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Syntheses, structures and reactions of some new benzyl-substituted cyclopentadienyl titanium complexes

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Abstract

Twenty eight new benzyl-substituted cyclopentadienyl titanium complexes have been synthesized. Among them, five typical molecular structures have been studied by X-ray analysis. It was found that in the preparation of *ortho*-MeO-containing benzyl-substituted titanium complexes, when both two substituents on benzylic carbon atom are Et or more large group, titanoxacycle complexes are always formed. The cyclization was promoted by the presence of halides. The activity order of halides for the cyclization is: LiI–NaI > LiBr–Br_2 > NaBr–KI > KBr > I_2. High temperature is favourable to the cyclization. At 80°C, the normal *ortho*-MeO benzyl-substituted cyclopentadienyl titanium complex **26** may be spontaneously converted into metallocyclic complex **19**. The position of the MeO group on the benzene ring is the key factor to the cyclization. In the case of *meta*- and *para*-MeO benzyl-substituted titanium complexes **23** and **25**, there was no possibility to form a titanoxacycle complex, such as **19**, because the MeO group is too far from titanium. A probable mechanism involving a four-membered transition state was proposed. © 1997 Elsevier Science S.A.

1. Introduction

Investigation of synthesis, structure and reactivity of metal complexes with cyclopentadienyl ligands remains an active research field in organometallic chemistry. A number of interests are related to the introduction of various kinds of substituents into the cyclopentadienyl ligand, aimed at studying the relationship between the structures of complexes and their catalytic activities. Among them, great attention has been paid to substituted titanocene and zirconocene complexes, which have been used as effective catalysts in a number of reactions, such as hydrogenation [1–3], isomerization [4–6] and polymerization [7–9] of olefin, hydrogenolysis [10] of halides, and reduction [11] of carbonyl compounds.

In recent years, there has been special interest in the synthesis of new types of titanocene and zirconocene complexes, because they enable highly effective single-site catalysis in olefin polymerization. Previous studies in our group have been focused on the chemistry of substituted cyclopentadienyl titanium and zirconium complexes, their syntheses, structures and catalytic reactions. To compare the substituent effects, more than 300 substituted titanocene and zirconocene complexes have been synthesized in our laboratory [12–18]. Among them, benzyl-substituted cyclopentadienyl titanium complexes were investigated in some detail, because of their unique features in catalytic isomerization of olefin. We used isomerization of 1,5-hexadiene as a model reaction to study the effect of substituents

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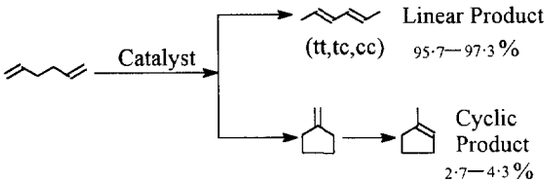
on the rings of the cyclopentadienyl titanium catalysts, and found [6] that benzyl substituents favour the formation of linear products:



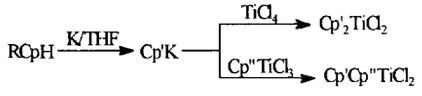
(1)

It seems that there is some interaction between the benzyl group and titanium atom, which control the reaction direction. To study the mechanism of the reaction catalyzed by benzyl-substituted cyclopentadienyl titanium complexes, we have synthesized a series of such complexes and studied their reactions. As in the previous communication [19], we reported part of the results; here, we present the full details.

2. Results and discussion

2.1. Benzyl-substituted cyclopentadienyl titanium complexes

Substituted cyclopentadienes prepared from the reaction of CpNa and RX or ROTs were converted into the corresponding potassium salts, which reacted with $TiCl_4$ to give bis(substituted cyclopentadienyl) titanium dichloride (Cp'_2TiCl_2), or reacted with $Cp''TiCl_3$ to give the differently substituted cyclopentadienyl titanium dichloride ($Cp'Cp''TiCl_2$) [20]. $Cp''TiCl_3$ was prepared from Cp''_2TiCl_2 and SO_2Cl_2 in $SOCl_2$ [21]:



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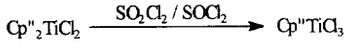
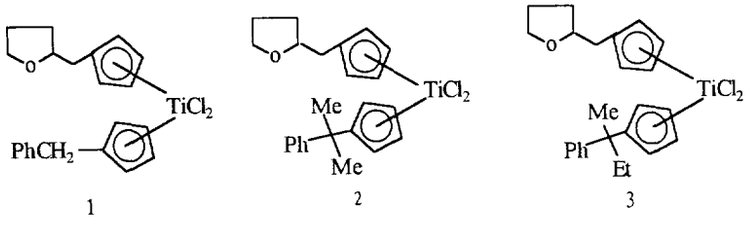
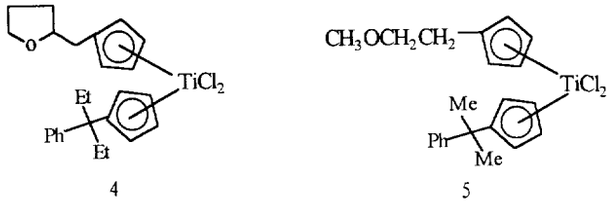


(3)

According to the above general synthetic route, the following complexes have been synthesized.





A single crystal of **5** was obtained by recrystallization from cool ether (−5°C), and its molecular structure was determined by X-ray diffraction and shown in Fig. 1. Crystal data, selected bond lengths and bond angles are listed in Tables 1 and 2.

The two Cp rings are staggered with the two substituents oriented in opposite directions. The ethereal oxygen atom does not chelate with the titanium as found in $CH_3OCH_2CH_2C_5H_4TiCl_3$ [21]. Because of the presence of a substituent on both Cp rings, the distances between the titanium and each carbon atom in the Cp rings are significantly

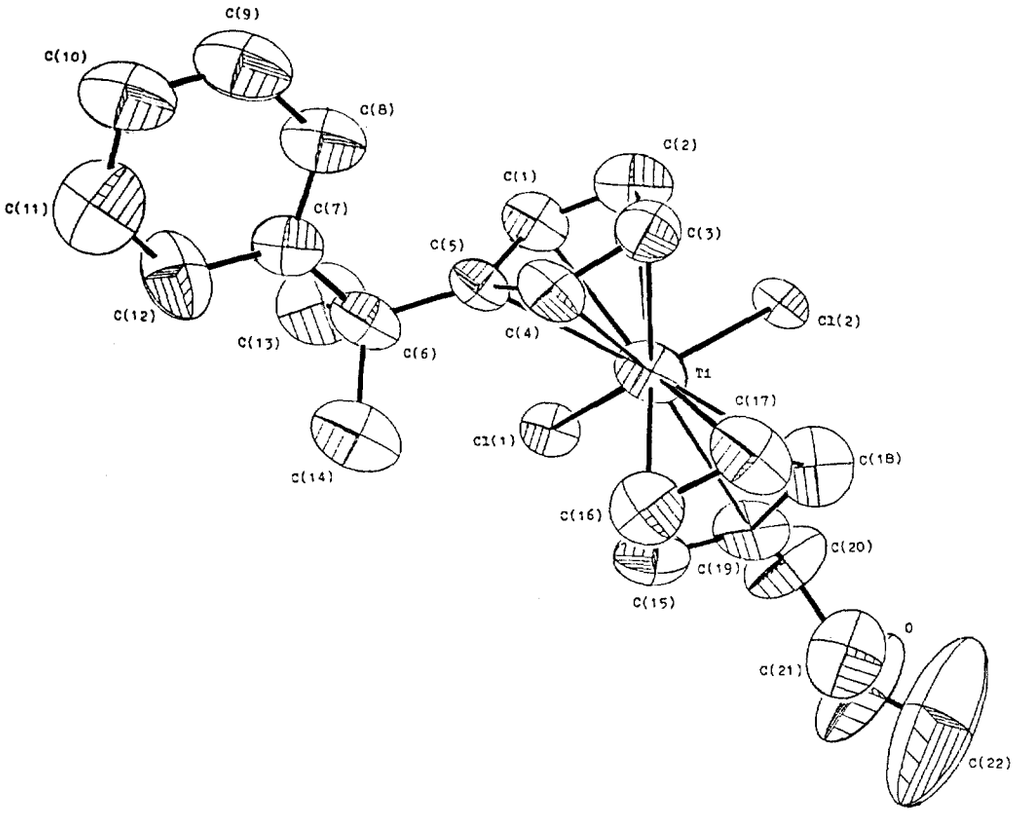
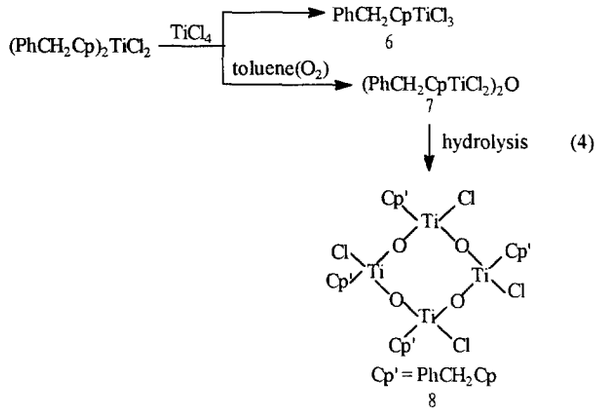


Fig. 1. Molecular structure of **5**.

unequal; the biggest differences for ring C(1)–C(5) and ring C(15)–C(19) are 0.176 Å and 0.107 Å, respectively. The more bulky the substituent is, the farther it is away from the titanium.

In the preparation of benzyl-substituted titanium trichloride, if a normal toluene was used, it gave $(PhCH_2CpTiCl_2)_2O$ **7** as main product that may be further hydrolysed into an eight-member ring compound **8**:



Complex **8** was air-stable and it may be recrystallized in cool ether; the yellow particle crystal was obtained. The molecular structure was determined by X-ray diffraction and is shown in Fig. 2, and the elemental cell of the crystal is shown in Fig. 3. The crystal data, selected bond lengths and bond angles are listed in Tables 1 and 2.

Table 1
The crystal data of complex **5**, **8**, **16**, **19** and **28**

Compound	**5**	**8**	**16**	**19**	**28**
Formula weight	$C_{22}H_{26}TiOCl_2$ /425.25	$C_{48}H_{44}Ti_4O_4Cl_4$ /1018.29	$C_{23}H_{26}TiOCl_2$ /437.27	$C_{21}H_{23}ClOTi$/374.77	$C_{34}H_{42}Cl_2O_4Ti_2$ /681.42
Colour and habit	Red/octahedral	Yellow/plates	Red	Orange, octahedral	
Crystal system	Monoclinic	Monoclinic		Monoclinic	Monoclinic
Space group	C_i^1-PT	C_{2h}^4-P2/n	$P_{z1/a}$	C_{2h}^5-P21/n	$P2_1/c$
a (Å)	6.774(7)	13.011(2)	13.511(6)	14.780(5)	6.882(3)
b (Å)	12.802(14)	10.141(2)	11.642(9)	13.420(3)	13.476(6)
c (Å)	13.822(13)	18.129(4)	14.380(9)	19.464(7)	18.222(6)
α (°)	114.50(7)		117.15(4)		
β (°)	101.65(8)	103.10(2)	117.15(4)	105.34(3)	100.50(3)
γ (°)	94.73(9)		117.15(4)		
V (Å^3)	1049	2330	2012	3723(2)	1661.6(12)
Z	2	2	4	8	2
D_c (g/cm^3)	1.35	1.45	1.44	1.34	1.362
μ (cm^{-1})	6.8 (Mo)	9.6 (Mo)	7.2 (Mo)	6.19 (Mo)	
F(000)	444	1144	912	1576	712
Scan method	W scan	W scan	W scan	W scan	W scan
Max. 2θ (°)	45	45	45	45	50
Crystal size (mm)	0.05×0.15×0.5	0.3×0.3×0.4	0.15×0.15×0.20	0.26×0.14×0.38	0.4×0.5×0.5
Scan rate (°/min)	4–29.3	4–29.3		4–29.3	5.90–29.3
No. of observed reflections	1511	2602 $F > 2.5\sigma(F)$	1786 $F > 250(F)$	2321	1956 $F > 4.0s(F)$
R	0.0917	0.0347	0.077	0.056	0.058
wR	0.0901	0.0327	0.066	0.052	0.0468
Goodness-of-fit	2.316	1.579			1.58

Table 2
Selected bond lengths and bond angles of **5**, **8**, **16**, **19**, **28**

Compound	**5**		**8**		**16**		**19**		**28**	
Bond lengths (Å)	Ti–Cl(1)	2.394(7)	Ti(1)–Cl(1)	2.280(1)	Ti–Cl(1)	2.364(3)	Ti(1)–Cl(1)	2.420(3)	Ti–Cl	2.331(2)
	Ti–Cl(2)	2.436(7)	Ti(1)–C(1)	2.334(3)	Ti–Cl(2)	2.418(4)	Ti(1)–O(1)	1.879(6)	Ti–O	1.874(3)
	Ti–C(15)	2.418(24)	Ti(1)–C(2)	2.361(4)	Ti–Cp(1)	2.464(11)	Ti(1)–C(9)	2.383(8)	Ti–O(1)	2.462(3)
	Ti–C(16)	2.331(22)	Ti(1)–C(3)	2.377(3)	Ti–Cp(2)	2.413(11)	Ti(1)–C(10)	2.384(8)	Ti–C(2)	2.359(5)
	Ti–C(17)	2.363(18)	Ti(1)–C(4)	2.352(4)	Ti–Cp(3)	2.356(12)	Ti(1)–C(11)	2.384(8)	Ti–C(3)	2.337(5)
	Ti–C(18)	2.427(20)	Ti(1)–C(5)	2.348(3)	Ti–Cp(4)	2.300(10)	Ti(1)–C(12)	2.383(8)	Ti–C(4)	2.365(5)
	Ti–C(19)	2.438(21)	Ti(1)–O(1)	1.797(1)	Ti–Cp(5)	2.361(12)	Ti(1)–C(8)	2.383(8)	Ti–C(5)	2.423(4)
	C(1)–Tia	2.393(21)	Ti(1)–O(3)	1.802(2)					Ti–C(6)	2.432(4)
	C(2)–Tia	2.314(29)							Ti–TiA	2.773(2)
	C(3)–Tia	2.407(27)							Ti–OA	1.810(3)
	C(4)–Tia	2.434(20)							O–TiA	1.810(3)
	C(5)–Tia	2.490(18)								
Bond angles	Cl(1)–Ti–Cl(2)	92.5(2)	Cl(1)–Ti(1)–C(1)	146.2(1)	Cl(1)–Ti–Cl(2)	92.5(1)	Cl(1)–Ti–O(1)	94.5(2)	Cl–Ti–O	92.7(1)
	Cl(1)–Ti–C(15)	78.4(6)	Cl(1)–Ti(1)–C(2)	117.7(1)	Cl(1)–Ti–Cp(1)	86.2(2)	Cl(1)–Ti–C(9)	135.1(2)	Cl–Ti–O(1)	77.6(1)
	Cl(2)–Ti–C(15)	117.9(5)	C(1)–Ti(1)–C(2)	34.8(1)	Cl(2)–Ti–Cp(1)	129.6(3)	O(1)–Ti–C(9)	102.9(3)	O–Ti–O(1)	148.8(1)
	Cl(1)–Ti–C(16)	105.9(8)	Cl(1)–Ti(1)–C(3)	89.1(1)	Cl(1)–Ti–Cp(2)	80.3(3)	O(1)–Ti–(10)	134.3(3)	Cl–Ti–C(2)	146.3(1)
	Cl(2)–Ti–C(16)	134.9(6)	C(1)–Ti(1)–C(3)	57.5(1)	Cl(2)–Ti–Cp(2)	96.1(4)	Cl(1)–Ti–(1 1)	78.1(2)	O–Ti–C(2)	107.4(1)
	C(15)–Ti–C(16)	34.1(8)	C(2)–Ti(1)–C(3)	34.0(1)	Cp(1)–Ti–Cp(2)	34.0(5)	O(1)–Ti–(1 1)	122.9(3)	O(1)–Ti–C(2)	95.9(1)
	Cl(1)–Ti–C(17)	134.6(8)	Cl(1)–Ti(1)–C(4)	92.3(1)	Cl(1)–Ti–Cp(3)	109.0(3)			Cl–Ti–C(3)	128.5(1)
	Cl(2)–Ti–C(17)	105.8(7)	C(1)–Ti(1)–C(4)	57.6(1)	Cl(2)–Ti–Cp(3)	76.8(4)			O–Ti–C(3)	82.2(1)
	C(15)–Ti–C(17)	56.2(10)	C(2)–Ti(1)–C(4)	57.0(1)	Cl(1)–Ti–Cp(4)	138.0(3)			Cl–Ti–C(4)	95.7(1)
	C(1 6)–Ti–C(17)	34.7(11)	C(3)–Ti(1)–C(4)	34.5(1)	Cl(2)–Ti–Cp(4)	96.1(4)			Cl–Ti–C(5)	89.3(1)
	Cl(1)–Ti–C(18)	119.6(7)			Cl(1)–Ti–Cp(5)	118.4(2)			Cl–Ti–TiA	110.2(1)
	Cl(2)–Ti–C(18)	76.9(6)			Cl(2)–Ti–Cp(5)	130.0(3)			O–Ti–TiA	40.3
	C(15)–Ti–C(18)	57.4(9)							Ti–O–TiA	97.6(1)
	C(16)–Ti–C(18)	58.1(9)							TiA–Ti–OA	42.1(1)
	C(17)–Ti–C(18)	34.0(7)								
	Cl(1)–Ti–C(19)	86.8(6)								
	Cl(2)–Ti–C(19)	84.7(6)								
	C(1 5)–Ti–C(19)	34.1(9)								
	C(16)–Ti–C(19)	56.5(8)								
	C(17)–Ti–C(19)	55.1(8)								
	C18–Ti–C(19)	33.7(10)								

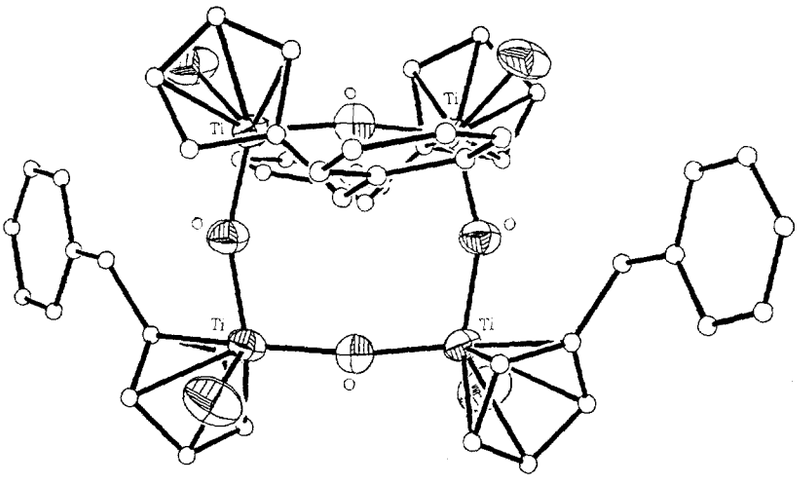


Fig. 2. The molecular structure of complex **8**.

2.2. *MeO-containing benzyl-substituted cyclopentadienyl complexes*

It is already proved in our previous work [21,22] that the oxygen atom in the side chain of Cp ring in titanium complexes may coordinate with titanium atom. Therefore, to compare the coordination ability of MeO and benzyl

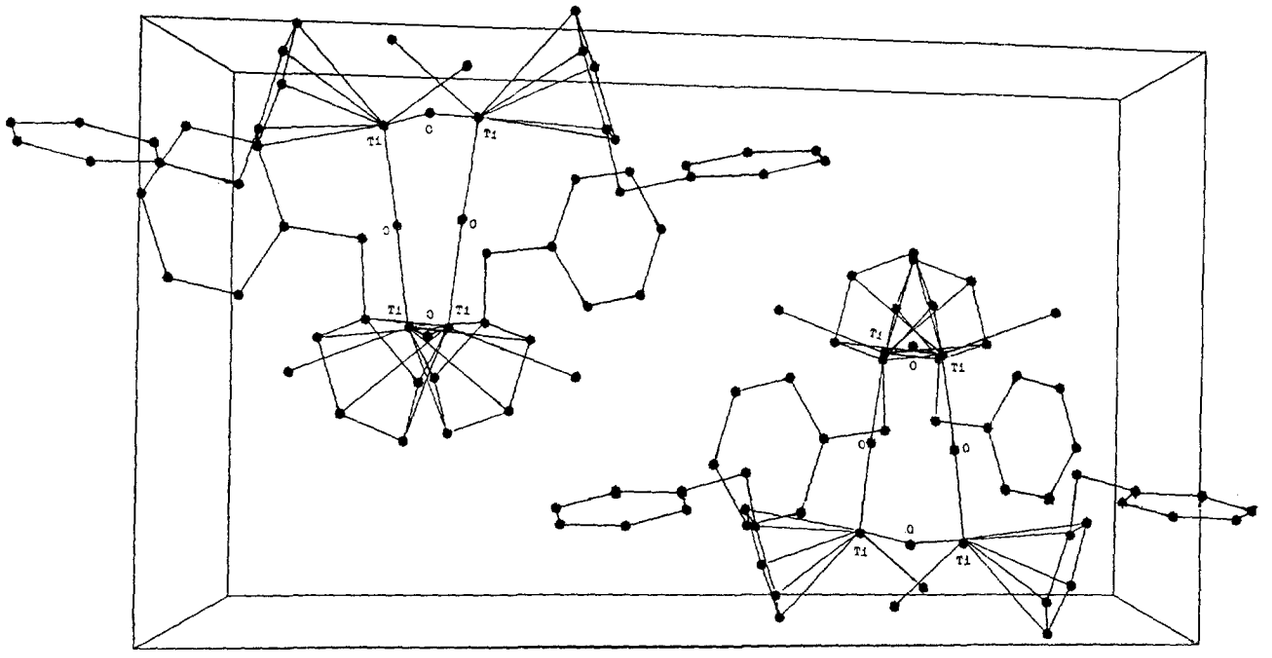


Fig. 3. The elemental cell of **8**.

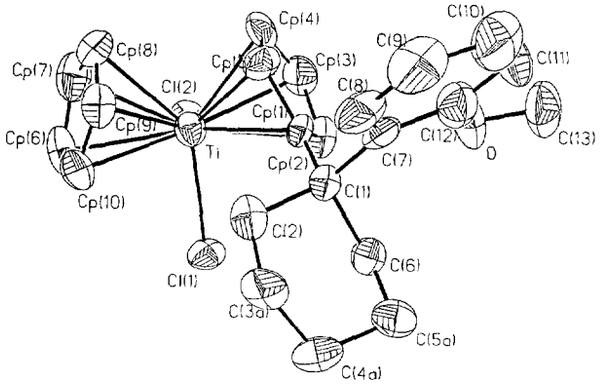
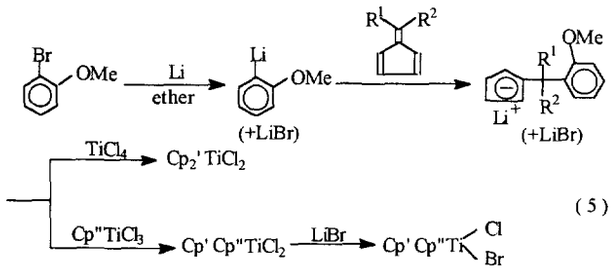
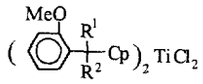


Fig. 4. The molecular structure of **16**.

group to titanium, a series of MeO-containing benzyl-substituted cyclopentadienyl titanium complexes have been synthesized in following way:

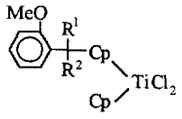


(5)



9 $R^1 = R^2 = Me$

10 $R^1 = Me$ $R^2 = Et$



11 $R^1 = R^2 = Me$

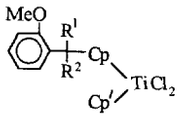
12 $R^1 = Me$ $R^2 = Et$

13 $R^1 = Me$ $R^2 = Pr^n$

14 $R^1 = Me$ $R^2 = Bu^n$

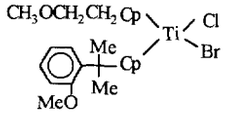
15 $R^1 = Me$ $R^2 = Bu^i$

16 $R^1, R^2 = -(CH_2)_5-$



17 $Cp' = PhCH_2Cp$

$R^1 = R^2 = Me$



18

The molecular structure of **16** was determined by X-ray diffraction, and shown as Fig. 4. The crystal data, selected bond lengths and bond angles are listed in Tables 1 and 2.

The structure shows that the MeO group on benzene ring in complex **16** is quite far from titanium, and the presence of (1,5)-pentylidene group seems to restrict free rotation along the C(1)–Cp(2) axis, thus leads less coordination possibility between Ti and O.

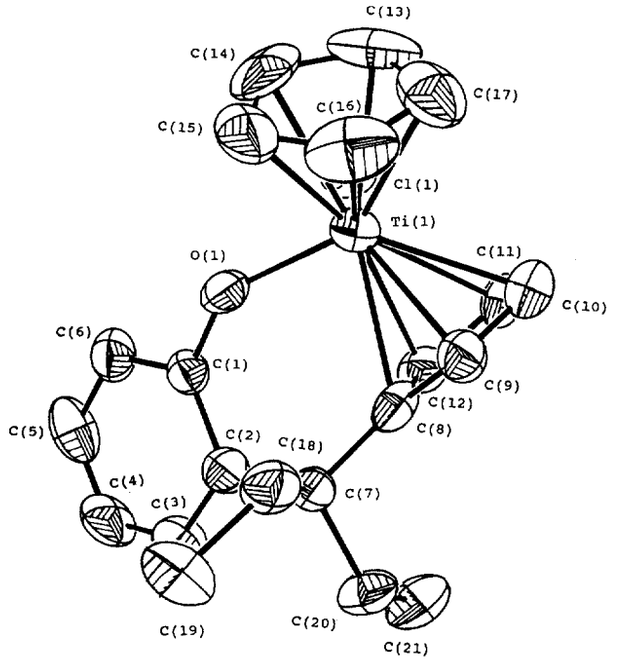
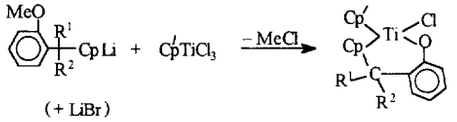


Fig. 5. The molecular structure of **19**.

3. A novel cyclization to titanocycle complexes

In the preparation of *o*-MeO-containing benzyl-substituted *cyclo*-pentadienyl titanium complexes, to our great surprise, when R^1 and R^2 are Et or more large group, the reaction always gives titanoxacycle complexes:



(6)

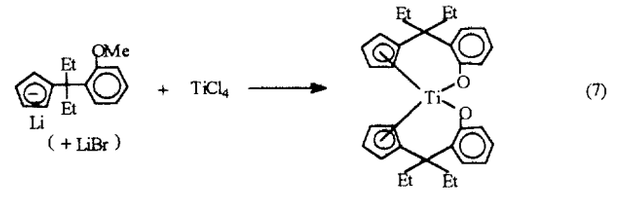
Cp′ = Cp
R¹ = R² = Et — 19

Cp′ = $CH_3OCH_2CH_2Cp$
R¹ = R² = Et — 20

Cp′ = Cp
R¹ = R² = Pr^n — 21

The molecular structure of **19** was proved by single crystal X-ray diffraction, and is shown in Fig. 5. Its crystal data, selected bond lengths and bond angles are listed in Tables 1 and 2.

If the *o*-MeO-containing benzyl-substituted cyclopentadienide reacted with $TiCl_4$, it gives a titanospiro complex **22**:



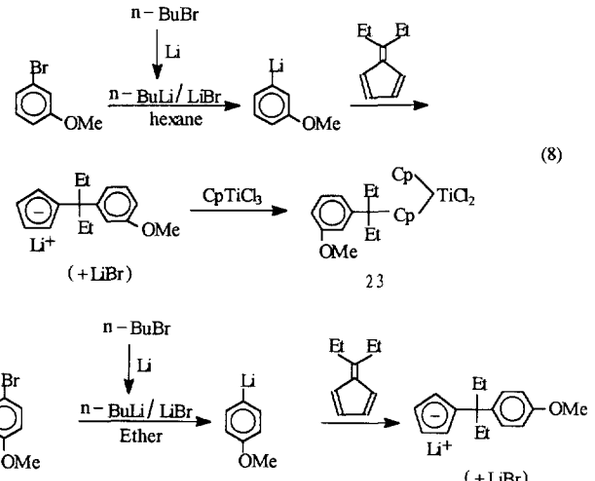
(7)

22

4. Factors affecting cyclization

4.1. Position of the MeO group on the benzene ring

To compare the effect of position of MeO group on the benzene ring to the cyclization, *m*- and *p*-MeO-containing benzyl-substituted titanium complexes have been synthesized, and it gives only normal-substituted cyclopentadienyl titanium complexes:



The red single crystal of **23** was obtained from recrystallization of benzene/petroleum mixed solvent.

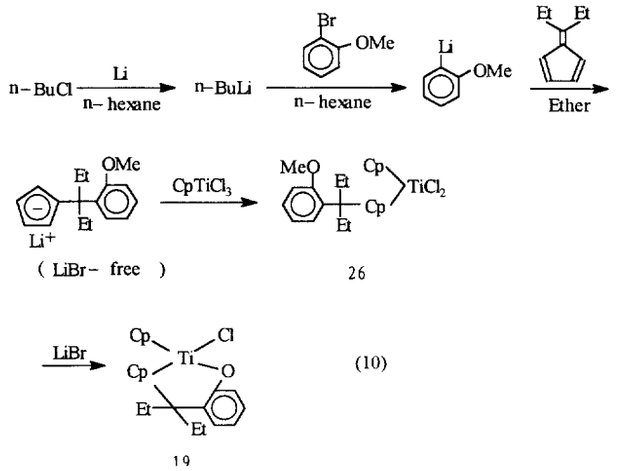
Table 3
Cyclization of **26** into **19** with halides

Halides	Titanium/Halide (mol/mol)	Time (h)	Conversion (%)
LiBr	3:1	0.5	31
	2:1	1	100
	1:3	0.5	100
NaBr	3:1	0.5	27
	1:3	0.5	78
		1	100
KBr	3:1	4	16
	1:3	4	68
Br_2	1:3	0.5	100
LiI	2:1	0.5	100
NaI	2:1	0.5	76
		1	100
KI	2:1	0.5	24
	1:1	0.5	38
	1:3	0.5	100
I_2	2:1	1.5	2
	1:1	1.5	12
	1:3	2	22

Reaction temperature: 5°C.

4.2. Halides as promotors

After further research, it was found that the presence of LiBr in the reaction mixture is an important factor for cyclization. To avoid the wrong effect of LiBr, a LiBr-free synthetic route was used, as follows:



When the LiBr-free substituted cyclopentadienide reacted with $CpTiCl_3$, it formed a normal-substituted cyclopentadienyl complex **26**, which may be easily converted into **19** quantitatively, at room temperature, in the presence of LiBr. It indicated that LiBr played an important role for the cyclization.

In addition to LiBr, many other halides can also promote the cyclization (see Table 3).

Table 3 shows that LiI and NaI are the most effective promotors for the cyclization. The activity order of halides for the cyclization is as follows:

$$LiI\text{–}NaI > LiBr\text{–}Br_2 > NaBr\text{–}KI > KBr\text{–}I_2$$

4.3. Temperature

In the absence of halides and below 10°C, in principle, there is no cyclization, but in the case of high temperature, **26** may be converted into **19** spontaneously (see Table 4).

4.4. Substituents on benzylic carbon atom

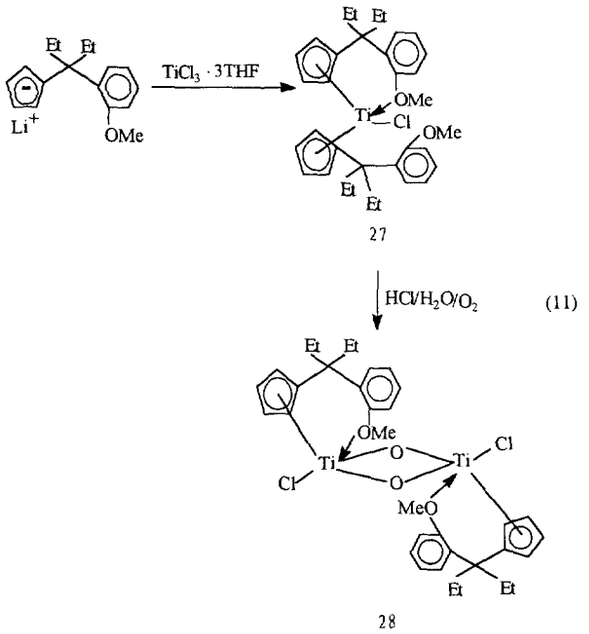
It seems that if one of the substituents on benzylic carbon atom of the complexes is a methyl group, like complexes **9–15**, and **18**, or 1,5-pentylidene group, like **16**, then the cyclization will not easily take place. The large substituents on benzylic carbon atom lead the benzene ring near the titanium atom, thus forming a favourable space condition for the cyclization.

Table 4
Effect of temperature on the cyclization of **26** into **19**

Temperature (°C)	Time (h)	Conversion
15	2	15
30	0.5	20
	1	30
	2	44
60	0.5	24
	1	50
	2	74
80	0.5	60
	1	88

4.5. Ti(III) derivative

The reaction of *o*-MeO-containing benzyl-substituted cyclopentadienide with $TiCl_3 \cdot 3THF$ gave a very sensitive complex **27** in which an intramolecular Ti–O coordination bond was confirmed by the lower shift of its C–O stretching vibration frequency in IR. Some crystals of **28** were obtained from the reaction mixture of **27** with concentrated hydrochloric acid. It seems to be affected by the 'aerial' of **27**.



A single crystal of **28** was obtained from CH_2Cl_2/*n*-hexane and sealed in capillary under argon atmosphere. The molecular structure of **28** is shown in Fig. 6. The crystal data, selected bond length and bond angles are listed in Tables 1 and 2. The structure of **28** reveals that there are two intramolecular Ti–O coordination bonds and a Ti · · · Ti nucleus bridged by two oxygen atoms.

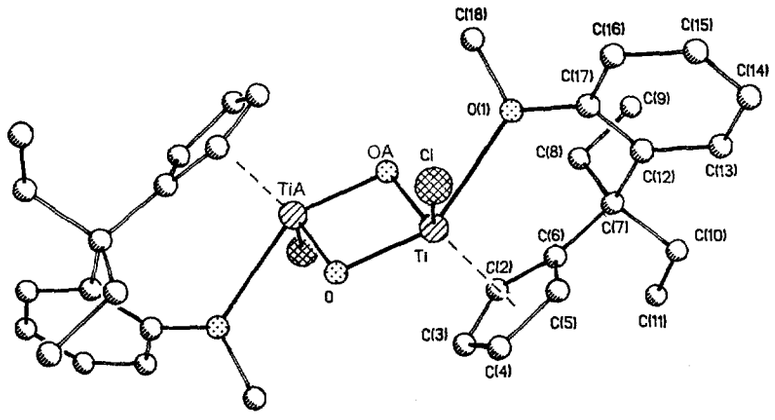
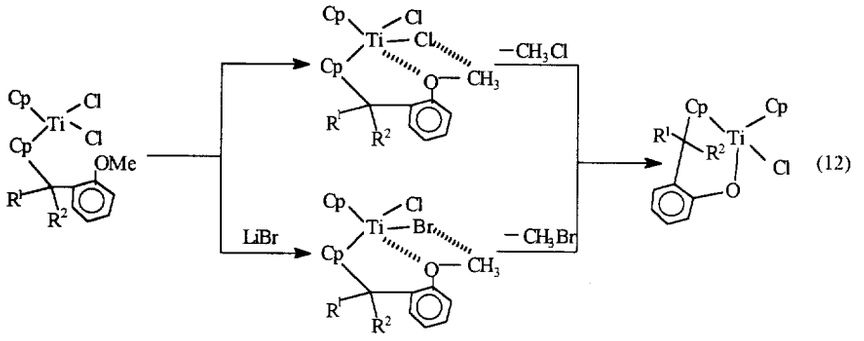


Fig. 6. The molecular structure of complex **28**.

4.6. The mechanism of the cyclization

The mechanism of four-membered transition state may be proposed as follows:



In the case of thermocyclization, the four-membered transition state between Ti–Cl and $-OCH_3$ group was formed at first, then followed by a elimination of CH_3Cl. In the presence of halide, for example, LiBr, the first step was halogen-exchanging, then also formed a four-membered transition state between Ti–Br and $-OCH_3$ group, followed by a elimination of CH_3Br instead of CH_3Cl, to give a titanoxacycle complex. The CH_3Br was found by MS and GC among the gas phase of the reaction mixture. In bromide or iodide as promotors, the cyclization was much faster than thermocyclization. It seems to attribute to the large atomic volume of bromine and iodine, which makes the elimination of CH_3Br or CH_3I easier than CH_3Cl. A further study on the mechanism is now in progress.

5. Experimental

All reactions were carried out at argon atmosphere using standard Schlenk techniques. Solvents were refluxed over the appropriate dried agents and distilled before use under argon. Melting points were uncorrected. ^1H NMR was measured on a varian EM-60 and Bruker AM-300 NMR Spectrometer using $CDCl_3$ as solvent and Me_4Si as an internal standard. IR was recorded on a Shimadzu IR-40 and a Perkin-Elmer 980 IR Spectrometer. [1] MS was obtained on a Finnigan 4021 Mass Spectrometer. $CH_3OCH_2CH_2CpTiCl_3$ and *cyclo*-C_4H_7O-2-$CH_2CpTiCl_3$ were synthesized according to Refs. [21,22].

5.1. Synthesis of 1

A solution of $PhCH_2Br$ (14 ml, 0.118 mol) in 50 ml of THF was dropped into a solution of CpNa (100.7 ml, 1.3 mmol/ml, 0.13 mol) in THF. After the mixture was stirred for 1 h, 10 ml of ether and 2 ml of water were added to dissolve all solid, 1N hydrochloric acid was added until pH = 7 of the solution. Then the organic phase was separated, and the aqueous phase was extracted with ether (20 ml × 3). The combined organic extracts were distilled under reduced pressure after removal of solvent. $PhCH_2CpH$ (9.10 g) was collected at 58–2°C/0.1 mm Hg yield = 49.4%. To a mixture of potassium (2.3 g) in 110 ml of THF was dropped $PhCH_2CpH$ (9.10 g) in 10 ml of THF. It was stirred for 4 h. The excess potassium was removed. 130 ml of $PhCH_2CpK$ solution (51 mmol, 0.4 mmol/ml) was obtained.

Into a solution of *cyclo*-C_4H_7O-2-$CH_2CpTiCl_3$ (1.69 g, 5.57 mmol) in 30 ml of THF was added a solution of $PhCH_2CpK$ (6.12 ml, 0.91 mmol/ml) in THF. It was stirred for 2 h and the solvent was removed. The residue was washed with petroleum and extracted with ether. A red solid (0.91 g) was obtained in 39%, m.p. = 121–122°C. ^1H NMR (δ, ppm): 7.22 (s, 5H), 6.94 (m, 4H), 6.43 (m, 4H), 4.01 (s, 2H), 3.29 (m, 3H), 2.88 (d, 2H), 1.82(m, 4H). MS (m/e): 387 (18, M–Cl), 352 (44, M–2Cl), 273 (14, $PhCH_2CpTiCl_2$), 267 (100, M–$PhCH_2Cp$). Anal. calc. for $C_{22}H_{24}Cl_2OTi$: C, 62.42; H, 5.73; Ti, 11.32. Found: C, 62.03; H, 5.88; Ti, 11.25.

5.2. Synthesis of 2

To solution of 7 ml PhLi in ether (1 mmol/ml) was dropped a solution of 0.8 ml of 6,6′-dimethylfulvene in 2 ml of ether in 5 min. It was stirred for 0.5 h, filtered, washed with 2 ml of ether, and then dried. 1.26 g of white solid

[1] The IR data are not listed here, but had been deposited with the editor.

($PhC(CH_3)_2CpLi$) was obtained, yield = 65%. It was dissolved in 14 ml of THF and was added dropwise into a solution of *cyclo*-C_4H_7O-2-$CH_2CpTiCl_3$ (1.42 g, 4.54 mmol) in 20 ml of THF. It was stirred for 1–2 h at 60°C, and stood over night. After removal of solvent, it was passed through a column of microcrystalline cellulose with ether as eluent. From the solution, 1.16 g of red solid was obtained, yield = 55%. The crude product was treated with $MgCl_2$ in THF, and an analytical sample was obtained, m.p. = 130–131°C. ^1H NMR (δ, ppm): 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). MS (m/e): 415 (60, M–Cl), 301 (20, $PhC(CH_3)_2CpTiCl_2$), 267 (100, *cyclo*-C_4H_7O-$CH_2CpTiCl_2$). Anal. calc. for $C_{24}H_{28}Cl_2OTi$: C, 63.87; H, 6.27; Ti, 10.61. Found: C, 63.51; H, 6.15; Ti, 10.76.

5.3. Synthesis of **3**

It was made in the same way from 6-methyl-6′-ethyl-fulvene. A dark red solid (1.43 g) was obtained in 52%, m.p. = 125–126°C. ^1H NMR (δ, ppm): 7.33 (s, 5H), 6.83 (m, 2H), 6.46 (m, 4H), 5.95 (m, 2H), 3.82 (m, 3H), 2.95 (m, 2H), 2.15 (m, 2H), 1.90 (m, 4H), 1.71 (s, 3H), 0.73 (t, 3H). MS (m/e): 429 (26, M–Cl), 394 (8, M–2Cl), 315 (13, $PhC(CH_3)(C_2H_5)CpTiCl_2$), 267 (52, *cyclo*-$C_4H_7O$-2-$CH_2CpTiCl_2$). Anal. calc. for $C_{25}H_{30}Cl_2OTi$: C, 64.52; H, 6.51; Ti, 10.29. Found: C, 63.56; H, 6.44; Ti, 11.16.

5.4. Synthesis of **4**

It was made in the same way from 6,6′-diethyl-fulvene. A dark red solid was obtained in 43%. After recrystallization with ether, an analytical sample was gained, m.p. = 166–167°C. ^1H NMR (δ, ppm): 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). MS (m/e): 443 (9, M–Cl), 408 (1, M–2Cl), 329 (9, $PhC(C_2H_5)_2CpTiCl_2$), 294 (7, $PhC(C_2H_5)_2CpTiCl$), 267 (100, *cyclo*-C_4H_7O-2-$CH_2CpTiCl_2$), 232 (12, *cyclo*-C_4H_7O-2-$CH_2CpTiCl$). Anal. calc. for $C_{26}H_{32}Cl_2OTi$: C, 65.14; H, 6.74; Ti, 9.99. Found: C, 65.02; H, 6.80; Ti, 10.27.

5.5. Synthesis of **5**

Compound **5** was made in the same way from $CH_3OCH_2CH_2CpTiCl_3$. A red solid was obtained after extraction with ether, yield = 54%. An analytical sample was obtained by recrystallization with ether, m.p. = 106–107°C. ^1H NMR (δ, ppm): 7.26 (s, 5H), 6.55 (m, 2H), 6.45 (m, 2H), 6.19 (m, 2H), 6.01 (m, 2H), 3.58 (t, 2H), 3.30 (s, 3H), 2.97 (t, 2H), 1.71 (s, 6H). MS (m/e): 389 (10, M–Cl), 301 (12, $PhC(CH_3)_2CpTiCl_2$), 241 (99, $CH_3OCH_2CH_2CpTiCl_2$), 205 (24, $CH_3OCH_2CH_2CpTiCl$-1). Anal. calc. for $C_{22}H_{26}Cl_2OTi$: C, 62.14; H, 6.16; Ti, 11.26. Found: C, 61.15; H, 6.18; Ti, 11.23.

5.6. Synthesis of **6–8**

Into a solution of $(PhCH_2Cp)_2TiCl_2$ (2.0 g, 4.6 mmol) in 6 ml of toluene was added a mixture of $TiCl_4$ (1.5 ml, 13.6 mmol) and 6 ml of toluene with stirring over a period of 10 min. The mixture was allowed to heat to 115°C and stirred for 25 h. The solvent was removed and the residue was extracted with petroleum (30–60°C). After cooling, two different solids were obtained. The air-sensitive orange solid (compound **6**): ^1H NMR (δ, ppm): 7.32 (s, 5H), 6.90 (m, 4H), 4.22 (s, 2H). MS (m/e): 273 (100, M–Cl), 238 (8, M–2Cl), 153 (42, $PhCH_2Cp$). Anal. calc. for $C_{12}H_{11}Cl_3Ti$: C, 46.57; H, 3.59; Ti, 15.48. Found: C, 46.63; H, 3.59; Ti, 15.62. The yellow solid (compound **7**), yield = 76.2%. MS (m/e): 272 (100, $PhCH_2CpTiCl_2$), 237 (7, $PhCH_2TiCpCl$), 153 (69, $PhCH_2Cp$); Anal. calc. for $C_{24}H_{22}Cl_4OTi_2$: C, 51.11; H, 3.93; Ti, 16.98; Cl, 25.14. Found: C, 51.08; H, 3.90; Ti, 17.34; Cl, 25.30. Compound **7** was recrystallized with toluene and ether (without deoxygenation treatment), a single crystal (compound **8**) was obtained and the crystal structure was determined by X-ray diffraction. The result showed an eight-membered Ti–O heterocyclic compound.

5.7. Synthesis of **9**

To a solution of metal lithium (0.75 g, 0.11 mol) in 20 ml of ether was added a solution of 6.25 ml (9.35 g, 0.05 mol) of 2-bromo anisole with gentle reflux, then it was stirred for 1 h at room temperature. After filtration, a solution of 2-lithium anisole in ether was titrated with standard hydrochloric acid. Into the above solution of 27 ml of 2-lithium anisole (1.21 mmol/ml, 33 mmol) in ether was added dropwise a solution of equimolecular 6,6′-dimethyl-fulvene in ether. It was stirred again for 2 h. A solution of the equivalent above lithium salt was added into a mixture of 10 ml of

benzene and 1 ml of $TiCl_4$ at 0°C. It was stirred for 2 h and filtrated, and the solvent was removed at reduced pressure. The residue was passed through a microcrystalline cellulose column with benzene as eluent. After the solvent was removed, a red crystal was obtained, yield = 29%, m.p. = 185–186°C. ^{1}H NMR (δ, ppm): 7.15–7.33 (m, 4H), 6.75–7.05 (m, 4H), 6.45–6.65 (m, 4H), 6.15–6.35 (m, 4H), 3.70 (s, 1H), 1.80 (s, 12H). MS (m/e): 494 (15, M–CH_3Cl), 493 (31, M–H–CH_3Cl), 443 (100, M–2CH_3Cl–H), 331 (3, M–Cp′), 213 (25, Cp′), Anal. calc. for $C_{30}H_{34}Cl_2O_2Ti$: C, 66.06; H, 6.30. Found: C, 66.02; H, 6.32.

5.8. Synthesis of **10**

To 10 ml of THF was added $TiCl_4$ (2 ml, 18.0 mmol), and in situ a yellow precipitated was formed. Then 22.6 ml (18.8 mmol) of a corresponding lithium salt in ether was dropped in the above mixture. It was stirred for 2 h, and the solvent was removed. The residue was passed through a microcrystalline cellulose column with $CHCl_3$ as eluent. It was condensed and petroleum ether was added. A red crystal (0.1 g) was obtained after cooling in refrigerator, yield = 1.2%. It was recrystallized with $CHCl_3$/petroleum ether to give analytical samples, m.p. = 163–165°C. ^{1}H NMR (δ, ppm): 6.94–7.44 (m, 8H), 5.78–6.79 (m, 8H), 3.55 (s, 6H), 2.75 (m, J = 7.4, 2H), 2.10 (m, 2H), 1.72 (s, 6H), 0.60 (t, J = 7.4, 6H). MS (m/e): 522(7, M^+–CH_3Cl), 472 (27, M2–CH_3Cl), 345 (6, M–Cp′), 227 (23, Cp′). Anal. calc. for $C_{32}H_{38}Cl_2O_2Ti$: C, 67.02; H, 6.68. Found: C, 67.23; H, 6.79.

5.9. Synthesis of **11**

Into a solution of $CpTiCl_3$ (0.66 g, 3 mmol) in THF was added the solution of equimolecular corresponding lithium salt in ether as used in synthesis of compound **9**. After stirred for 2 h, it was passed through a column with microcrystalline cellulose with chloroform–ether as eluent, concentrated at reduced pressure to remove part solvent, kept in refrigerator, and 0.25 g of an orange crystal was obtained, yield = 63%, m.p. = 159–160°C. ^{1}H NMR (δ, ppm): 6.65–7.33 (m, 4H), 6.40–6.60 (m, 9H), 3.56 (s, 3H), 1.76 (s, 6H). MS (m/e): 361 (6, M^+–Cl), 346 (27, M–CH_3Cl), 331 (77, M^+–Cp), 183 (2, $CpTiCl_2$). Anal. calc. for $C_{20}H_{22}Cl_2OTi$: C, 60.48; H, 5.58; Ti, 12.06. Found: C, 60.46; H, 5.54; Ti, 12.18.

5.10. Synthesis of **12**

The corresponding lithium salt was formed from the reaction of 2–lithium anisole with 6-methyl-6′-ethyl fulvene. Then compound **12** was synthesized in the same way as compound **11**. An orange solid was obtained, yield = 54%, m.p. = 132–133°C. ^{1}H NMR (δ, ppm): 6.70–7.45 (m, 4H), 6.35–6.60 (m, 9H), 3.68 (s, 3H), 2.00 (q, 2H), 1.65 (d, 3H), 0.65 (t, 3H). MS (m/e): 376 (6, M–Cl), 361 (37, M–CH_3Cl), 326 (100, M–Cl–CH_3Cl), 346 (5, M–Cp), 183 (2, $CpTiCl_2$–H). Anal. calc. for $C_{21}H_{24}Cl_2OTi$: C, 61.34; H, 5.88. Found: C, 59.90; H, 5.77.

5.11. Synthesis of **13**

By using 6-methyl-6′-propyl fulvene as starting material, compound **13** was synthesized in the same way as compound **11**. A red crystal was obtained, yield = 76%, m.p. = 124–127°C. ^{1}H NMR (δ, ppm): 6.69–7.33 (m, 4H), 6.43 (s, 5H), 6.00–6.20 (m, 2H), 3.60 (s, 3H), 2.67 (m, 1H), 1.92 (m, 1H), 1.68 (s, 3H), 1.26 (m, 2H), 0.83 (m, 3H). MS (m/e): 388 (11, M^+–Cl), 374 (10, M–CH_3Cl), 358 (10, M–Cp), 241 (2, M–$CpTiCl_2$), 183 (3, $CpTiCl_2$). Anal. calc. for $C_{22}H_{26}Cl_2OTi$: C, 62.13; H, 6.17. Found: C, 62.05; H, 6.49.

5.12. Synthesis of **14**

By using a corresponding fulvene as starting material, compound **14** was synthesized in the same way as compound **11**. A red crystal was obtained, yield = 55%, m.p. = 118–121°C. ^{1}H NMR (δ, ppm): 6.71–7.29 (m, 4H), 6.42 (s, 5H), 5.95–6.70 (m, 4H), 3.63 (s, 3H), 2.71 (m, 1H), 2.02 (m, 1H), 1.69 (s, 3H), 1.21 (m, 4H), 0.79 (t, 3H). MS (m/e): 403 (58, M–Cl), 388 (65, M–CH_3Cl), 373 (4, M–Cp), 352 (100, M^+–CH_3Cl–Cl), 255 (5, Cp′), 183 (4, $CpTiCl_2$). Anal. calc. for $C_{23}H_{28}Cl_2OTi$: C, 62.89; H: 6.42. Found: C, 63.38; H, 6.33.

5.13. Synthesis of **15**

By using a corresponding fulvene as starting material, the compound **15** was synthesized in the same way as compound **11**. Red crystal, yield = 38%, m.p. = 140–141°C. ^{1}H NMR (δ, ppm): 7.39 (m, 1H), 7.23 (m, 1H), 6.95

(m, 2H), 6.75 (m, 2H), 6.44 (s, 5H), 6.30 (m, 1H), 5.95 (m, 1H), 3.60 (s, 3H), 2.68 (d-d, $J_1 = 13.5$, $J_2 = 5.9$, 1H), 2.00 (d-d, $J_1 = 13.5$, $J_2 = 4.8$, 1H), 1.70 (s, 3H), 1.33 (m, 1H), 0.98 (d, $J = 6.7$, 3H), 0.47 (d, $J = 6.7$, 3H). MS (m/e). 403 (17, M–Cl), 388 (6, M–CH_3Cl), 373 (100, M–Cp), 255 (12, M–$CpTiCl_2$), 183 (21, $CpTiCl_2$). Anal. calc. for $C_{23}H_{28}Cl_2OTi$:C, 62.89, H, 6.42. Found: C, 62.47, H, 6.33.

5.14. Synthesis of **16**

By using 6,6′-cyclohexyl fulvene as starting material, the compound **16** was synthesized in the same way as compound **11**. Red solid, yield = 50%, m.p. = 167–168°C. ^{1}H NMR (δ, ppm): 6.90–7.48 (m, 4H), 6.12–6.78 (m, 9H), 3.80 (s, 3H), 1.00–1.98 (m, 10H). MS (m/e): 402 (2, M^+–Cl), 387 (14, M^+–Cl), 372 (3, M–Cp), 1 83 (5, $CpTiCl_2$). Anal. calc. for $C_{23}H_{26}Cl_2OTi$: C, 63.20; H: 6.01. Found: C, 62.35; H, 6.03.

5.15. Synthesis of **17**

A solution of 2-lithium anisole (5.445 mmol) in ether was added into a solution of 6,6′-dimethyl fulvene (0.6 ml, 5.445 mmol) in petroleum ether. It was stirred for 2 h, then filtered. Obtained white solid was washed with petroleum ether and dissolved in 10 ml of THF. It was added into a solution of $(PhCH_2CpTiCl_2)_2O$ (1.36 g, 2.4 mmol) in THF. The mixture was stirred for 1 h. After 6 ml of hydrochloric acid (4 M) was added, the water phase was extracted with ether, and the combined organic phase was dried with Na_2SO_4. Then the solvent was removed. The residue was treated with benzene and petroleum ether, and gave 1.3 g red solid, yield = 55%, m.p. = 141–142°C. ^{1}H NMR (δ, ppm): 6.90–7.56 (m, 4H), 7.25 (s, 5H), 6.63 (m, 2H), 6.30 (m, 6H), 4.10 (s, 2H), 3.55 (s, 3H), 1.75 (s, 6H). MS (m/e): 436 (8, M–CH_3Cl), 400 (71, M^+–CH_3Cl–Cl), 331 (10, M–$PhCH_2Cp$), 281 (98, M–CH_3Cl–$PhCH_2Cp$). Anal. calc. for $C_{27}H_{28}Cl_2OTi$: C, 66.55; H, 5.79; Ti, 9.83. Found: C, 65.97; H, 5.71; Ti, 10.60.

5.16. Synthesis of **18**

A THF solution from the reaction of 6,6′-dimethyl fulvene (0.16 g) and 2-lithium anisole (1.3 ml, 1.57 mm) in ether was added into a solution of $CH_3OCH_2CH_2CpTiCl_3$ (0.44 g, 1.59 mmol) in 10 ml of THF. It was stirred for 1 h. After removal of the solvent, the residue was washed with petroleum ether, then extracted with ether. A dark red solid was obtained, yield = 54%, m.p. = 116–117°C. ^{1}H NMR (δ, ppm): 7.02–7.4 (m, 4H), 6.76 (m, 2H), 6.48 (m, 2H), 6.26 (m, 2H), 6.02 (m, 2H), 3.58 (s, 3H), 3.53 (t, 2H), 3.32 (s, 3H), 3.01 (t, 2H), 1.26 (s, 3H), 1.23 (s, 3H). MS (m/e): 448, 450 (3, M–CH_3Cl), 404 (19, M–CH_3Br), 369 (45, M–CH_3Br–Cl), 325, 327 (3, M–CH_3Cl–$CH_3OCH_2CH_2Cp$), 94, 96 (100, CH_3Br), 50 (2, CH_3Cl). Anal. calc. for $C_{23}H_{28}BrClO_2Ti$: C, 55.28; H, 5.65; Ti, 9.59; Cl, 7.09; Br, 15.99. Found: C, 55.03; H, 5.82; Ti, 9.98; Cl:7.09; Br, 15.96.

5.17. Synthesis of **19**

To 0.5 ml of 6,6′-diethylfulvene in 4 ml of petroleum ether was added 3 ml of *o*-methoxyphenyllithium (1.09 mmol/ml in Et_2O, prepared from Li and *o*-bromoanisole in Et_2O) with stirring at r.t. The mixture was stirred for another 0.5 h. The precipitated white solid was filtered, washed with 2 ml petroleum ether, and dissolved in 5 ml of THF. The THF solution was transferred to a dropping funnel and added to 0.66 g of $CpTiCl_3$ in 10 ml of THF under stirring during 10 min. After 2 h additional stirring at r.t., solvents were removed under reduced pressure and the residue was washed with 5 ml of petroleum ether, chromatographed on a column of microcrystalline cellulose, and eluted with petroleum ether/CH_3Cl (1/1). The eluate was concentrated and cooled to 0°C. Orange crystals (0.71 g) of **19** were obtained in 63%, m.p. = 141–142°C. ^{1}H NMR (δ, ppm): 6.48–6.86 (m, 4H), 6.15 (m, 2H), 6.52 (m, 2H), 1.85 (m, 4H), 0.65 (m, 6H). MS (m/e,): 374 (52, M^+), 339 (100, M–Cl), 309 (76, M–Cp), 281 (45, M–OPh), 244 (29, M–OC_6H_4–C_2H_4). Anal. calc. for $C_{21}H_{23}ClOTi$: C, 67.30; H, 6.19; Ti, 12.28. Found: C, 66.37; H, 6.23; Ti, 14.05.

5.18. Synthesis of **20**

Using similar runs as compound **19**, a THF solution of a corresponding lithium salt was added to 1.02 g $CH_3OCH_2CH_2CpTiCl_3$ in 10 ml of THF. It was stirred for 2 h at 60°C, and the solvent was removed. The residue was passed through a microcrystalline cellulose column with petroleum ether as eluent. A part of the solvent was removed, and 1 g of an orange crystal was obtained, yield = 62%, m.p. = 107–108°C. ^{1}H NMR (δ, ppm): 6.45–6.94 (m, 4H), 6.58 (m, 2H), 6.33 (m, 2H), 5.97 (m, 2H), 5.50 (m, 2H), 3.70 (t, 2H), 3.38 (s, 3H), 2.90 (t, 2H), 1.83 (m,

4H), 0.73 (t, 6H). MS (m/e):432 (9, M^+), 397 (100, M–Cl), 309 (6, M–$CH_3OCH_2CH_2Cp$), 275 (14, M^+–Cl–$CH_3OCH_2CH_2Cp$). Anal. calc. for $C_{24}H_{29}ClO_2Ti$: C, 66.60; H, 6.75; Ti, 11.07; Cl, 8.19. Found: C, 66.69; H, 6.66; Ti, 10.31; Cl, 7.08.

5.19. Synthesis of **21**

By using the same procedure as compound **20**, an orange solid was prepared, yield = 45%, m.p. = 150–151°C. ^1H NMR (δ, ppm): 6.55–7.2 (m, 4H), 6.10–6.45 (m, 5H), 6.05 (m, 2H), 5.35 (m, 2H), 0.5–1.98 (m, 14H). MS (m/e): 403 (19, M^+), 368 (100, M–Cl), 338 (12, M–Cp), Anal. calc. for $C_{23}H_{27}ClOTi$: C, 68.74; H, 6.73. Found: C, 68.58; H, 6.76.

5.20. Synthesis of **22**

To 2 ml of 6,6′-diethylfulvene in 10 ml of petroleum ether was added 20 ml of *o*-methoxyphenyllithium (0.606 mmol/ml in Et_2O, prepared from Li and *o*-bromoanisole in Et_2O). The mixture was stirred at r.t. for 2 h. The resulting white solid was filtered, washed with 3 ml of petroleum ether, dissolved in 5 ml of THF, and added to 0.16 ml of $TiCl_4$ in 10 ml of benzene during 10 min. The reaction mixture was stirred at r.t. for 4 h, then stored overnight. A yellow solid was obtained, after washing with petroleum ether, weight 0.91 g, yield = 30%, m.p. = 265–266°C. ^1H NMR (δ, ppm): 6.82–6.45 (m, 8H), 5.66–6.45 (m, 8H), 1.86 (m, 8H), 0.76 (m, 12H). MS (m/e): 500 (14, M^+), 407 (6, M–OPh), 377 (26, M–OPh–C_3H_6), 337 (33, M–$OC_6H_4CEt_2$–H), 78 (100, C_6H_6). Anal. calc. for $C_{32}H_{36}O_2Ti$: C, 76.36; H, 7.07; Ti, 9.73. Found: C, 76.79; H, 7.25; Ti, 9.59.

5.21. Synthesis of **23**

By using the 3-bromo anisole as starting material, compound **23** was synthesized in the same way. A red solid was obtained, yield = 47%, m.p. = 139–140°C. ^1H NMR (δ, ppm): 6.25–7.35 (m, 8H), 5.82 (s, 5H), 3.72 (s, 3H), 2.15 (m, 4H), 0.60 (t, 6H). MS (m/e): 390 (2, M + 1–Cl), 360 (5, M^+–Cp), 242 (1, M + 1–$CpTiCl_2$). Anal. calc. for $C_{22}H_{26}Cl_2OTi$: C, 62.14; H, 6.16; Ti, 11.26. Found: C, 62.86; H, 6.07; Ti, 10.93.

5.22. Synthesis of **24** and **25**

By using the 4-bromo anisole as starting material, the corresponding lithium salt was prepared. Then it reacted with $TiCl_4$ in the same way as compound **9**, and reacted with $CpTiCl_3$ as compound **11**, and gave compound **24** and **25**, respectively.

Obtained was compound **24**, red solid, yield = 59%, m.p. = 198–199°C. ^1H NMR (δ, ppm): 6.65–7.55 (m, 8H), 6.40 (m, 4H), 5.55 (m, 2H), 5.30 (m, 2H), 3.75 (s, 6H), 2.15 (m, 8H), 0.60 (t, 12H). MS (m/e): 565 (2, M–Cl), 359 (4, M–Cp′), 241 (13, Cp′). Anal. calc. for $C_{34}H_{42}Cl_2O_2Ti$: C, 67.89; H, 7.04. Found: C, 67.49; H, 6.95.

Also obtained was compound **25**, red solid, yield = 53%, m.p. = 200–201°C. ^1H NMR (δ, ppm): 6.40–7.60 (m, 8H), 6.00 (m, 5H), 3.80 (s, 3H), 2.20 (m, 4H), 0.65 (t, 6H). MS (m/e): 389 (34, M–Cl), 359 (19, M–Cp), 241 (100, Cp′). Anal. calc. for $C_{22}H_{26}Cl_2OTi$: C, 62.14: H, 6.16. Found: C, 61.39; H, 5.95.

5.23. Synthesis of **26**

To 6 mmol of *o*-bromoanisole in 20 ml of *n*-hexane was added 6 mmol of *n*-BuLi (originated from Li and *n*-BuCl in *n*-hexane) under stirring. Soon white solid precipitated. The reaction mixture was stirred at r.t. for 6 h. Then, the white solid was filtered, dissolved in 20 ml of ether and added to 6 mmol of 6,6′-diethylfulvene in 10 ml of ether. After it was stirred at r.t. for 2 h, the mixture was transferred to 6 mmol of $CpTiCl_3$ in 20 ml of ether under stirring at r.t. After additional 2 h stirring, the solvents were removed and the residue was chromatographed on a column of microcrystalline cellulose using $CHCl_3$ as eluent. Partial $CHCl_3$ was removed, and petroleum ether was added. The mixture was cooled to 0°C to give 1.4 g of red solid, yield = 55%, m.p. = 128–129°C. ^1H NMR (δ, ppm): 6.20–7.30 (m, 8H), 6.00 (s, 5H), 3.75 (s, 3H), 2.30 (m, 4H), 0.70 (t, 6H, J = 7 Hz). MS (m/e): 389 (2, M–Cl), 359 (2, M–Cp), 183 (15, $CpTiCl_2$), 65 (17, Cp). Anal. calc. for $C_{22}H_{26}Cl_2OTi$: C, 62.14; H, 6.16; Ti, 11.26. Found: C, 62.41; H, 6.04; Ti, 11.47.

5.24. Reaction of 26 with halides

In 10 ml of THF, 100 mg of **26** and 90 mg of LiBr was dissolved and stirred at r.t. for 7 h. The same treatment as **19** afforded 85 mg of orange crystalline **19** in 97% yield. The reaction of **26** with other halides was carried out in the same way.

5.25. Synthesis of 27 and 28

To 10.1 mmol of $TiCl_3 \cdot 3THF$ was added 20.1 mmol of LiBr-free sodium α,α'-diethyl-*o*-methoxybenzylcyclopentadienide (0.56 mmol/ml in THF). The mixture was stirred at r.t. for 5 h. Then the solvent was removed and the residue was washed with *n*-hexane (2 × 20 ml) followed by hot-extraction with mixed solvents of 80 ml of *n*-hexane and 20 ml of THF. After cooling to r.t., blue needles (compound **27**) weighing 3.42 g were obtained in 60% yield, which decomposed at 160°C, MS (m/e): 565 (100, M^+), 550 (5, M–Me), 530 (1, M–Cl), 515 (62, M–MeCl), 500 (26, M–MeCl–Me). Anal. calc. for $C_{34}H_{42}ClO_2Ti$: C, 72.14; H, 7.48. Found: C, 71.75; H, 7.31.

A small amount of compound **28** was obtained from the reaction mixture of **27** with concentrated hydrochloric acid, and the structure of single crystal was determined by X-ray diffraction. It seems to be the reaction product of **27** with a trace of oxygen.

6. Determination of crystal structures

The single crystal of **5**, **8**, **16**, **19**, **28** were sealed in capillary under argon atmosphere. Data collection was made on a Siemens R3m/v Diffractometer using Mo–Kα radiation ($g = 0.71073$ Å) and a highly oriented graphite crystal monochromator. The crystal structures were solved by direct methods using a Siemens SHELXTL PLUS (VMS) System and refined by Full-Matrix least-squares.

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References

[1] Y. Qian, G. Li, Y. Huang, J. Mol. Catal. 54 (1989) L19.
[2] Y. Zhang, S. Liao, Y. Xu, J. Organomet. Chem. 382 (1990) 695.
[3] Q. Sun, S. Liao, Y. Xu, Y. Qian, J. Huang, Chin. J. Catal., Cuihua Xuebao 17 (1996) 495.
[4] Y. Qian, J. Lu, W. Xu, J. Mol. Catal. 34 (1986) 31.
[5] Y. Qian, J. Zhuang, J. Lu, Q. Huang, W. Xu, S. Chen, J. Mol. Catal. 38 (1986) 331.
[6] Y. Qian, G. Li, Y. He, W. Chen, B. Li, S. Chen, J. Mol. Catal. 60 (1990) 19.
[7] T. Ushioda, M.L.H. Green, J. Haggitt, X. Yan, J. Organomet. Chem. 518 (1996) 155.
[8] P.C. Moehring, N.J. Coville, J. Organomet. Chem. 479 (1994) 1.
[9] R.L. Halterman, Chem. Rev. 92 (1992) 965.
[10] J. Lu, Y. Qian, Chin. J. Inorg. Chem. 1 (1985) 130.
[11] F. Sato, T. Jinbo, M. Sato, Tetrahedron Lett. 21 (1980) 2171.
[12] Y. Qian, R. Guo, J. Huang, Q. Yang, Polyhedron 16 (1997) 195, and references therein.
[13] Y. Qian, J. Huang, T. Huang, S. Chen, Transition Met. Chem. 21 (1996) 393.
[14] Y. Qian, R. Guo, J. Huang, K. Jonas, Chin. Chem. Lett. 7 (1996) 1139.
[15] Y. Qian, J. Huang, Macromol. Symp. 105 (1996) 205.
[16] Y. Qian, K. Hong, H. Zong, J. Huang, Polymers Adv. Technol. 7 (1996) 619.
[17] J. Liu, J. Huang, Y. Qian, F. Wang, A.S.C. Chan, Polymer J. 29 (1997) 182.
[18] J. Liu, J. Huang, Y. Qian, F. Wang, A.S.C. Chan, Polymer Bull. 37 (1996) 719.
[19] Y. Qian, J. Huang, X. Chen, G. Li, W. Chen, B. Li, X. Jin, Q. Yang, Polyhedron 13 (1994) 1105.
[20] Y. Qian, G. Li, W. Chen, B. Li, X. Jin, Transition Met. Chem. 15 (1990) 478.
[21] Q. Huang, Y. Qian, G. Li, Y. Tang, Transition Met. Chem. 15 (1990) 483.
[22] Y. Qian, G. Li, W. Chen, B. Li, X. Jin, J. Organomet. Chem. 373 (1989) 185.