Pergamon

0277-5387(95)00113-1

Polyhedron Vol. 14, No. 20 21, pp. 3005 3009, 1995

0277 5387/95 \$9.50+0.00

PREPARATION OF SOME CYCLOPENTADIENYL TITANIUM COMPLEXES AND CRYSTAL STRUCTURE OF (η^5-PENTAMETHYLCYCLOPENTADIENYL) {(1*R*,2*S*,3*R*)-*EXO*-3 [(*R*)-2-PHENYL-2-OLATO-ETHYL] SULPHENYL-1,7,7-TRIMETHYLBICYCLO[2.2.1]HEPTAN-2-OLATO} CHLOROTITANIUM(IV): [$Cp^*Ti(OC_{18}H_{24}SO)Cl]\cdot C_6H_6$

CHU-CHIEH LIN

Department of Chemistry, National Chung-Hsing University, Taichung 403,
Taiwan, R.O.C.

(*Received* 4 *January* 1995; *accepted* 2 *March* 1995)

Abstract—The reaction of (1*R*,2*S*,3*R*)-*exo*-3[(*R*)-2-phenyl-2-hydroxyethyl]sulphenyl-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (**1**) with Cp^*TiCl_3 in the presence of Et_3N furnishes the product $Cp^*Ti(OC_{18}H_{24}SO)Cl$ in high yield {Cp* = pentamethylcyclopentadienyl; $OC_{18}H_{24}SO$ = (1*R*,2*S*,3*R*)-*exo*-3[(R)-2-phenyl-2-olato-ethyl]sulphenyl-1,7,7-trimethylbicyclo[2.2.1]heptan-2-olato}. The structure of $Cp^*Ti(OC_{18}H_{24}SO)Cl\cdot C_6H_6$ (**2**) has been determined by X-ray crystallography. The reaction of $Cp_2Ti(X)Cl$ (X = Me, Cl) with 2-methoxybenzyl alcohol in the presence of Et_3N under refluxing benzene gave the product $Cp_2Ti(X)(o\text{-}OCH_2C_6H_4OMe)$ (X = Cl, Me).

Titanocene alkoxides have been known for many years and used in a number of organic reactions. It has been proposed that substrate molecules can be cooperatively activated by an early transition metal centre and a late-transition metal centre.[1] Alcohols associated with a phenyl ring are interesting due to their capability to act as a spacer by linking bimetallic centres.[2] The importance of chiral Lewis acid catalysts in organic synthesis has been demonstrated in recent years.[3] Difunctional ligands containing oxygen, sulphur or one sulphur and one oxygen have attracted considerable attention recently,[4] due to their ability to form bimetallic complexes of a variety of structures and their potential for the synthesis of asymmetric compounds.

In this paper, the high yield preparation of several titanium alkoxide derivatives is described. The complexes prepared are $Cp_2Ti(X)(o\text{-}OCH_2C_6H_4OMe)$ (X = Me or Cl) and [$Cp^*Ti(OC_{18}H_{24}SO)Cl$]. X-ray structural characterization of [$Cp^*Ti(OC_{18}H_{24}SO)Cl]\cdot C_6H_6$ (**2**) is also presented.

EXPERIMENTAL

General

All manipulations were carried out under dry nitrogen. Solvents were dried by refluxing for at least 24 h over sodium–benzophenone (benzene, hexane, ether) and freshly distilled prior to use. Deuterated solvents (Aldrich) were dried over molecular sieves. The compounds Cp^*TiCl_3,[5] $Cp_2TiMeCl$[6] and compound **1**[7] were prepared according to the literature methods. Cp_2TiCl_2 was purchased and used without further purification. 2-Methoxybenzyl alcohol (Aldrich) was purchased and stored over molecular sieves prior to use. Melting points were determined with a Buchi 535 digital melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-300 spectrometer with chemical shifts given in ppm from internal TMS. Mass spectra were recorded on a Jeol Jms-HX 110. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument.

Preparation of complex **2**

A mixture of **1** (0.460 g, 1.5 mmol) and Et_3N (0.42 cm^3, 3.0 mmol) in benzene (15 cm^3) was added slowly at 27°C to a benzene (15 cm^3) solution of Cp^*TiCl_3 (0.449 g, 1.5 mmol). White smoke was produced and the colour of the solution changed from deep red to orange. After stirring for 1 h, an orange solution was separated from a white powder by filtration. Volatile materials were removed *in vacuo* to give a yellow crystalline solid. Yield: 0.76 g (84.3%). Found: C, 67.5; H, 7.5. Calc. for $C_{34}H_{45}ClO_2STi$: C, 67.9; H, 7.6%. ^1H NMR ($CDCl_3$): 7.37 (s, 5H), 7.30 (s, 6H, C_6H_6), 5.34 (dd, 1H), 4.64 (d, 1H), 2.7–3.0 (m, 3H), 2.20 (s, 1H), 2.04 [s, 15H, $C_5(CH_3)$], 1.72–1.86 (m, 3H), 1.55 (s, 1H), 1.07 (s, 3H), 0.99 (s, 3H), 0.73 (s, 3H). Other ^1H resonances are not assigned.

Preparation of $Cp_2Ti(Cl)(o\text{-}OCH_2C_6H_4OMe)$

To a refluxing solution of Cp_2TiCl_2 (0.996 g, 4.0 mmol) in benzene (100 cm^3), a benzene (10 cm^3) solution of Et_3N (1.20 cm^3, 8.6 mol) and *o*-$MeOC_6H_4CH_2OH$ (1.066 g, 7.7 mmol) was added slowly, and the mixture was refluxed for 4 h. The orange-yellow clear solution was cooled to room temperature (27°C) and separated from a white powder by filtration. Volatile materials were removed under reduced pressure to afford an orange powder. The powder was then washed three times with ether (3 cm^3). The orange residue was then dried *in vacuo*. Yield: 1.14 g (81.3%). ^1H NMR ($CDCl_3$, ppm): 7.17 (d, 2H, 6.8 Hz), 6.94 (dt, 1H, 0.6–7.8 Hz), 6.81 (d, 1H, 8.4 Hz), 6.32 (s, 10H), 5.48 (s, 2H), 3.81 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): 155.70, 130.65, 127.67, 127.24, 120.18, 116.59 (Cp), 109.81, 78.69 (OCH_2), 55.15 (OCH_3). Found: C, 61.7; H, 5.5. Calc.: C, 61.7; H, 5.5%. Mass spectrum: 315 (0.92, M^+-Cl), 287, 285 (69.4, M^+-Cp). M.p. 140.2–141.0°C (dec.).

Table 1. Crystallographic data of $Cp^*TiCl(OC_{18}H_{24}SO)\cdot C_6H_6$

Formula	$C_{34}H_{45}ClO_2STi$
Formula weight	601.1
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	10.452(2)
b (Å)	14.975(2)
c (Å)	20.634(3)
V (Å^3)	3229.7(8)
Z	4
D_{calc} (g cm^{-3})	1.236
λ(Mo-K_α) (Å)	0.71073
Absorption coefficient (mm^{-1})	0.440
2θ range (°)	3.0–50.0
Scan type	θ–2θ
Reflections collected	3216
Independent reflections	3191
Observed reflections	2243 ($F > 2.0\sigma(F)$)
No. of refined parameters	352
R^a for significant reflections	0.0463
$R_w{}^b$ for significant reflections	0.0367
GoF^c	1.14

[a] $R = [\Sigma(|F_0|-|F_c|)/\Sigma|F_0|]$.

[b] $R_w = [\Sigma w(|F_0|-|F_c|)^2/\Sigma w|F_0|^2]^{1/2}$; $w = 1/\sigma^2(F)$.

[c] $GoF = [\Sigma w(|F_0|-|F_c|)^2/(N_{rflns}-N_{params})]^{1/2}$.

Preparation of $Cp_2Ti(Me)(o\text{-}OCH_2C_6H_4OMe)$

To a refluxing solution of $Cp_2TiMeCl$ (0.914 g, 4.0 mmol) in benzene (100 cm^3), a benzene (10 cm^3) solution of Et_3N (0.60 cm^3, 4.3 mol) and *o*-$MeOC_6H_4CH_2OH$ (0.552 g, 4 mmol) was added slowly. After all of the latter solution was added, the mixture was heated to 50°C for 2 h. The clear yellow solution was cooled to room temperature (27°C) and separated from a white powder by filtration. Volatile materials were removed *in vacuo* to give a yellow powder. Yield 1.25 g (94.6%). ^1H NMR ($CDCl_3$, ppm): 7.42–7.52 (m, 1H), 7.00–7.12 (m, 2H), 6.56 (d, 1H, 7.8 Hz), 5.68 (s, 10H, Cp), 5.43 (s, 2H), 3.34 (s, 3H), 0.80 (s, 3H). $^{13}C\{^1H\}$ NMR (C_6D_6, ppm): 156.04, 132.41, 127.38, 127.15, 120.73, 112.18 (Cp), 109.72, 74.99 (OCH_2), 54.51 (OCH_3), 33.94 ($TiCH_3$). Found: C, 69.1; H, 6.9. Calc.: C, 69.1; H, 6.7%. M.p. 99.7–101.5°C.

X-ray crystallographic studies

A suitable crystal of complex **2** was sealed in a thin-walled glass capillary under a nitrogen atmosphere and mounted on a Siemens R3m/V diffractometer. The crystallographic data were collected using a θ–2θ scan mode with Mo-K_α radiation. Cell constants were obtained by least-squares analysis on positions of 25 random reflections in the 2θ range of 7–25°. The space group determination was based on a check of the Laue symmetry and systematic absences, and was confirmed by the structure solution. The structure was solved by direct methods using the Siemens SHELXTL PLUS (VMS) program. All non-hydrogen atoms were located from successive Fourier maps. Anisotropic thermal parameters were used for all non-hydrogen atoms and fixed isotropic for hydrogen atoms, which were refined using a riding model. An ORTEP drawing is shown in Fig. 1 with 30% probability ellipsoids. Crystallographic data are given in Table 1.

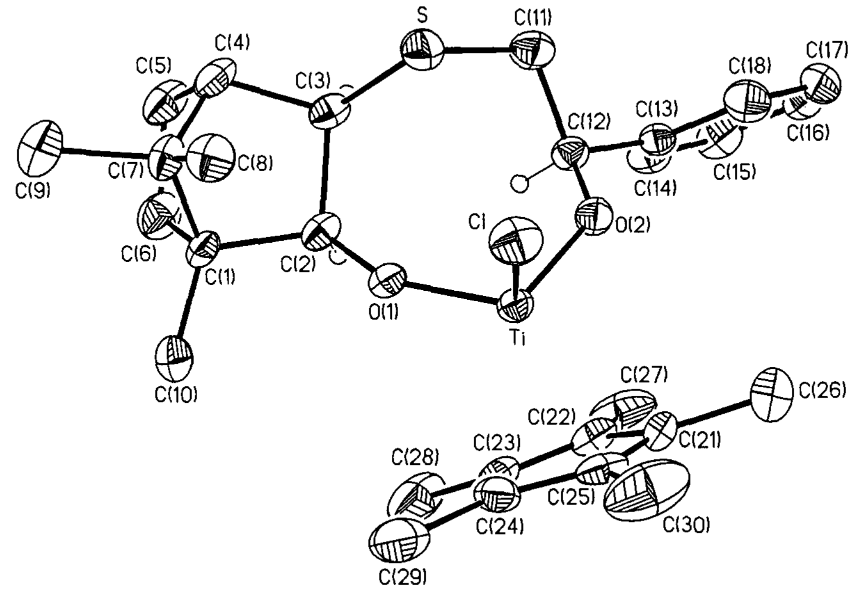


Fig. 1.

RESULTS AND DISCUSSION

Syntheses

Complex **2** was obtained from the reaction of compound **1** with Cp*TiCl$_3$ in the presence of Et$_3$N at room temperature in high yield, according to eq. (1).

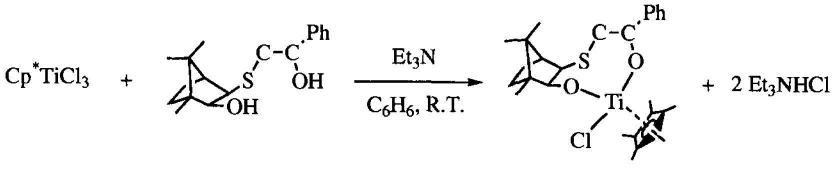
The reaction was observed by the sharp colour change from deep red to orange. The reaction was so rapid that white smoke was observed due to the formation of triethylammonium chloride during the addition of the mixture of compound **1** with Et$_3$N. The ^{1}H NMR spectrum of complex **2** showed that one benzene molecule was present per complex **2** molecule, which was verified by the elemental analysis and X-ray crystal structure determination.

The preparation of Cp$_2$Ti(X)(*o*-OCH$_2$PhOMe) (X = Me, Cl) was carried out by refluxing Cp$_2$Ti(X)Cl with 2-methoxybenzyl alcohol in the presence of Et$_3$N according to eq. (2).

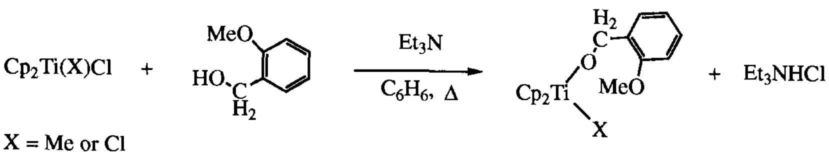
The reaction was unusually slow, with the colour changing from deep red to orange slowly. No reaction occurred without refluxing. Unlike Cp$_2$Ti(OPh)$_2$,[8] the disubstituted complex Cp$_2$Ti(*o*-OCH$_2$PhOMe)$_2$ was not obtained, even with the addition of an excess of 2-methoxybenzyl alcohol, probably due to the steric hindrance on the titanium centre.

Molecular structure of Cp*Ti(OC$_{18}$H$_{24}$SO)Cl·C$_6$H$_6$ (2)

Suitable crystals of Cp*Ti(OC$_{18}$H$_{24}$SO)Cl·C$_6$H$_6$ {OC$_{18}$H$_{24}$SO = (1*R*,2*S*,3*R*)-*exo*-3[(*R*)-2-phenyl-2-olato - ethyl]sulphenyl - 1,7,7 - trimethylbicyclo [2.2.1]heptan-2-olato} for X-ray structure determination were recrystallized from benzene. Difference Fourier maps revealed the presence of six peaks that were not within bonding distance of the complex. Examination of the bond distances and peaks leads to the conclusion of the exist-



(1)



(2)

Table 2. Selected bond lengths (Å) for **2**[a]

Ti—Cl	2.313(2)	Ti—O(1)	1.778(4)
Ti—O(2)	1.816(4)	Ti—C(21)	2.411(7)
Ti—C(22)	2.355(6)	Ti—C(23)	2.342(7)
Ti—C(24)	2.375(6)	Ti—C(25)	2.429(6)
S—C(3)	1.800(6)	S—C(11)	1.818(7)
O(1)—C(2)	1.403(7)	O(2)—C(12)	1.414(7)
Ti—X1	2.064(7)		

[a] X1 represents the centroid of the cyclopentadienyl ring.

Table 3. Selected bond angles (°) for **2**[a]

Cl—Ti—O(1)	105.4(1)	Cl—Ti—O(2)	107.1(1)
O(1)—Ti—O(2)	103.3(2)	O(1)—Ti—C(21)	143.0(2)
O(2)—Ti—C(21)	87.5(2)	Cl—Ti—C(21)	104.8(2)
O(1)—Ti—C(22)	110.6(2)	O(2)—Ti—C(22)	86.0(2)
Cl—Ti—C(22)	137.5(2)	O(1)—Ti—C(23)	87.6(2)
O(2)—Ti—C(23)	116.5(2)	Cl—Ti—C(23)	130.0(2)
O(1)—Ti—C(24)	99.4(2)	O(2)—Ti—C(24)	141.8(2)
Cl—Ti—C(24)	95.7(2)	O(1)—Ti—C(25)	133.0(2)
O(2)—Ti—C(25)	118.9(2)	Cl—Ti—C(25)	82.2(2)
Ti—O(1)—C(2)	152.7(4)	Ti—O(2)—C(12)	133.1(3)
X1—Ti—O(1)	117.1	X1—Ti—O(2)	117.1
X1—Ti—Cl	111.4	X1—Ti—S	170.8

[a] X1 represents the centroid of the cyclopentadienyl ring.

ence of a benzene molecule in the crystal. Selected bond lengths and bond angles are listed in Tables 2 and 3, respectively. An ORTEP diagram with atomic numbering is shown in Fig. 1.

The complex crystallizes in the non-centrosymmetric orthorhombic space group $P2_12_12_1$ (No. 18). The coordination geometry around titanium is approximately a three-legged "piano-stool" type geometry with an O(1)—Ti—Cl angle of 105.4(1)°, O(2)—Ti—Cl angle of 107.1(1)° and O(1)—Ti—O(2) angle of 103.3(2)°. The average angle (105.3°) is smaller than the average angle (115.0°)[4] of the regular four-legged "piano-stool" type complexes, but is somewhat larger than the average angle (101.8°)[4,9] of the normal three-legged "piano-stool" type complexes. The Ti—O(1) and Ti—O(2) distances are 1.778(4) and 1.816(4) Å, respectively, which are within the normal range for a Ti—O bond. The distance between the centre (X1) of the cyclopentadienyl and titanium is 2.064(7) Å and the Ti—Cl distance of 2.313(2) Å appears to be normal compared to other titanocene chloride complexes.[4,9]

Supplementary material available

Tables giving full details of the crystal data collection, structure solution parameters, atomic coordinates of all atoms, bond distances, bond angles and anisotropic and isotropic thermal parameters of non-hydrogen atoms have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements—Financial support from The National Science Council of the Republic of China is gratefully acknowledged. I also thank Professor T. K. Yang and H. M. Gau for helpful discussions.

REFERENCES

1. (a) D. W. Stephan, *Coord. Chem. Rev.* 1989, **95**, 42; (b) S. A. Stevenson, J. A. Dumesic, R. T. K. Baker and E. Ruckenstein (Eds), *Metal–Support Interactions in Catalysis, Sintering, and Redispersion*. Van Nostrand-Reinhold, New York (1987).
2. (a) H. M. Gau, C. T. Chen, T. T. Jong and M. Y.

Chien, *J. Organomet. Chem.* 1993, 99; (b) H. M. Gau, C. T. Chen and C. C. Schei, *J. Organomet. Chem.* 1992, 307; (c) T. Y. Huang, C. T. Chen and H. M. Gau, *J. Organomet. Chem.*, in press.

3. (a) A. Hafner, R. O. Duthaler, R. Marti, G. Rihs, P. Rothe-Streit and F. Schwarzenbach, *J. Am. Chem. Soc.* 1992, **114**, 2321; (b) U. Pindur, G. Lutz and C. Otto, *Chem. Rev.* 1993, 741.
4. (a) H. M. Gau, C. A. Chen, S. J. Chang, W. E. Shih, T. K. Yang, T. T. Jong and M. Y. Chien, *Organometallics* 1993, **12**, 1314; (b) T. T. Nadasdi, Y. Huang and D. W. Stephan, *Inorg. Chem.* 1993, **32**, 347; (c) A. Hafner, R. O. Duthaler, R. Marti, G. Rihs, P. Rothe-Streit and F. Schwarzenbach, *J. Am. Chem. Soc.* 1992, **114**, 2321.
5. G. H. Liinas, M. Mena, F. Palacios, P. Royo and R. Serrano, *J. Organomet. Chem.* 1988, **340**, 37.
6. H. C. Beachell and S. A. Butter, *Inorg. Chem.* 1965, **4**, 1133.
7. S. M. Hung, M.S. Thesis, National Chung-Hsing University (1990).
8. K. Andra, *J. Organomet. Chem.* 1968, **11**, 567.
9. (a) C. H. Winter, X. X. Zhou, D. A. Dobbs and M. J. Heeg, *J. Organomet. Chem.* 1991, **10**, 210; (b) U. Thewalt and D. Schomburg, *J. Organomet. Chem.* 1977, **127**, 169.