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Organotitanium chemistry

XVI *. Synthesis and crystal structure of tetrahydrofurfurylcyclopentadienyltitanium trichloride and its derivatives

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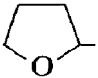
Abstract

The synthesis of tetrahydrofurfurylcyclopentadienyltitanium trichloride $-CH_2CpTiCl_3$ (**1**) and its derivatives $(R^1Cp)(R^2Cp)TiCl_2$ (R^1 = $-CH_2$; R^2 = allyl (**2**), $PhCH_2$ (**3**), $PhC(C_2H_5)_2$ (**4**), $PhC(CH_3)_2$ (**5**), $PhC(CH_3)(C_2H_5)$ (**6**)) is described. The crystal structure of **1** is determined by X-ray diffraction and refined to a *R* factor of 0.054 for 1651 observed reflections. The ethereal oxygen atom of the ring-substituent chelates with the titanium atom with a Ti–O bond length of 2.165(4) Å. The crystal belongs to the monoclinic space group $P2_1/n$ with unit cell parameters: *a* 7.894(2), *b* 13.082(5), *c* 12.123(3) Å, β 100.26(2)°, $Z = 4$, and its spectral properties are also discussed.

Introduction

In our previous work [1], we observed that the substituents on the Cp rings have important effects on the isomerization modes of 1,5-hexadiene catalyzed by $(RCp)_2TiCl_2/{}^iPrMgBr$ or $(RCp)CpTiCl_2/{}^iPrMgBr$. In this connection, a number

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* For part XV see ref. 9.

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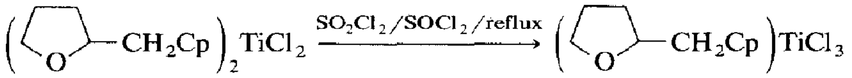
of compounds of the formulae $(RCp)_2TiCl_2$ and $(RCp)CpTiCl_2$ [2–8] have been prepared, but few dicyclopentadienyltitanium complexes of the type $(R^1Cp)(R^2Cp)TiCl_2$ with two different cyclopentadienyl rings have been reported. In this paper, we present the synthesis and crystal structure of tetrahydrofurfurylcyclopentadienyltitanium trichloride and its derivatives.

Results and discussion

In our laboratory, some functionally substituted cyclopentadienyltitanium complexes such as ( $CH_2Cp)_2TiCl_2$ (**7**) have been synthesized. The crystal structure of **7** determined by X-ray diffraction showed that the oxygen atom does not chelate with the titanium atom [9]. Reaction of **7** with SO_2Cl_2 in $SOCl_2$ [10], after recrystallization from benzene, affords tetrahydrofurfurylcyclopentadienyltitanium trichloride (**1**), which is an orange crystalline solid, sensitive to moisture.

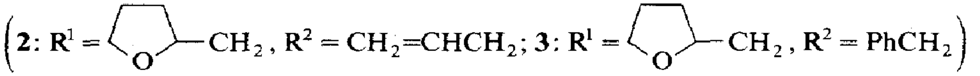


(**7**) (**1**)

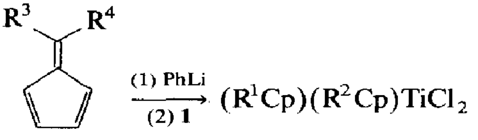
Reactions of potassium salts of allyl and benzyl cyclopentadienes with **1** produce compounds **2** or **3**.

$$R^2C_5H_5 \xrightarrow{K/THF} R^2C_5H_4K \xrightarrow{\mathbf{1}} (R^1Cp)(R^2Cp)TiCl_2$$

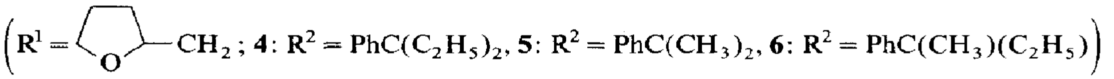
(**2,3**)



Phenyllithium easily reacts with fulvenes [11] to form lithium salts of substituted cyclopentadienes. Reaction of the lithium salts with **1** leads to compounds **4**–**6**.



(**4–6**)



The spectral data for compounds (**1**–**6**) are given in Table 4. The mass spectra of the related substituted cyclopentadienyltitanium complexes $(RCp)_2TiCl_2$ and $(RCp)CpTiCl_2$ have been studied [12]. The main fragments are $M - Cl$, $M - RCp$ and $M - Cp$. For our $(R^1Cp)(R^2Cp)TiCl_2$ compounds, the peaks due to $(M - R^2Cp)^+$ are, without exception, much stronger than those due to $(M - R^1Cp)^+$ and are frequently the base peaks. This indicates that the species $(M - R^2Cp)^+$ is more stable than $(M - R^1Cp)^+$ in the gas phase, possibly because of chelation of the ethereal oxygen atom of the R^1 group in $(M - R^2Cp)^+$, thereby stabilizing the species.

In general, the chemical shifts of the hydrogens on the Cp rings in compounds

$(R^1Cp)(R^2Cp)TiCl_2$, while nearly equal, are split into very complicated multiple peaks. Additionally, the CH_2 signals due to the ethyl groups in **4** and **6** are not as simple as the expected quartets. In all of these compounds, the distances between the titanium and each of the five carbons on the Cp rings are expected to be unequal, thus the hydrogens on the Cp ring are chemically non-identical and appear as one or several groups of multiple peaks in the NMR spectra. The bulky substituents on the Cp rings may also hinder the free rotation along the Cp–C bond, leading to a slight difference between the protons of CH_2 in **4** and **6**. Thus the CH_2 forms multiplets instead of the usual quartet.

The intense stretching vibration of C–O in **2–6** is observed at 1050–1060 cm^{-1}, while the C–O for **1** is shifted to 960 cm^{-1}. This is consistent with the chelation of the oxygen atom with the titanium atom (also confirmed by X-ray diffraction) weakening the C–O bond and shifting the C–O absorption to lower wavelength.

Crystal structure of 1

The atom coordinates and temperature factors are listed in Table 1. The bond lengths and bond angles are given in Table 2 and Table 3 respectively. The molecular configuration is shown in Fig. 1.

The molecular structure of **1**, compared with its unsubstituted analog, $CpTiCl_3$ [13], has the following different features. First of all, the ethereal oxygen atom in the tetrahydrofurfuryl moiety chelates with the titanium atom with moderate strength. The Ti–O bond in **1** (2.165(4) Å) is shorter than the Ti–O coordinate bond in $(\eta^5\text{-}Cp)_2Ti\text{-}\mu\text{-}(\eta^1:\eta^5\text{-}C_5H_4)Ti(\eta^5\text{-}Cp)\cdot THF\cdot THF$ (2.26 Å) [14] and longer than the Ti–O σ-bond in $Cp_2Ti(OEt)Cl$ (1.855 Å) [15]. Secondly, the distances between titanium and the carbons on the Cp ring are no longer equal, but instead increase gradually in the order Ti–C(2) (2.342(6) Å) or Ti–C(3) (2.345(7) Å), Ti–C(1) (2.369(6) Å) or Ti–C(4) (2.373(7) Å), Ti–C(5) (2.392(6) Å), the bond length between titanium and the carbon possessing the substituent being the longest. In addition, one of the three Ti–Cl, Ti–Cl(2), is longer than the remaining two by about 0.05 Å.

Table 1

Atom coordinates ($\times 10^4$) and temperature factors (Å $\times 10^3$)

atom	x	y	z	U^a
Ti	8326(1)	489(1)	2597(1)	34(1)
Cl(1)	9899(2)	1971(1)	2969(2)	52(1)
Cl(2)	10848(2)	−298(1)	2222(2)	61(1)
Cl(3)	8137(2)	−834(1)	3810(2)	60(1)
O(1)	6834(5)	1240(4)	3696(3)	47(2)
C(1)	6796(8)	1350(5)	1007(5)	46(2)
C(2)	7657(10)	522(6)	635(5)	58(3)
C(3)	6986(10)	−396(6)	996(6)	65(3)
C(4)	5666(9)	−134(5)	1599(5)	52(2)
C(5)	5532(8)	958(5)	1617(5)	43(2)
C(6)	4444(8)	1568(6)	2237(5)	52(2)
C(7)	5089(11)	1429(10)	3431(7)	123(5)
C(8)	4566(9)	2069(6)	4322(6)	60(3)
C(9)	5961(10)	1859(8)	5337(7)	84(4)
C(10)	7484(10)	1430(7)	4904(5)	80(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U tensor.

Table 2

Bond lengths (Å)

Ti–Cl(1)	2.303(2)	Ti–Cl(2)	2.356(2)
Ti–Cl(3)	2.293(2)	Ti–O(1)	2.165(4)
Ti–C(1)	2.369(6)	Ti–C(2)	2.342(6)
Ti–C(3)	2.345(7)	Ti–C(4)	2.373(7)
Ti–C(5)	2.392(6)	O(1)–C(7)	1.380(10)
O(1)–C(10)	1.485(8)	C(1)–C(2)	1.396(10)
C(1)–C(5)	1.438(9)	C(2)–C(3)	1.413(11)
C(3)–C(4)	1.418(11)	C(4)–C(5)	1.433(9)
C(5)–C(6)	1.472(10)	C(6)–C(7)	1.459(10)
C(7)–C(8)	1.482(13)	C(8)–C(9)	1.523(10)
C(9)–C(10)	1.504(12)		

Table 3

Selected bond angles (deg.)

Cl(1)–Ti–Cl(2)	87.8(1)	Cl(1)–Ti–Cl(3)	127.2(1)
Cl(2)–Ti–Cl(3)	87.0(1)	Cl(1)–Ti–O(1)	80.3(1)
Cl(2)–Ti–O(1)	152.6(1)	Cl(3)–Ti–O(1)	80.9(1)
Ti–O(1)–C(7)	124.6(5)	Ti–O(1)–C(10)	123.6(4)
C(7)–O(1)–C(10)	110.8(6)	Ti–C(5)–C(6)	117.1(4)
C(1)–C(5)–C(6)	126.2(6)	C(4)–C(5)–C(6)	126.8(6)
C(5)–C(6)–C(7)	107.8(6)	O(1)–C(7)–C(6)	114.3(7)
O(1)–C(7)–C(8)	109.2(6)	C(6)–C(7)–C(8)	124.0(8)
C(7)–C(8)–C(9)	103.4(6)	C(8)–C(9)–C(10)	107.0(6)
O(1)–C(10)–C(9)	104.5(5)		

Thirdly, because the oxygen atom takes part in the coordination, the electron count of the titanium is 14. The plane of Cl(2)–Ti–O approximately divides the plane of Cl(3)–Ti–Cl(1) into two equivalent parts. The bond angles of Cl(1)–Ti–Cl(2) and Cl(3)–Ti–Cl(2) (ca. 87°) are smaller than that of Cl–Ti–Cl (ca. 102°) in $CpTiCl_3$ whereas the angle of Cl(1)–Ti–Cl(3) (127°) is larger. The interaction between the substituent and the titanium, especially in reaction intermediates may be an important factor determining the behaviours of these substituted cyclopentadienyl titanium complexes.

Experimental

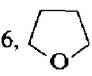
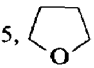
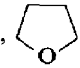
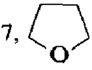
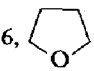
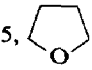
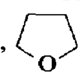
Melting points were uncorrected. Mass spectra were measured on a Finnigan 4021 Mass Spectrometer. Infrared spectra were measured on Shimadzu IR-40 spectrometer. Measurement of the infrared spectrum of **1** was carried out under a nitrogen atmosphere. ^1H NMR were measured on a Varian EM-360A NMR Spectrometer using tetramethylsilane (TMS) as an internal standard. Solvents were purified in the usual ways.

Preparation of 1

Bis(tetrahydrofurfurylcyclopentadienyl)titanium dichloride (4.57 g) was placed in a reaction vessel and flushed with argon several times. Under argon, SO_2Cl_2 (5 ml) and $SOCl_2$ (20 ml) were added. The resulting mixture was refluxed for 2 h. The

Table 4

MS, IR and ^{1}H NMR of compounds **1–6**

Entry	MS	IR (cm^{-1})	NMR (ppm)
1	267(100, $M-$Cl) 71 (76, )	3120(m), 2950(m), 2870(m) 1495(m), 1438(m), 1385(m) 1055(m), 1027(m), 960(s) 875(m), 835(m), 820(m)	6.95(s, 4H) 4.08(m 3H) 3.05(m, 2H) 2.10(m, 4H)
2	337(19, $M-$Cl) 267(59, $M-\mathrm{R}^2_1$Cp) 243(14, $M-\mathrm{R}^1$Cp) 71 (95, ) 43 (100, )	3100(m), 2910(m), 2790(m) 1484(m), 1420(S), 1375(w) 1050(s), 1080(w), 1020(w) 850(m), 830(s), 805(m)	6.43(m, 8H), 5.76(m, 1H) 5.17(d, 1H), 4.95(d, 1H) 3.88(d, 2H), 3.80(m, 3H) 3.46(m, 2H), 1.88(m, 4H)
3	387(18, $M-$Cl) 267(100, $M-\mathrm{R}^2$Cp) 273(14, $M-\mathrm{R}^1$Cp) 71 (77, )	3100(m), 2911(m), 2810(m) 1600(m), 1495(s), 1425(s) 1380(w), 1050(s), 1170(w) 1075(w), 1030(m), 850(s) 820(m), 720(s), 695(s)	7.22(s, 5H), 6.94(m, 4H) 6.34(m, 4H), 4.01(s, 2H) 3.79(m, 3H), 2.89(m, 2H) 1.82(m, 4H)
4	443(60, $M-$Cl) 329(9, $M-\mathrm{R}^1$Cp) 267(100, $M-\mathrm{R}^2$Cp) 71 (86, )	3100(m), 2900(m), 2750(m) 1495(m), 1470(s), 1440(s) 1060(s), 1190(m), 1055(s) 1020(m), 815(s), 763(s) 701(s)	7.40(s, 5H), 6.60(m, 2H) 6.42(m, 2H), 5.96(m, 2H) 5.25(m, 2H), 3.71(m, 3H) 2.90(m, 2H), 2.20(m, 4H) 1.80(m, 4H), 0.66(t, 6H)
5	415(60, $M-$Cl) 301(20, $M-\mathrm{R}^1$Cp) 267(100, $M-\mathrm{R}^2$cp) 71 (45, )	3100(m), 2900(m), 2750(m) 1490(m), 1475(s), 1440(s) 1380(m), 1050(s), 1145(m) 1030(m), 821(s), 765(s) 700(s)	7.26(s, 5H), 6.62(m, 2H) 6.45(m, 2H), 6.23(m, 2H) 6.05(m, 2H), 3.80(m, 3H) 2.95(m, 2H), 1.82(m, 4H) 1.73(s, 6H)
6	419(26, $M-$Cl) 315(13, $M-\mathrm{R}^1$Cp) 267(52, $M-\mathrm{R}^2$Cp) 71 (100, )	3100(m), 2950(m), 2890(m) 1480(m), 1445(s), 1425(s) 1365(m), 1060(s), 1035(m) 840(m), 825(s), 765(s) 705(s)	7.33(s, 5H), 6.83(m, 2H) 6.46(m, 4H), 5.95(m, 2H) 3.82(m, 3H), 2.95(m, 2H) 1.90(m, 4H), 2.15(m, 2H) 1.71(s, 3H), 0.73(t, 3H)

excess of SO_2Cl_2 and $SOCl_2$ was removed under reduced pressure. The orange solid was recrystallized from benzene under argon. Orange crystals of **1** were obtained in 88% yield (m.p. 101–103°C), Found: C, 39.61; H, 4.31. $C_{10}H_{13}Cl_3OTi$ calcd. C, 39.58; H, 4.32%.

*Synthesis of **2** and **3***

The potassium salt of allylcyclopentadiene (ca. 5.4 mmol in THF) was added to 1.64 g of **1** in 15 ml of THF under argon. The resulting mixture was stirred magnetically at room temperature for 2 h. The solvent was then removed and the residue was extracted with ether. The crude product was obtained in 48% yield.

Recrystallization from ether gave a pure red solid (m.p. 71–72° C), Found: C, 57.62; H, 5.68; Ti, 12.84. $C_{18}H_{28}Cl_2OTi$ calcd.: C, 57.93; H, 5.95; Ti, 12.81%.

Compound **3** was synthesized similarly in 39% yield (m.p. 121–122° C). Found: C, 62.03; H, 5.18; Ti, 11.25. $C_{22}H_{24}Cl_2OTi$ calcd.: C, 62.42; H, 5.73; Ti, 11.32%.

*Synthesis of **4**, **5**, and **6***

Under argon, 7 ml of PhLi (1 mmol/ml in ether) was added to 0.8 ml of 6.6′-diethylfulvene in ether. The white precipitate formed was filtered under argon and washed with a small amount of ether. $PhC(C_2H_5)_2CpLi$ (1.26 g) was obtained in 82% yield. Its solution in 10 ml of THF was added to 1.32 g of **1** in THF and stirred for about 2 h. After the solvent was removed, the residual solid was washed with petroleum (2 × 10 ml) and extracted with ether. The red product (0.88 g) was obtained in 43% yield (m.p. 166–167° C), Found: C, 65.02; H, 6.80; Ti, 10.27. $C_{26}H_{32}Cl_2OTi$ calcd.: C, 65.14; H, 6.74; Ti, 9.99%.

Compounds **5** and **6** were synthesized as above.

5: red, yield 74%, m.p. 106–107° C, Found: C, 61.15; H, 6.18; Ti, 11.22. $C_{24}H_{28}Cl_2OTi$ calcd.: C, 62.14; H, 6.16; Ti, 11.26%.

6: red, yield 52%, m.p. 125–125° C, Found: C, 63.56, H, 6.44; Ti, 11.16. $C_{25}H_{30}Cl_2OTi$, calcd.: C, 64.52; H, 6.51; Ti, 10.29%.

*X-ray determination of **1***

The single crystal of **1**, for molecular structure see Fig. 1, was obtained by recrystallization several times from dry benzene. The selected crystal, 0.4 × 0.3 × 0.3 mm^3 in size, was sealed in a capillary under argon for X-ray determination. It belongs to the monoclinic space group $P2_1/n$ with unit cell parameters: a 7.894(2), b 13.082(5), c 12.123(3) Å, β 100.26(2)°, V 1232 $Å^3$, $Z = 4$, D_c 1.64 g/cm^3, μ 13.1 cm^{-1} (Mo), $F(000) = 792$. Collection of intensity data and determination of the crystal structure were made on a Syntex R3 Crystallographic System. The intensity data were collected in the range of $0° < 2\theta < 50°$ in a ω scan mode at rate of 4–29.3°/min. Independent reflections totalling 1797 were collected. The SHELXTL programme was used to solve and refine the structure. The coordinates of Ti and Cl atoms were solved by direct methods, while the rest of non-hydrogen atoms were

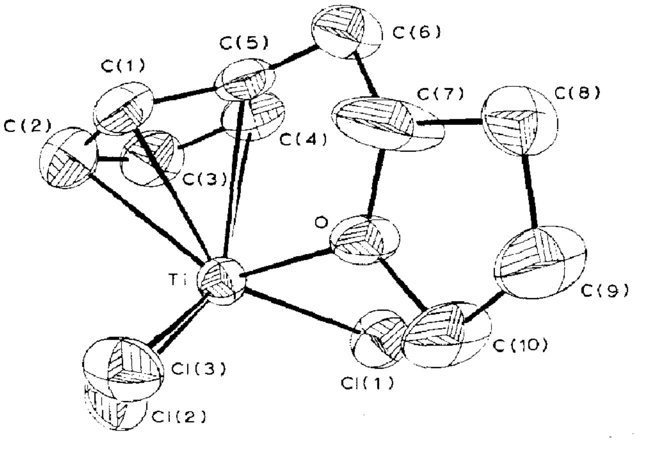


Fig. 1. Molecular structure of **1**.

found by means of difference Fourier map. The coordinates of hydrogen atoms were calculated theoretically. Refinement by full-matrix-block-least-squares for 1651 observed reflections gave the final *R* factor, 0.054.

Acknowledgement

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