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Intramolecular cyclization of benzyl-substituted cyclopentadienyl titanium dichlorides promoted by boron tribromide

Yanlong Qian [a,*], Jiling Huang [a], Kai Ding [a], Yue Zhang [a], Qinglan Huang [a], Xiao Ping Chen [a], Albert S.C. Chan [b,*], Wing Tak Wong [c]

[a] *Laboratory of Organometallic Chemistry, East China University of Science and Technology, 130 Meilong Road, P.O. Box 421, Shanghai 200237, China*

[b] *Department of Applied Biology and Chemical Technology, Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China*

[c] *Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong, China*

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Abstract

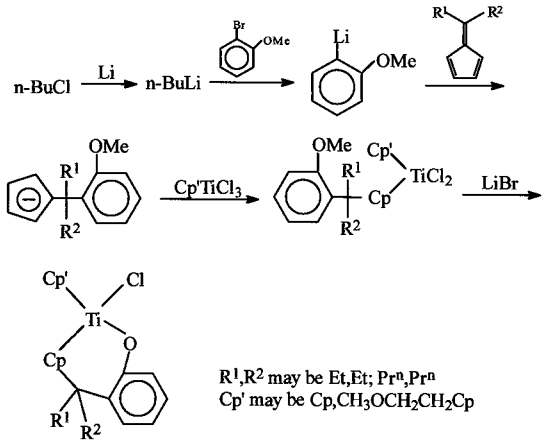
Intramolecular cyclization of α,α-alkyl-*ortho*-methoxybenzylcyclopentadienyl titanium complexes to form titanoxacycle complexes promoted by BBr_3 has been studied. A probable two-step mechanism involving halogen exchange and intramolecular elimination was proposed. Four related benzyl-substituted cyclopentadienyl titanium complexes have been studied by X-ray crystallography. © 2002 Published by Elsevier Science B.V.

Keywords: Titanoxacycle; Halogen exchange; Intramolecular cyclization; Boron tribromide

1. Introduction

Because of the importance of the cyclopentadiene ligand in organometallic chemistry, much attention has been paid to the synthesis of new types of substituted cyclopentadienes and their transition metal complexes. Recent interest in our laboratory is focused on the chemistry of new types of substituted titanocene and zirconocene complexes [1–5], which may be used as effective catalysts for hydrogenation [6–8], isomerization [9–12] and polymerization [13–21]. One of the main themes of this study is an understanding of intramolecular coordination and elimination of α,α-dialkyl-*ortho*-methoxybenzylcyclopentadienyl titanium complexes to form titanoxacycle complexes [22,23], which seem to have potential use as catalysts in olefin polymerization. Our previous investigations have demonstrated that in the preparation of *ortho*-MeO-containing benzyl-substituted titanium complexes, when the benzylic carbon atom is substituted with an ethyl or larger group, titanoxacycle complexes are always formed, as shown in Scheme 1 [22,23].

The cyclization reaction is promoted by halides, such as LiBr. If one of the substituents on the benzylic carbon atom of the complexes is a methyl group or 1,5-pentylidene group, the cyclization will not easily take place, usually only mixtures were obtained. The large substituents on the benzylic carbon atom cause the benzene ring to shift towards the titanium atom,



Scheme 1.

* Corresponding authors. Tel./fax: +86-21-64702573.
E-mail address: qianling@online.sh.cn (Y. Qian).

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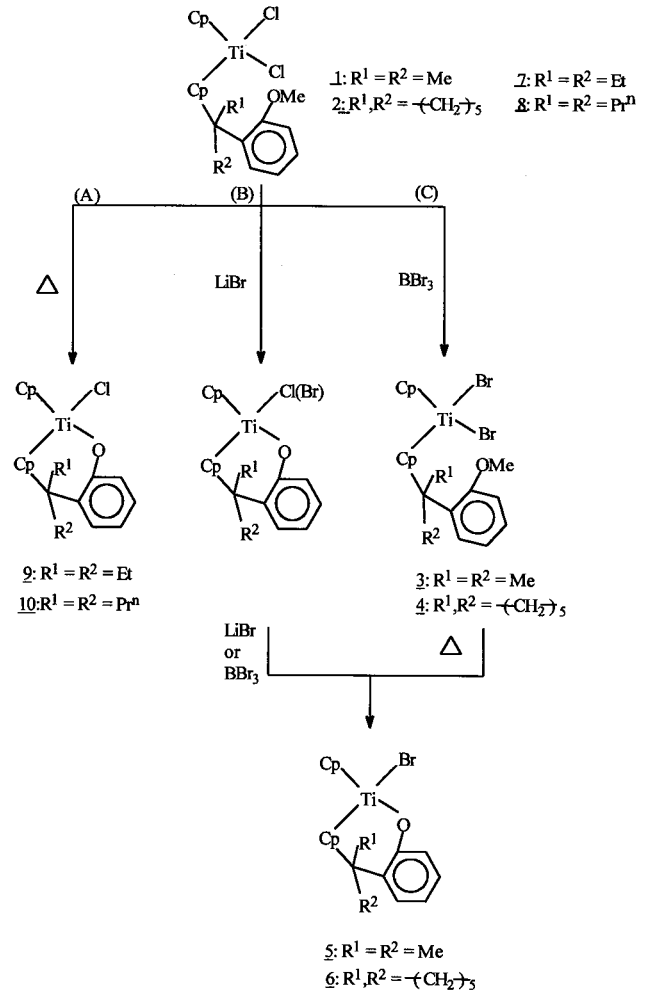


Scheme 2.

thus facilitating a favorable spatial orientation for the cyclization. In order to extend this work, we have performed the corresponding cyclizations using α,α-dimethyl or $-(CH_2)_5$-*ortho*-methoxybenzylcyclopentadienyl titanium complexes, in an attempt to obtain a series of novel titanoxacycle complexes. Thus, a series of benzyl-substituted cyclopentadienyl titanium complexes has been synthesized. Such pure complexes have never been isolated by using our previous method, by heating or by the LiBr-promoted reaction [23], and four of them have been studied by X-ray crystallography.

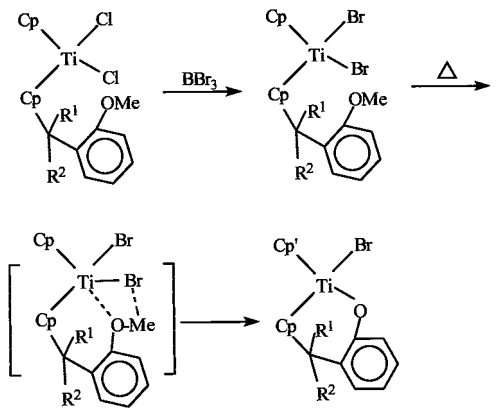
2. Results and discussion

After further study on such cyclization methodology the reaction may be outlined as shown in Scheme 2.

In the case of $R_1 = R_2 = Et$ or Pr^n, the cyclization takes place readily [23] on heating without halide as promoter (see pathway A). In the presence of halide, such as LiBr, the cyclization may be completed, but it is sometimes accompanied by halogen exchange to give a mixture of chloride and bromide. If the reaction time is prolonged for more than 100 h on heating, it is possible to isolate a pure bromide product (see pathway B). In this case, we believe that dibromides **3** and **4** should also formed as intermediates in the reaction mixtures, but never were isolated as pure products. After extensive screening of metal halides as promoters, BBr_3 was found to be a more effective and controllable promoter for the cyclization. In the presence of BBr_3, the reaction may be stopped after the halogen-exchange step. Therefore, two dibromides **3** and **4**, were isolated as pure products which may be converted into titanoxacycle complexes easily on heating, or in the presence of BBr_3 for a longer reaction time (see pathway C). Of course, the dichlorides may be converted into titanoxacycle complexes directly by BBr_3 and a mixture of titanoxacycle chloride and bromide was also converted conveniently into pure bromide.

In the present work, a series of benzyl-substituted cyclopentadienyl titanium compounds have been synthesized and well characterized. Among them, the molecular structures of complexes **1**, **4**, **5**, and **6**, have been studied by X-ray diffraction. Their crystal data, selected bond lengths and angles are listed in Tables 1 and 2. The structures are shown in Figs. 1–4.

The attempts to prepare titanocene dibromides by the reaction of titanocene dichlorides with KBr or LiBr were unsuccessful, and the products isolated proved to be mixtures of unconverted chloro complex, corresponding bromo compound and mixed halo compounds [24]. Instead, BBr_3 is a more effective halogen exchanging reagent for preparative reactions of metallocenes dibromides from corresponding dichlorides in high yields [25]. Therefore, the mechanism of the cyclization may be proposed as follows (Scheme 3):



Scheme 3.

The first step is halogen exchange from the dichloride to the dibromide. The second step is intramolecular coordination between Ti···O and Br···CH_3 through a four-membered ring transition state; then the titanoxacycle bromide complex is formed by elimination of

CH_3Br. Besides, BBr_3 is a good Lewis acid which easily producing a Br^- anion and thus promotes demethylation of aryl methyl ether [26,27]. In our case, it seems to be that the BBr_3 as a Lewis acid for demethylation is also involved, and thus in the fact formation of titanocyclic compounds with BBr_3 is a complicated reaction. A further study of the mechanism will be done in the future.

3. Experimental

All reactions were carried out under an inert atmosphere using standard Schlenck techniques. Solvents were refluxed over Na wire and benzophenone and distilled under Ar prior to use. Melting points were uncorrected. ^{1}H-NMR spectra were recorded on a GERMINI-300 spectrometer using $CDCl_3$ as solvent and Me_4Si as an internal standard. IR spectra were measured on a NICOLET MAGNA-IR550. MS were obtained on a HP5989A Mass Spectrometer. The compounds **1**, **2**, **7**, **8**, **9** and **10** were synthesized according to our previous method [23].

X-ray data were collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo–K_α radiation and a 12 kW rotating anode generator.

3.1. Synthesis of *3*

A solution of BBr_3 (2.4 ml, 0.22 mol) in 5 ml of CH_2Cl_2 was added dropwise to a solution of **1** (400 mg, 1 mmol) in 10 ml of CH_2Cl_2 with stirring at 0 °C. It was stirred for 2 h at room temperature (r.t.). After the solvent was removed, a dark black solid was obtained as crude product. It was passed though a microcrystal column with petroleum ether–$CHCl_3$ as eluant. The solvent was removed, and the remaining solid was recrystallized from $CHCl_3$–petroleum in the refrigerator to afford 100 mg of dull red pure sample in 20% yield, m.p. 174–176 °C, ^{1}H-NMR (δ ppm): 6.95–6.94 (m, 4H), 6.66 (s, 5H), 6.59–6.85 (m, 4H), 3.67 (s, 3H), 1.78 (s, 6H). MS (m/e): 405 ($M-Br$, 2), 390 ($M-CH_3Br$, 32), 325 ($M-CH_3Br-Cp$, 56), 311 ($M-CH_3Br-Br$, 42), 94 (CH_3Br, 100). IR (KBr, cm^{-1}): 3136w, 3114m, 3082m, 2998w, 2935w, 2874w, 2831m, 1593w, 1580w, 1490m, 1479m, 1444m, 1434m, 1291m, 1243s, 1181w, 1148w, 1091m, 1031m, 835s, 824s, 744s. Anal. Calc. for $C_{20}H_{22}Br_2OTi$: C, 49.41; H, 4.57. Found: C, 48.74; H, 4.49%.

3.2. Synthesis of *4*

To a solution of **2** (440 mg, 1 mmol) in 7 ml of CH_2Cl_2, BBr_3 (0.1 ml, 1 mmol) in 6 ml of CH_2Cl_2 was added dropwise with stirring at 0 °C. It was stirred for 2 h. The solvent was removed. It was passed through a microcrystal column with petroleum ether–$CHCl_3$ as eluant. After the solvent was removed, the remaining solid was recrystallized from chloroform and petroleum ether in refrigerator. Black crystals (70 mg) were ob-

Table 1
Crystallographic data

Compound	**1**	**4**	**5**	**6**
Empirical formula	$C_{20}H_{22}TiOCl_2$	$C_{23}H_{26}TiOBr_2$	$C_{19}H_{19}TiOBr$	$C_{22}H_{23}TiOBr$
Formula weight	397.20	526.17	391.16	431.23
Color and habit	Orange, block	Red, block	Orange, block	Red, block
Crystal system	Triclinic	Monoclinic	Orthorhombic	Triclinic
Space group	$P\bar{1}$ (#2)	$P2_1/a$ (#14)	$P2_12_12_1$ (#19)	$P\bar{1}$ (#2)
a (Å)	6.684(1)	13.881(2)	11.028(1)	10.126(2)
b (Å)	10.870(1)	11.652(2)	14.992(2)	12.340(2)
c (Å)	13.450(1)	14.632(2)	9.976(1)	8.269(2)
α (°)	101.74(1)			100.58(2)
β (°)	101.27(1)	117.447(9)		95.44(2)
γ (°)	100.15(1)			112.58(1)
V (Å^3)	914.3(2)	2100.1(6)	1649.2(3)	922.2(3)
Z	2	4	4	2
D_{calc} (g cm^{-3})	1.443	1.664	1.575	1.553
μ(Mo–K_α) (cm^{-1})	7.64	42.35	29.48	26.44
F(000)	412.00	1056.00	792.00	440.00
Scan type	ω–2θ	ω–2θ	ω–2θ	ω–2θ
Max. 2θ (°)	47.9	48.0	45.0	48.0
Crystal size (mm)	$0.19\times0.20\times0.31$	$0.23\times0.28\times0.29$	$0.21\times0.21\times0.32$	$0.14\times0.22\times0.34$
Scan rate (° min^{-1})	4–16.0	6–16.0	6–16.0	6–16.0
Reflections observed	3154	3639	1275	3091
R	0.030	0.050	0.054	0.033
R_w	0.030	0.047	0.047	0.032
Goodness-of-fit	1.99	3.20	2.90	1.48

Table 2
Selected bond lengths (Å) and angles (°) of **1**, **4**, **5**, **6**

1	**4**	**5**	**6**				
Bond lengths							
Ti(1)–Cl(1)	2.3739(9)	Ti(1)–Br(1)	2.539(2)	Ti(1)–Br(1)	2.535(4)	Ti(1)–Br(1)	2.565(1)
Ti(1)–Cl(2)	2.3490(9)	Ti(1)–Br(2)	2.496(2)	Ti(1)–O(1)	1.86(1)	Ti(1)–O(1)	1.878(3)
Ti(1)–C(1)	2.357(3)	Ti(1)–C(1)	2.37(1)	Ti(1)–C(1)	2.32(2)	Ti(1)–C(1)	2.369(5)
Ti(1)–C(2)	2.398(3)	Ti(1)–C(2)	2.34(1)	Ti(1)–C(2)	2.30(2)	Ti(1)–C(2)	2.373(5)
Ti(1)–C(3)	2.389(3)	Ti(1)–C(3)	2.37(1)	Ti(1)–C(3)	2.35(2)	Ti(1)–C(3)	2.405(5)
Ti(1)–C(4)	2.389(3)	Ti(1)–C(4)	2.38(1)	Ti(1)–C(4)	2.36(2)	Ti(1)–C(4)	2.372(5)
Ti(1)–C(5)	2.351(3)	Ti(1)–C(5)	2.38(1)	Ti(1)–C(5)	2.36(2)	Ti(1)–C(5)	2.332(5)
Ti(1)–C(6)	2.482(3)	Ti(1)–C(6)	2.49(1)	Ti(1)–C(15)	2.44(2)	Ti(1)–C(18)	2.377(5)
Ti(1)–C(7)	2.389(3)	Ti(1)–C(7)	2.38(1)	Ti(1)–C(16)	2.41(2)	Ti(1)–C(19)	2.402(5)
Ti(1)–C(8)	2.317(3)	Ti(1)–C(8)	2.30(1)	Ti(1)–C(17)	2.35(3)	Ti(1)–C(20)	2.382(5)
Ti(1)–C(9)	2.363(3)	Ti(1)–C(9)	2.35(1)	Ti(1)–C(18)	2.34(3)	Ti(1)–C(21)	2.378(5)
Ti(1)–C(10)	2.417(3)	Ti(1)–C(10)	2.41(1)	Ti(1)–C(19)	2.39(2)	Ti(1)–C(22)	2.387(5)
Bond angles							
Cl(1)–Ti(1)–Cl(2)	92.80(3)	Br(1)–Ti(1)–Br(2)	91.63(8)	Br(1)–Ti(1)–O(1)	93.8(4)	Br(1)–Ti(1)–O(1)	96.3(1)
Cl(1)–Ti(1)–C(1)	104.89(9)	Br(1)–Ti(1)–C(1)	106.2(4)	Br(1)–Ti(1)–C(1)	116.1(5)	Br(1)–Ti(1)–C(1)	121.2(2)
Cl(1)–Ti(1)–C(2)	77.53(8)	Br(1)–Ti(1)–C(2)	134.2(3)	Br(1)–Ti(1)–C(2)	83.3(5)	Br(1)–Ti(1)–C(2)	87.3(1)
Cl(1)–Ti(1)–C(3)	84.78(9)	Br(1)–Ti(1)–C(3)	117.1(3)	Br(1)–Ti(1)–C(3)	81.3(5)	Br(1)–Ti(1)–C(3)	77.4(1)
Cl(1)–Ti(1)–C(4)	117.86(9)	Br(1)–Ti(1)–C(4)	84.5(4)	Br(1)–Ti(1)–C(4)	109.9(6)	Br(1)–Ti(1)–C(4)	103.0(1)
Cl(1)–Ti(1)–C(5)	133.85(9)	Br(1)–Ti(1)–C(5)	78.1(4)	Br(1)–Ti(1)–C(5)	136.3(5)	Br(1)–Ti(1)–C(5)	134.3(1)
Cl(2)–Ti(1)–C(6)	85.07(7)	Br(2)–Ti(1)–C(6)	86.6(3)	Br(1)–Ti(1)–C(15)	91.0(10)	Br(1)–Ti(1)–C(18)	135.3(1)
Cl(2)–Ti(1)–C(7)	116.82(8)	Br(2)–Ti(1)–C(7)	118.5(3)	Br(1)–Ti(1)–C(16)	123.3(10)	Br(1)–Ti(1)–C(19)	112.7(2)
Cl(2)–Ti(1)–C(8)	137.35(9)	Br(2)–Ti(1)–C(8)	137.3(3)	Br(1)–Ti(1)–C(17)	132.0(9)	Br(1)–Ti(1)–C(20)	81.4(1)
Cl(2)–Ti(1)–C(9)	109.81(9)	Br(2)–Ti(1)–C(9)	109.3(3)	Br(1)–Ti(1)–C(18)	102.0(1)	Br(1)–Ti(1)–C(21)	80.8(2)
Cl(2)–Ti(1)–C(10)	80.89(8)	Br(2)–Ti(1)–C(10)	81.4(3)	Br(1)–Ti(1)–C(19)	79.5(7)	Br(1)–Ti(1)–C(22)	111.3(2)
				O(1)–Ti(1)–C(1)	78.0(5)	O(1)–Ti(1)–C(1)	77.8(1)
				O(1)–Ti(1)–C(2)	88.7(6)	O(1)–Ti(1)–C(2)	85.0(2)
				O(1)–Ti(1)–C(3)	124.2(7)	O(1)–Ti(1)–C(3)	57.1(2)
				O(1)–Ti(1)–C(4)	135.0(6)	O(1)–Ti(1)–C(4)	57.9(2)
				O(1)–Ti(1)–C(5)	103.5(6)	O(1)–Ti(1)–C(5)	34.7(2)

tained in 15% yield, m.p. 190–196 °C. ^{1}H-NMR (δ ppm): 7.50–6.90 (m, 4H), 6.70–6.20 (m, 9H), 3.80 (s, 3H), 1.98–1.00 (m, 10H). MS (m/e): 430 ($M - CH_3Br$, 6), 365 ($M - CH_3Br - Cp$, 10), 351 ($M - CH_3Br - Br$, 6). IR (KBr, cm^{-1}): 1595w, 1480m, 1460m, 1235s, 1175s, 1100s, 1020s, 820s, 750s.

3.3. Synthesis of **5**

3.3.1. Method 1

BBr_3 (0.2 ml, 2 mmol) was added to a solution of **1** (400 mg, 1 mmol) in 15 ml of CH_2Cl_2 with stirring under Ar. The reaction mixture changed in color from red to black immediately. It was stirred for 2 h at r.t. After the solvent was removed, it was passed through a microcrystal column with $CHCl_3$ as eluant. It was stirred overnight at 50 °C. Under reduced pressure the solvent was removed. The remaining solid was recrystallized from C_6H_6 and petroleum ether. An analytically pure sample was obtained as red crystals in 52% yield, m.p. 192–194 °C.

^{1}H-NMR (δ ppm): 7.35–6.88 (m, 4H), 6.52 (s, 5H), 6.47–5.54 (m, 4H), 1.59 (s, 3H),1.30 (s, 3H). MS (m/e):

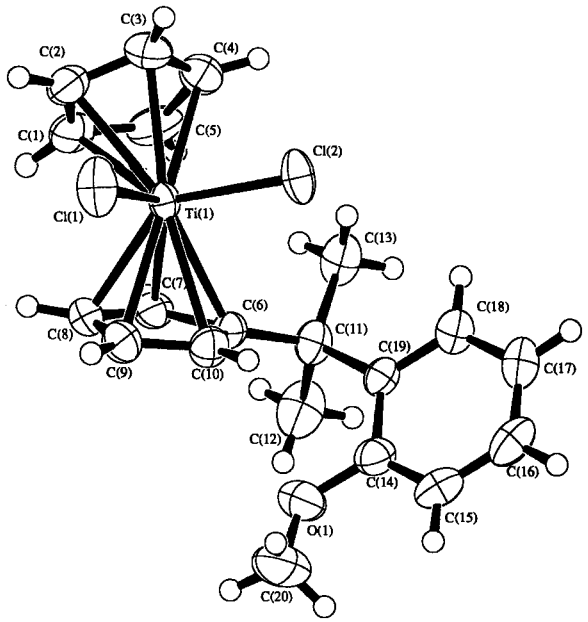


Fig. 1. Molecular structure of **1**.

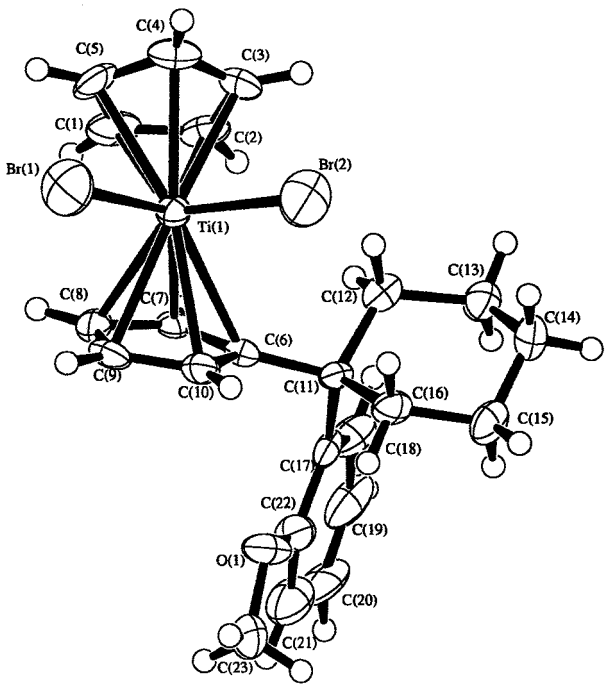


Fig. 2. Molecular structure of **4**.

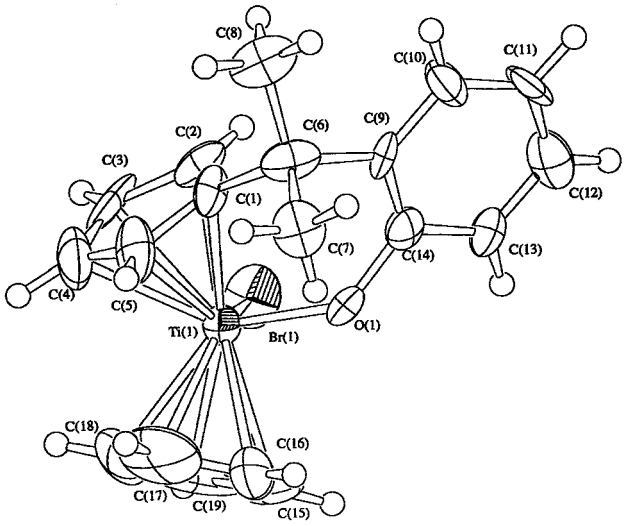


Fig. 3. Molecular structure of **5**.

390 (M, 36), 325 (M − Cp, 55), 311 (M − Br, 100), 310 (M − Cp − CH_3, 30), 296 (M − Br − CH_3, 24), 65 (Cp, 12). IR (KBr, cm^{-1}): 3110m, 2960m, 2870m, 1593m, 1571w, 1475s, 1446s, 1362m, 1255s, 1020m, 840s, 820s, 750s. Anal. Calc. for $C_{19}H_{19}BrOTi$: C, 58.33; H, 4.91. Found: C, 58.39; H, 4.91%.

3.3.2. Method 2

A solution of LiBr (227 mg, 2.2 mmol) and **1** (215 mg, 0.5 mmol) in 30 ml of THF was stirred for 100 h at 40 °C. Then after the solvent was removed it was passed through a microcrystal column with $CHCl_3$ as eluant. The eluant was concentrated, petroleum ether was added, and orange red crystals were obtained in 45% yield. ^{1}H-NMR spectrum was identical with the authentic sample.

3.3.3. Method 3

A solution of **3** (485 mg, 1 mmol) in 5 ml of $CHCl_3$ with stirring for 20 h at 60 °C. The solvent was removed and it was recrystallized from $C_6H_5CH_3$ and n-C_6H_{14}. Compound **5** was obtained in 50% yield.

3.4. Synthesis of **6**

By using compound **2** as starting material, compound **6** was synthesized in the same way as in Section 3.3.1. Red crystals were obtained, in 30% yield, m.p. 195–196 °C. ^{1}H-NMR (δ ppm): 7.48 (d-m, 1H), 7.04 (t-m, 1H), 6.87 (t-m, 1H), 6.51, 6.47 (s, 5H), 6.49 (m, 1H), 6.38 (m, 1H), 6.29 (m, 1H), 6.13 (m, 1H), 5.43–5.34 (m, 1H), 1.30–1.80 (m, 10H). MS (m/e): 430 (M, 41), 365 (M − Cp, 100), 351 (M − Br, 42). IR (KBr, cm^{-1}): 3200–3100w, 2970m, 2950m, 2880m, 1600m, 1580m, 1480s, 1440s, 1300w, 1230s, 1160m, 1120m, 1040m, 880s, 820s, 770s. Anal. Calc. for $C_{22}H_{23}BrOTi$: C, 61.27; H, 5.39. Found: C, 61.47; H, 5.39%.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 135658, 135659, 135660 and 135661 for compounds **1**, **4**, **5** amd **6**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.ac.uk).

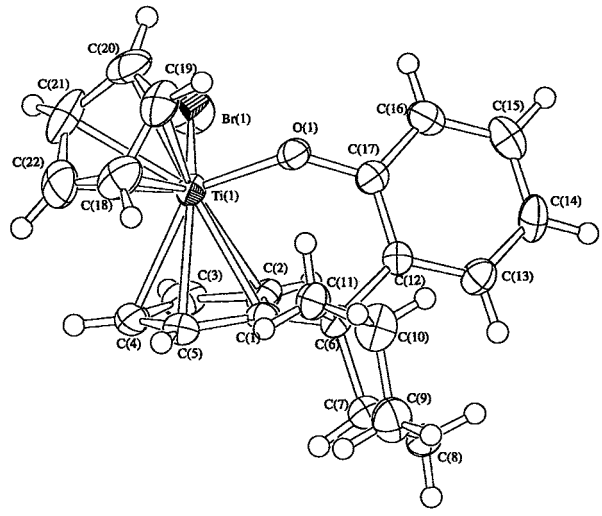


Fig. 4. Molecular structure of **6**.

Acknowledgements

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