Journal of Organometallic Chemistry, 445 (1993) 107–109

JOM 23140

Ketene acetal metallocene complexes. Crystal structure of $(C_5H_5)_2Ti(Cl)OC(OCH_3)=C(CH_3)_2$

Kai Hortmann, Josef Diebold and Hans-Herbert Brintzinger

Fakultät für Chemie, Universität Konstanz, Postfach 5560, 7750 Konstanz (Germany)

(Received July 20, 1992)

Abstract

Titanocene and zirconocene ketene acetal derivatives have been prepared by reaction of the respective metallocene dichloride with the lithium enolate of isobutyric acid methyl ester. The crystal structure of $(C_5H_5)_2Ti(Cl)OC(OCH_3)=C(CH_3)$ is reported.

1. Introduction

Silyl ketene acetals, such as $(CH_3)_3SiOC(OCH_3)=C(CH_3)_2$ (**1**), are highly reactive species of substantial interest for use in aldol condensations and Michael additions [1] or for group-transfer polymerisation of acrylic acid derivatives [2]. Related titanium compounds, in which a tris(alkoxy)titanium [3] or bis(alkoxy)(cyclopentadienyl)titanium [4] group replaces the trimethylsilyl group of **1**, have been reported to be useful polymerisation initiators and organic synthons, respectively. More recently, Collins and Ward [5] have described catalyst systems for group-transfer polymerisation of methyl methacrylate, which are derived from zirconocene dimethyl or dienolate compounds by addition of a proton source. These authors have presented substantial evidence that cationic zirconocene ketene acetal complexes are the reactive species in these catalyst systems.

Here, we describe the synthesis of neutral titanocene (**2**) and zirconocene (**3**) ketene acetal complexes, and the crystal structure of **2**, $(C_5H_5)_2Ti(Cl)OC(OCH_3)=C(CH_3)_2$.

2. Results and discussion

The titanocene ketene acetal $(C_5H_5)_2Ti(Cl)OC(OCH_2)=C(CH_3)_2$, **2**, was prepared by the addition of $LiOC(OCH_3)=C(CH_3)_2$ (obtained by deprotonation of isobutyric acid methyl ester with lithium diisopropylamid) to an equimolar amount of $(C_5H_5)_2TiCl_2$ in THF at −78°C (see Section 3). Warming the reaction mixture to room temperature, removal of the solvent, extraction with toluene, and crystallisation from the extract at −80°C afforded **2** in *ca.* 30% yield, as a black solid extremely air- and moisture-sensitive, especially in solution. *

An analogous reaction with zirconocene dichloride gave a yellow oily product that we were unable to crystallise. As judged from its ^1H NMR spectrum, this product is predominantly $(C_5H_5)_2Zr(Cl)OC(OCH_3)=C(CH_3)_2$, **3**, containing *ca.* 10–20% of the bis(ketene acetal) complex $(C_5H_5)_2Zr(OC(OCH_3)=(CH_3)_2)_2$. **

The ^1H NMR spectra of the ketene acetal derivatives (Table 1) are quite similar to those of the trimethylsilyl ketene acetal **1**. The protons of the methyl substituents on the alkene carbon atoms show higher and more unequal chemical shifts in **2** and **3** than in **1**.

In the case of the titanocene complex **2**, we obtained crystals suitable for an X-ray diffraction study. The structure obtained for this compound (Fig. 1, Table 2) is entirely in accordance with expectation. The ketene

---

Correspondence to: Professor H.-H. Brintzinger.

* Neither treatment of $(C_5H_5)_2Ti(Cl)OCH_3$ with dimethyl ketene in THF nor that of $(C_5H_5)_2TiCl_2$ with **1** in THF at room temperature gave **2**.

** A related t-butoxy species, $(C_5H_5)_2Zr(OC(OC(CH_3)_3)=C(CH_3)_2)_2$, has been described by Collins and Ward [5].

0022-328X/93/$6.00

TABLE 1. ^1H NMR spectra of **1**, **2** and **3** in C_6D_6 solution. Shifts in p.p.m. relative to tetramethylsilane

Compound	$-CH_3$ [a]	$-OCH_3$	C_5H_5	$-Si(CH_3)_3$
1	1.52, 1.57	3.50 s		0.20 s
2	1.60, 1.89	3.50 s	5.97 s	
3	1.66, 1.84	3.42 s	6.05 s	

[a] Non-resolved quadruplets with $^4J \approx 0.5$ Hz.

acetal ligand is planar within the standard deviation; its mean plane intersects the Ti–O–Cl plane at an angle of 40°.

Of interest are the Ti–O distance of 189 pm and the Ti–O–C angle of 142°. In Cp_2Ti-bound alkoxylate, enolate and carboxylate complexes, variation of the Ti–O distances in the range 175–193 pm, in conjunction with that of Ti–O–C angles in the range 133–166° [6] have been ascribed to different degrees of donation of the O-atom lone pairs to the formally electron-deficient metal centre. In complex **2**, this π-type Ti–O interaction appears to be relatively minor, as judged by the rather long Ti–O distance and the small Ti–O–C bond angle. It remains to be determined what effects different electron distributions in these ketene acetal derivatives have on the reactivities of these compounds, *e.g.* in group transfer polymerisation.

3. Experimental details

Solvents were thoroughly dried and stored under nitrogen. Air-sensitive materials were handled by standard Schlenk techniques.

3.1. $(C_5H_5)_2Ti(Cl)OC(OCH_3)=C(CH_3)_2$ (2)

To a solution of $(C_5H_5)_2TiCl_2$ (12.45 g, 50 mmol) in 750 ml THF at −78°C was added a solution of $LiOC(OCH_3)=C(CH_3)_2$, prepared by the addition of 60 mmol of isobutyric acid methyl ester to a solution of 52 mmol of lithium diisopropyl amide in 120 ml THF. The mixture was allowed to warm to room temperature overnight, during which time the colour of the mixture darkened. The THF was then removed *in vacuo*, and the black solid was dissolved in 100 ml of toluene. This solution was filtered to remove the LiCl and the filtrate concentrated *in vacuo*. Cooling of the solution slowly to −80°C yielded 5.0 g (32%) of a black solid. More product (5.9 g, 38%) was isolated as a thick black oil upon further concentration of the mother liquor. Slow vapour-diffusion-controlled recrystallisation from toluene–pentane gave **2** as clusters of black needles.

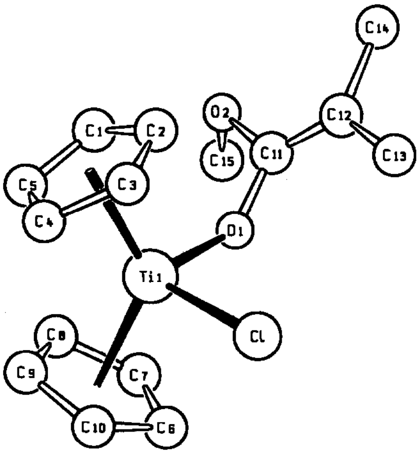

Fig. 1. Structure of $(C_5H_5)_2Ti(Cl)OC(OCH_3)=C(CH_3)_2$, **2** (H atoms omitted for clarity).

TABLE 2. Selected bond lengths (in pm) and bond angles (in degrees) for complex **2**. C_5-ring centroids: CR(1): C(1)–C(5); CR(2): C(6)–C(10); mean planes: PL(1): Ti(1), O(1), C1; PL(2): O(1), O(2), C(11)–C(14); PL(3): Ti(1), CR(1), CR(2); PL(4): C(1)–C(5); PL(5): C(6)–C(10)

Ti(1)–C1	240.3(9)	Ti(1)–O(1)	188.8(7)
Ti(1)–C(1)	236.2(16)	Ti(1)–C(6)	242.9(9)
Ti(1)–C(2)	239.5(10)	Ti(1)–C(7)	240.5(12)
Ti(1)–C(3)	241.7(10)	Ti(1)–C(8)	234.7(18)
Ti(1)–C(4)	236.7(12)	Ti(1)–C(9)	240.3(17)
Ti(1)–C(5)	233.7(19)	Ti(1)–C(10)	241.7(12)
C(11)–O(1)	135.7(13)	C(11)–O(2)	136.7(32)
C(11)–C(12)	133.1(35)	O(2)–C(15)	137.9(17)
Cl–Ti(1)–O(1)	96.5(4)	Ti(1)–O(1)–C(11)	141.5(8)
CR(1)–Ti(1)–CR(2)	130.8	C(11–O(2)–C(15)	114.0(11)
PL1–PL2	39.9	PL1–PL3	89.7
PL4–PL5	52.4		

TABLE 3. Fractional coordinates ($\times 10^4$) (with esds) and isotropic displacement coefficients ($pm^2 \times 10^{-1}$) for complex **2**

	x	*y*	*z*	U_{eq} [a]
Ti(1)	1026(1)	895(1)	6577(8)	35(3)
Cl	936(1)	1347(2)	3549(11)	36(4)
O(1)	1010(3)	−162(4)	6029(16)	28(8)
O(2)	1413(3)	−1183(5)	7548(24)	76(10)
C(1)	1888(5)	545(8)	8085(34)	50(4)
C(2)	2056(4)	718(6)	6379(30)	35(3)
C(3)	1964(4)	1481(6)	6075(27)	36(3)
C(4)	1708(4)	1805(6)	7635(28)	35(3)
C(5)	1686(5)	1219(7)	8834(32)	55(4)
C(6)	−20(4)	1036(6)	6347(27)	37(3)
C(7)	87(4)	498(6)	7637(28)	35(3)
C(8)	399(5)	810(7)	9046(28)	52(4)
C(9)	448(5)	1591(7)	8706(28)	47(4)
C(10)	210(5)	1746(7)	7016(26)	43(3)
C(11)	1358(5)	−791(7)	5972(41)	37(4)
C(12)	1638(5)	−1012(7)	4500(37)	39(4)
C(13)	1610(5)	−594(8)	2748(32)	56(4)
C(14)	2002(5)	−1757(6)	4563(27)	62(4)
C(15)	905(5)	−1519(9)	8134(26)	81(5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalised U_{ij} tensor.

3.2. $(C_5H_5)_2Zr(Cl)OC(OCH_3)=C(CH_3)_2$ (**3**)

An analogous procedure starting from 10 mmol $(C_5H_5)_2ZrCl_2$ gave 2.35 g (66%) of a yellow oil that did not solidify after the addition of pentane.

3.3. *Crystal structure determination*

$C_{15}H_{19}ClO_2Ti$, $M = 000.00$, space group *Pccn*, with *a* 2303.0(7), *b* 1742.1(7), *c* 746.8(3) pm and $Z = 8$; $V = 2996(2) \cdot 10^6$ pm^3, $d_{calc} =$ 1.395 g cm^{-3} was determined for a crystal of **2** (0.2 · 0.2 · 0.2 mm^3) at 213 K on a Syntex-P3 four-circle diffractometer (Mo Kα, λ 71.073 pm; graphite monochromator; ω-scan with $\Delta\omega$ 0.75°; $2.0 \leq \dot{\omega} \leq 29.3°$ min^{-1}; $4.0° \leq 2\theta \leq 52.0°$). Of 1260 reflections collected, 740 independent reflections with $F > 2\sigma(F)$ were used, without absorption correction, for solving and refining the structure. The structure was solved by direct methods (SHELXTL PLUS) and refined, using the weighting scheme $w^{-1} = \sigma^2(F) + 0.0008F^2$, with thermal parameters anisotropic for Ti, Cl and O atoms and isotropic for C and H atoms, the latter in calculated positions (riding model). The refinement converged at $R = 0.079$ and $R_w = 0.095$, with goodness-of-fit of 2.16 and residual electron density $\leq 0.45 \cdot 10^{-6}$ e pm^{-3}. The structural parameters for complex **2** thus obtained are presented in Table 3. *

Acknowledgments

Financial support of this work by Volkswagen-Stiftung is gratefully acknowledged.

References

1 E. W. Colvin, *Silicon in Organic Synthesis*, Butterworths, London, 1981.

2 O. W. Webster, W. R. Hertler, D. Y. Sogah, W. B. Farnham and T. V. Rajanbabu, *J. Am. Chem. Soc., 105* (1983) 5706.

3 M. T. Reetz, *Pure Appl. Chem., 57* (1985) 1781.

4 M. Riediker and R. O. Duthaler, *Angew. Chem., 101* (1989) 488.

5 S. Collins and D. G. Ward, *J. Am. Chem. Soc., 114* (1992) 5460.

6 M. D. Curtis, S. Thanedar and W. M. Butler, *Organometallics, 3* (1984) 1855.

---

* Structural data are available on request from Fachinformationszentrum Karlsruhe, W-7514 Eggenstein-Leopoldshafen 2, upon quotation of deposit number CSD-56519, the authors, and the journal reference for this article.