95 (17.09)
$CpTiCl(hfa)_2$ 2.63	Hexafluoroacetylacetone (excess) 4.05	1 : 4 : 2	Reddish brown solid $CpTi(hfa)_3$ 75	6.45 (6.54)

[a] 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 $CpTiCl(OEt)_2$, calcd.: Ti, 20.08; Cl, 14.88%.)

3 Reactions of Cp_2MCl_2 with glycols or fluoro-β-diketones at room temperature in acetonitrile in presence of Et_3N

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 Cp_2TiCl_2 or $CpTiCl(G)$ or $CpTiCl(hfa)_2$ with excess hydroxylic species in presence of Et_3N

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.

Acknowledgement

The author is grateful to Prof. R.C. Mehrotra for his continuous encouragement throughout this work. He is also thankful to the Council of Scientific and Industrial Research, New Delhi, for providing a post-doctoral fellowship.

References

1 H. Kopf and M. Schmidt, Angew. Chem. Int. Ed. Engl., 4 (1965) 953.
2 M.A. Choudhary and F.G.A. Stone, J. Chem. Soc. A, (1966) 838.
3 R.S.P. Coutts and P.C. Wailes, Aust. J. Chem., 19 (1966) 1377.
4 S.A. Giddings, Inorg. Chem., 6 (1967) 849.
5 H. Kopf, J. Organometal. Chem., 14 (1968) 353.
6 M.Kh. Minacheva and E.M. Brainina, Izv. Akad. Nauk. SSSR, Ser. Khim., (1972) 139.
7 A.N. Nesmeyanov, O.V. Nogina, A.M. Berlin, A.S. Gershovich and G.V. Shatalov, Izv. Akad. Nauk. SSSR, (1961) 2146.
8 M.J. Frazer and W.E. Newton, Inorg. Chem., 10 (1971) 2137.
9 V.D. Gupta, Ph.D. Thesis, University of Rajasthan, Jaipur, 1965.