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Isodicyclopentadienes and related molecules

LVII *. Solid state structural studies of the diastereomeric *exo*- and *endo*-(η^5-cyclopentadienyl)(η^5-(1*S*,8*R*)-9,9-dimethyltricyclo[6.1.1.0^{2,6}]deca-2,5-dienyl)dichlorotitaniums and a stereopure *exo*-(η^5-pentamethyl-cyclopentadienyl) congener

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Abstract

The lithium salt of optically pure (1*S*,8*R*)-9,9-dimethyltricyclo[6.1.1.0^{2,6}]deca-2,5-diene (**9**) has been transformed in highly stereoselective fashion to the dichlorotitanium complexes **5–7**. Temperature and reaction conditions can be suitably controlled to attain proper π-facial selectivity in those condensations involving $CpTiCl_3$. Direct condensation with Cp^*TiCl_3, on the other hand, leads only to **7** in a more sluggish reaction. A stereochemical crossover to arrive at **8** was attempted by taking advantage of the inversion of configuration that operates during condensation of silane **10** with $TiCl_4$. Unfortunately, steric hindrance precluded the successful reaction of **11** with Cp^*M (M = Li, K, Tl, $SiMe_3$, $SnMe_3$) to provide **8**. Crystal structure analyses of the three available complexes were completed and detailed comparison of their structural features are presented. The absolute configurational assignments rest securely on the synthetic pathway developed earlier for gaining access to **9**.

A fundamental problem for the organometallic chemist is understanding how electronic, steric and stereochemical modifications within a series of transition metal complexes translate into modulation of chemical reactivity and changes in a host of other properties. Since its first utilization as a ligand [2], isodicyclopentadiene (**1**) has attracted considerable attention and widespread use [3]. Both of its π-surfaces can be complexed stereoselectively [4], with attendant alteration in chemical behavior. More recently, optically active ligands likewise constituted of bicyclic substructures fused across a cyclopentadiene ring have been reported. Those derived from (1*R*)-(+)-camphor (*e.g.*, **2**) [5], (1 *R*)-(−)-nopol (*e.g.*, **3**) [6] and (1*S*,5*S*)-(−)-verbenone (*e.g.*, **4**) [7] have been accorded specific attention by us [8,9]. To the present time, emphasis has been placed chiefly on the synthesis of complexes derived from **2–4** and on detailed assessment of their catalytic potential. Their use as reagents for accomplishing useful asymmetric organic synthesis is especially being explored.

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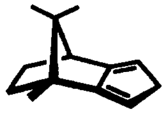

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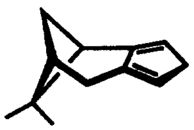

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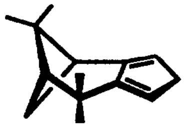

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Correspondence to: Professor L.A. Paquette or Professor R.D. Rogers.

[*] For Part LVI see ref. 1.

[**] National Need Fellow, 1989, 1990; Amoco Foundation Fellow, 1991.

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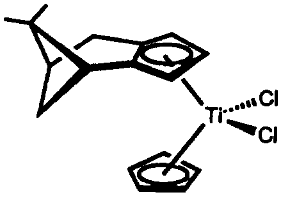

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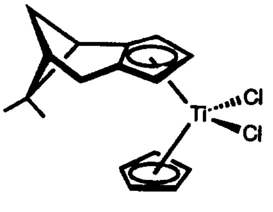

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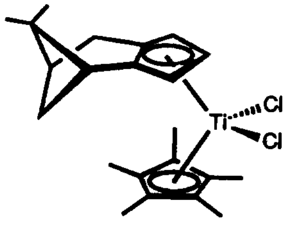

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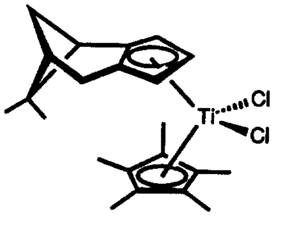

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We are attempting to show that valuable information can be derived by coupling fulll knowledge of the solid state structural characteristics of a group of complexes with the binding energies exhibited by these materials as determined by X-ray photoelectron spectroscopic methods [10]. Attention is focused here particularly on the dichlorotitaniums **5**–**8**, where systematic variation of the steric bulk of the second ligand (Cp or Cp*) and its stereochemical orientation on structure are examined crystallographically in three examples [11*,12*].

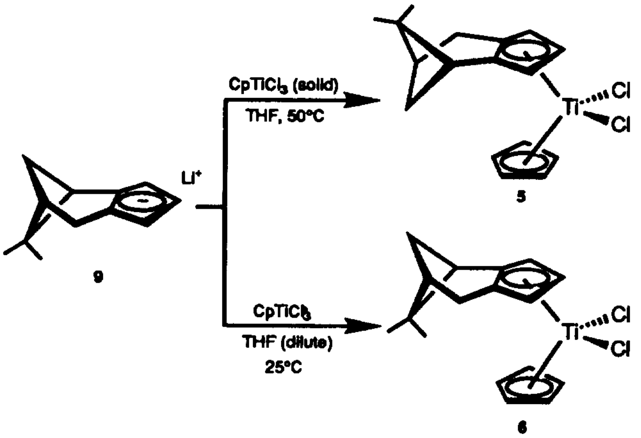
1. Results

In the synthesis of **5** and **6** described earlier [6c], mixtures of the two complexes were invariably obtained. Although the **5**:**6** ratios could be varied by taking advantage of the established temperature dependence to π-face complexation in **9**, the need remained for tedious separation of these diastereomers. As a consequence, their availability was lessened dramatically. As detailed in the Experimental section, these complications have now been completely resolved.

To achieve stereocontrolled above-plane complexation as in **5**, we have found it most convenient to add a warm (50°C) tetrahydrofuran solution of **9** to solid CpTiCl$_3$. These conditions conveniently provide **5** as a red solid in 69% yield after a single recyrstallization. Reversal of stereoselectivity rests on adding **9** slowly to dilute solutions of CpTiCl$_3$ (< 100 mg/10 ml) in tetrahydrofuran at room temperature. Shiny purple-brown crystals of **6** were isolated from toluene–hexane in 70% yield.

Moriarty has reported that attempted reaction of **9** with Cp*TiCl$_3$ [13] gave rise to ill-defined products [6c]. Although steric factors do complicate matters, further examination of this reaction has shown that reasonable levels of condensation can be effected if reaction times are prolonged. Thus, the green-brown solution that is obtained by mixing excess **9** with Cp*TiCl$_3$ in benzene was stirred at room temperature for 5 days and subsequently heated at reflux for 12 h. Direct isolation gave **7** (23%) as brown-black crystals exhibiting $[\alpha]_D^{19}$ −356° (*c* 0.1, toluene). That above-plane complexation had materialized was immediately evident from the appearance of the pair of methyl singlets at δ 1.36 and 0.50. For comparison, the related signals in **5** are seen at entirely comparable chemical shifts (δ 1.34, 0.49), while those in **6** reflect the increased deshielding at the *syn* methyl group brought on by its proximity to the metal center (δ 1.37, 0.74) [6].

To achieve the stereochemical crossover demanded by the maximally congested below-plane isomer **8**, advantage was initially taken of the established propensity of trimethylsilyl-substituted isodicyclopentadienes [14] to undergo electrophilic attack with inversion of configuration [4c,15]. To this end, solutions of **9** in cold (−78°C) tetrahydrofuran were allowed to react with chlorotrimethylsilane. The stereochemically homogeneous silane **10**, formed as an 8:1 mixture with its epimer, was isolated as a colorless, crystalline solid in 71% yield. Proper definition of the newly introduced stereocenter was achieved by Diels–Alder condensation with *N*-phenylmaleimide in benzene at 25°C. The resulting adducts **12** and **13**, produced in a 5:1 ratio, were chromatographically separated and identified by their high-field ^{1}H NMR features (see Experimental



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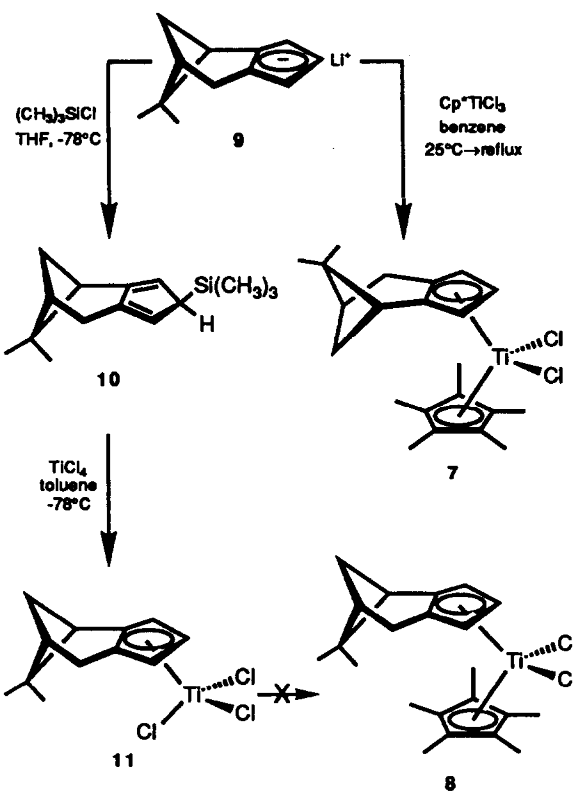
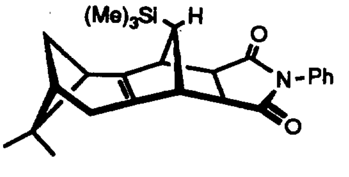
* Reference number with asterisk indicates a note in the list of references.



section) in the manner detailed elsewhere [6] for the parent system. The proximity of the methyl groups on silicon to the *syn*-methano proton of the pinene subunit was established convincingly by appropriate nuclear Overhauser effect measurements.



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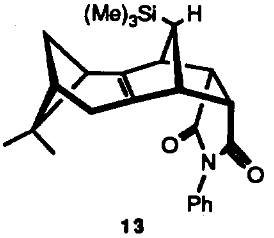

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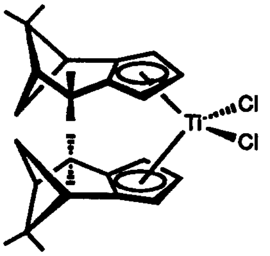
Exposure of **10** to titanium tetrachloride in toluene at −78°C resulted in immediate development of a brick-red color. After warming to room temperature, the trichloride **11** was obtained in good yield. The ^{1}H and ^{13}C NMR spectra of **11** showed the complex to be that stereoisomer in which coordination to titanium operates on that π-face proximal to the *gem*-dimethyl substituents. This important feature was revealed by the very telling appearance of the *syn*-methyl singlet absorption at δ 0.94, indicative of its projection into a region affected strongly by the anisotropy of the transition metal [6]. In tandem with this observation, the *syn*-methano bridge proton on the opposite surface resonates at its more shielded position (δ 0.78) in accord with its remoteness from the metal center. Therefore, the silyl substituent in **10** has directed the complexation event to the opposite face of the cyclopentadienyl ring, as anticipated [15].

Although **11** enters into reaction with cyclopentadienide anions that are not heavily substituted, it proved unwilling to condense with Cp*Li, Cp*K, or Cp*Ti [16] in THF or toluene at temperatures up to 25°C. Since recourse to Cp*SiMe$_3$ [17] or to Cp*SnMe$_3$ [18] likewise did not engage **11** in formation of the mixed titanocenes, further pursuit of this objective was dropped.

The three-dimensional stereochemical features of the three available complexes were ascertained by X-ray crystallography (Tables 1–4). The ORTEP illustrations of **5**–**7** are presented in Fig. 1–3. While **5** and **6** exhibit minor differences, they are actually remarkably similar to two structurally related compounds previously studied, *viz.* **14** [7a] and **15** [7b]. The C5 rings are eclipsed in **5** and very nearly eclipsed in **6**. The substituted portion of each molecule is directed towards one side. This brings the bulkiest portion of the substituted Cp closer to one of the Cl ligands (Cl(2) in **5** and Cl(1) in **6**). This Cl position is the one that exhibits the shorter of the two Ti–Cl contacts in each case.



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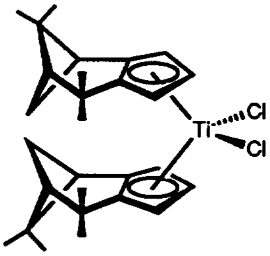

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In the Cp* analogue of **5**, *viz.* **7**, differences related to steric effects are manifested. Thus, the Cp rings are now staggered and the substituted carbon positions are directed immediately over the Cl–Ti–Cl bonds. This is presumably a result of unreasonably short contacts with the Cp* methyl substituents that would result if the molecule were to adopt the sideways conformations observed in **5** and **6**. A major difference stemming from this orientation is expansion of the Cl–Ti–Cl bond angle to 97.0(2)° from 91.80(5)° in **6** and 92.02(2)° in **5** (Table 5). It is noteworthy that the closest approach of the substituted portions of the Cp ring in **7** most likely to result in steric interferences are between Cl(1) and C(17), with Cl(1) exhibiting a closer approach to Ti than does Cl(2). Cl(1) also has the shortest contacts to the Cp* ligand.

In the three compounds, the sterically congested portion of the Cp ligand makes its closest approach to

TABLE 1. Experimental crystallographic data for **5**–**7**

	5	**6**	**7**
F.W.	343.13	343.13	413.27
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Temperature (°C)	21	22	23
Cell constants [a]			
a (Å)	6.812(2)	6.902(8)	12.101(2)
b (Å)	9.620(4)	9.249(8)	12.319(7)
c (Å)	24.170(7)	24.600(9)	13.897(4)
Cell volume (Å^3)	1584	1570	2071.6
Formula units/unit cell	4	4	4
D_{calc} (g cm^{-3})	1.44	1.45	1.32
μ_{calc} (cm^{-1})	8.82	8.88	6.85
Diffractometer/scan	Enraf-Nonius CAD-4/ω–2θ	Enraf-Nonius CAD-4/ω–$s\theta$	Enraf-Nonius CAD-4/ω–2θ
Radiation, graphite monochromator	Mo Kα ($\lambda = 0.71073$)	Mo Kα ($\lambda = 0.71073$)	Mo Kα ($\lambda = 0.71073$)
Max crystal dimensions (mm^3)	$0.18 \times 0.23 \times 0.45$	$0.10 \times 0.15 \times 0.18$	$0.14 \times 0.18 \times 0.40$
Scan width	$0.80 + 0.35 \tan \theta$	$0.80 + 0.35 \tan \theta$	$0.80 + 0.35 \tan \theta$
Standard reflections	400; 040, 0, 0, 12	020; 102; 0, 0, 10	600; 020; 002
Decay of standards	±1.5%	±2%	±3.5%
Reflections measured	1644	1640	2107
2θ range (°)	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$
Range of h, k, l	+8, +11, +28	+8, +11, +29	+14, +14, +16
Reflections observed [$F_o \geq 5\sigma(F_o)$] [b]	1383	693	997
Computer programs [c]	SHELX [23]	SHELX [23]	SHELX [23]
Structure solution	SHELXS [25]	Coordinates from M = Zr	SHELXS [25]
No. of parameters varied	187	187	137
Weights	$[\sigma(F_o)^2 + 0.00018\ F_o{}^2]^{-1}$	$[\sigma(F_o)^2 + 0.003\ F_o{}^2]^{-1}$	$[\sigma(F_o)^2 + 0.00032\ F_o{}^2]^{-1}$
GOF	2.02	1.22	4.10
$R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert \Sigma \lvert F_o \rvert$	0.031	0.056	0.064
R_w	0.040	0.071	0.077
R inverse configuration	0.034	0.057	0.065
Largest feature final diff. map (e Å^{-3})	0.3	0.3	0.3

[a] Least-squares refinement of $((\sin)/\lambda)^2$ values for 25 reflections $\theta > 20°$ (for **5**), $> 8°$ (for **6**), and $> 11°$ (for **7**). [b] Corrections: Lorentz-polarization. [c] Neutral scattering factors and anomalous dispersion corrections from ref. 26.

the shorter of the Ti–Cl separations. At *ca.* 0.05 Å, the difference between the two Ti–Cl bonds is nearly identical in all three instances. A similar difference of 0.06 Å was noted in **14** and **15**. For comparison, the Ti–Cl bonds are equivalent in Cp_2TiCl_2 (2.364(3) Å) [19], $Cp_2^*TiCl_2$ (2.349(4) Å) [20], $Cp^*CpTiCl_2$ (2.3518(9) Å) [21] and $(CpMe)_2TiCl_2$ (2.360(2) Å) [22].

The bonding of each Ti atom to the Cp fragments is similar in **5**–**7**. In **5** and **6**, there is a narrow range of Ti–Cp separations, 0.08 Å in **5** and 0.04 Å in **6**. The average distance in each, 2.36(3) and 2.38(2) Å, respectively, is considered to be statistically identical. The range of Ti–C(Cp*) separations in **7** (0.17 Å) is larger, once again a likely consequence of steric compression. The C(5) position in **7** makes the closest approach, with C(3) and C(2) having the longest separations. Its overall Ti–Cp* average appears to be longer at 2.42(6) Å as expected; however, the difference is statistically insignificant.

The achiral Cp ring is tilted in **5**–**7** such that the substituted carbon positions make the longest approach to Ti and the carbon atom opposite these makes the closest approach. The two carbon atoms between these positions have intermediate Ti–C separations. In **5**, the range is 0.15 Å (2.34(2)–2.49(2) Å) while in **6** it is 0.16 Å (2.317(4)–2.479(4) Å). For comparison, the range in **7** is 0.20 Å (2.31(1)–2.51(2) Å). This tilt was observed in both rings of **14** and **15**. The preceding relationships very likely impact on the level of reactivity at the metal center. The differing abilities of **5**–**7** to function in highly stereocontrolled chemical reactions is currently under investigation and will be described at a later date.

2. Experimental section

Melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 1320 spectrometer. ^1H NMR were recorded at 300 MHz and ^{13}C NMR spectra at 75 or 62.5 MHz as indicated. Mass spectra were recorded on a Kratos MS-30 instrument by Mr. Dick Weisenberger at the Ohio State University

TABLE 2. Bond distances (Å) and angles (°) for **5**

Bond distances			
Ti–Cl(1)	2.331(1)	Ti–Cl(2)	2.366(1)
Ti–C(1)	2.357(5)	Ti–C(2)	2.383(5)
Ti–C(3)	2.402(5)	Ti–C(4)	2.395(4)
Ti–C(5)	2.361(4)	Ti–C(6)	2.449(4)
Ti–C(7)	2.377(4)	Ti–C(8)	2.317(4)
Ti–C(9)	2.394(4)	Ti–C(10)	2.479(4)
C(1)–C(2)	1.387(8)	C(1)–C(5)	1.399(7)
C(2)–C(3)	1.379(8)	C(3)–C(4)	1.399(7)
C(4)–C(5)	1.400(7)	C(6)–C(7)	1.408(6)
C(6)–C(10)	1.413(6)	C(6)–C(14)	1.501(6)
C(7)–C(8)	1.380(6)	C(8)–C(9)	1.409(7)
C(9)–C(10)	1.419(6)	C(10)–C(11)	1.515(6)
C(11)–C(12)	1.526(7)	C(12)–C(13)	1.539(6)
C(12)–C(15)	1.567(7)	C(13)–C(14)	1.551(6)
C(14)–C(15)	1.579(6)	C(15)–C(16)	1.522(6)
C(15)–C(17)	1.542(7)	Cent1 [a]–Ti	2.06
Cent2–Ti	2.08		
Angles			
Cl(1)–Ti–Cl(2)	91.80(5)	C(2)–C(1)–C(5)	107.6(5)
C(1)–C(2)–C(3)	108.8(5)	C(2)–C(3)–C(4)	108.2(5)
C(3)–C(4)–C(5)	107.4(5)	C(1)–C(5)–C(4)	107.9(5)
C(7)–C(6)–C(10)	107.1(4)	C(7)–C(6)–C(14)	134.4(4)
C(10)–C(6)–C(14)	117.9(4)	C(6)–C(7)–C(8)	108.8(4)
C(7)–C(8)–C(9)	109.2(4)	C(8)–C(9)–C(10)	106.6(4)
C(6)–C(10)–C(9)	108.3(4)	C(6)–C(10)–C(11)	118.5(4)
C(9)–C(10)–C(11)	132.4(4)	C(10)–C(11)–C(12)	109.0(4)
C(11)–C(12)–C(13)	110.6(4)	C(11)–C(12)–C(15)	112.4(4)
C(13)–C(12)–C(15)	87.2(3)	C(12)–C(13)–C(14)	87.3(3)
C(6)–C(14)–C(13)	107.9(4)	C(6)–C(14)–C(15)	106.2(3)
C(13)–C(14)–C(15)	86.4(3)	C(12)–C(15)–C(14)	85.3(3)
C(12)–C(15)–C(16)	119.8(5)	C(14)–C(15)–C(16)	119.3(4)
C(12)–C(15)–C(17)	112.1(4)	C(14)–C(15)–C(17)	110.7(4)
C(16)–C(15)–C(17)	108.1(4)	Cent1–Ti–Cent2	131.1
Cent1–Ti–Cl(1)	105.6	Cent1–Ti–Cl(2)	106.6
Cent2–Ti–Cl(1)	107.1	Cent2–Ti–Cl(2)	107.6

[a] Cent1 is the centroid of the C(1)–(C)5 ring, Cent2 the C(6)–C(10) ring.

Chemical Instrument Center. Elemental analyses were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark. All MPLC separations were conducted on Merck Lobar columns (Licroprep Si-60) with the help of a Fluid Metering INC pump and a Waters Associates Model R403 differential refractometer detector. Solvents were dried and distilled from sodium/benzophenone ketyl or calcium hydride prior to use. All manipulations were performed under argon, nitrogen, and/or a vacuum using standard Schlenk-line techniques. Chlorotrimethylsilane (Huls) and titanium tetrachloride (Aldrich) were purified prior to use.

2.1. *exo-(η^5-Cyclopentadienyl)(η^5-(1S,8R)-9,9-dimethyltricyclo[6.1.1.0^{2,6}]deca-2,5-dienyl)dichlorotitanium* (*5*)

In a dry box under nitrogen, (η^5-cyclopentadienyl)-titanium trichloride (137 mg, 0.63 mmol) was placed in a dry 100ml round-bottomed flask fitted with a side-arm. To another dried flask was added the dry, powdery lithium salt **9** (112 mg, 0.68 mmol). The two flasks were connected to a Schlenk line under argon. To **9** was added 5 ml of dry tetrahydrofuran and this solution was warmed to 50°C prior to being transferred via cannula onto the solid $CpTiCl_3$. As addition took place, the stirred slurry turned deep red and was stirred vigorously at room temperature for 8 h before being concentrated *in vacuo*. The residue was taken up in toluene (15 ml), filtered through a pad of Celite, and concentrated by rotary evaporation. Recrystallization of the residue from toluene dichloromethane at −20°C provided powdery red microcyrstals of **5** (148 mg, 69%), m.p. 202–203.5°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.51 (s, 5 H); 6.31 (t, $J = 3.0$ Hz, 1H); 6.11 (q, $J = 2.0$ Hz, 1H); 6.01 (t, $J = 2.3$ Hz, 1H); 3.42 (dd, $J = 14.5$, 2.9 Hz, 1H); 2.82 (m, 2H); 2.48 (m, 1H); 2.15 (m, 1H); 1.37 (s, 3H); 1.30 (d, $J = 10.0$ Hz, 1H); 0.50 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 142.22, 120.22, 119.17, 113.92, 112.41, 43.71, 42.43, 40.46, 31.37, 29.19, 26.08, 21.17 ppm. MS: m/z ($M^+ - Cl$) calcd. 307.0732, obsd. 307.0734; $[\alpha]^{19}_{D} + 817°$ (c 0.05, toluene). Anal. Found: C, 59.67; H, 6.16. $C_{17}H_{20}Cl_2Ti$ calcd.: C, 59.50; H, 5.87%.

2.2. *endo-(η^5-Cyclopentadienyl)(η^5(1S,8R)-9,9-dimethyltricyclo[6.1.1.0^{2,6}]-deca-2,5-dienyl)dichlorotitanium* (*6*)

A solution of **9** (398 mg, 2.39 mmol) in dry tetrahydrofuran (20 ml) was transferred via cannula during 20 min into a magnetically stirred solution of $CpTiCl_3$ (532 mg, 2.43 mmol) in 30 ml of the same solvent under argon. The resulting red solution was stirred at room temperature for 3 days, filtered through Celite, and freed of solvent *in vacuo*. Recyrstallization of the residue from toluene/hexane afforded shiny brown-black crystals of **6** in two crops (571 mg, 70%). The physical and spectral properties of **5** have been reported previously [6c].

2.3. *exo-(η^5-Pentamethylcyclopentadienyl)(η^5-(1S,8R)-9,9-dimethyltricyclo-[6.1.1.0^{2,6}]deca-2,5-dienyl)dichlorotitanium* (*7*)

To a solution of (η^5-pentamethylcyclopentadienyl) titanium trichloride (321 mg, 1.11 mmol) in benzene (50 ml) was added a solution of **9** (267 mg, 1.61 mmol) in a solvent system composed of tetrahydrofuran (5 ml), 1,2-dimethoxyethane (15 ml), and benzene (25 ml) via cannula under argon. The reaction mixture developed a green-brown color after being stirred for 12 h at room temperature. After a total reaction time of 5 days, the mixture was refluxed for 12 h, cooled, filtered through a Celite pad, and concentrated *in vacuo*. The residual oil was taken up in a minimum amount of toluene and hexane and allowed to stand at −20°C.

TABLE 3. Bond distances (Å) and angles (°) for **6**

Bond distances			
Ti–Cl(1)	2.389(5)	Ti–Cl(2)	2.336(5)
Ti–C(1)	2.35(2)	Ti–C(2)	2.36(2)
Ti–C(3)	2.40(2)	Ti–C(4)	2.38(2)
Ti–C(5)	2.32(2)	Ti–C(6)	2.49(2)
Ti–C(7)	2.39(2)	Ti–C(8)	2.34(2)
Ti–C(9)	2.36(2)	Ti–C(10)	2.48(2)
C(1)–C(2)	1.41(2)	C(1)–C(5)	1.38(3)
C(2)–C(3)	1.44(3)	C(3)–C(4)	1.38(3)
C(4)–C(5)	1.34(3)	C(6)–C(7)	1.41(3)
C(6)–C(10)	1.38(3)	C(6)–C(14)	1.50(2)
C(7)–C(8)	1.38(2)	C(8)–C(9)	1.39(2)
C(9)–C(10)	1.43(2)	C(10)–C(11)	1.56(3)
C(11)–C(12)	1.53(2)	C(12)–C(13)	1.58(3)
C(12)–C(15)	1.56(2)	C(13)–C(14)	1.58(2)
C(14)–C(15)	1.56(3)	C(15)–C(16)	1.52(2)
C(15)–C(17)	1.52(2)		
Cent1[a]–Ti	2.04	Cent2–Ti	2.09
Angles			
Cl(1)–Ti–Cl(2)	92.0(2)	Cl(1)–Ti–C(1)	135.4(5)
Cl(2)–Ti–C(1)	108.2(4)	Cl(1)–Ti–C(2)	120.2(5)
Cl(2)–Ti–C(2)	78.8(5)	C(1)–Ti–C(2)	35.0(6)
Cl(1)–Ti–C(3)	85.6(5)	Cl(2)–Ti–C(3)	86.3(6)
C(1)–Ti–C(3)	57.6(7)	C(2)–Ti–C(3)	35.3(6)
Cl(1)–Ti–C(4)	78.6(5)	Cl(2)–Ti–C(4)	119.1(5)
C(1)–Ti–C(4)	56.8(6)	C(2)–Ti–C(4)	57.4(6)
C(3)–Ti–C(4)	33.6(6)	Cl(1)–Ti–C(5)	105.4(5)
Cl(2)–Ti–C(5)	135.7(5)	C(1)–Ti–C(5)	34.4(6)
C(2)–Ti–C(5)	57.1(7)	C(3)–Ti–C(5)	55.8(7)
C(4)–Ti–C(5)	33.0(6)	Cl(1)–Ti–C(6)	134.6(4)
Cl(2)–Ti–C(6)	104.2(4)	C(1)–Ti–C(6)	79.3(5)
C(2)–Ti–C(6)	104.6(6)	C(3)–Ti–C(6)	136.6(6)
C(4)–Ti–C(6)	124.9(6)	C(5)–Ti–C(6)	92.0(6)
Cl(1)–Ti–C(7)	109.4(5)	Cl(2)–Ti–C(7)	134.2(5)
C(1)–Ti–C(7)	84.6(7)	C(2)–Ti–C(7)	118.9(7)
C(3)–Ti–C(7)	133.7(8)	C(4)–Ti–C(7)	104.8(7)
C(5)–Ti–C(7)	77.9(7)	C(6)–Ti–C(7)	33.4(6)
Cl(1)–Ti–C(8)	79.4(5)	Cl(2)–Ti–C(8)	122.4(5)
C(1)–Ti–C(8)	117.5(7)	C(2)–Ti–C(8)	152.5(7)
C(3)–Ti–C(8)	147.7(7)	C(4)–Ti–C(8)	114.6(7)
C(5)–Ti–C(8)	101.0(7)	C(6)–Ti–C(8)	56.0(6)
C(7)–Ti–C(8)	34.0(6)	Cl(1)–Ti–C(9)	83.2(5)
Cl(2)–Ti–C(9)	88.3(6)	C(1)–Ti–C(9)	135.0(7)
C(2)–Ti–C(9)	153.3(6)	C(3)–Ti–C(9)	167.4(7)
C(4)–Ti–C(9)	147.3(7)	C(5)–Ti–C(9)	133.4(8)
C(6)–Ti–C(9)	55.3(6)	C(7)–Ti–C(9)	56.5(7)
C(8)–Ti–C(9)	34.4(6)	Cl(1)–Ti–C(10)	116.2(5)
Cl(2)–Ti–C(10)	79.3(5)	C(1)–Ti–C(10)	106.6(6)
C(2)–Ti–C(10)	119.6(6)	C(3)–Ti–C(10)	153.9(6)
C(4)–Ti–C(10)	157.1(7)	C(5)–Ti–C(10)	124.4(7)
C(6)–Ti–C(10)	32.3(6)	C(7)–Ti–C(10)	55.0(6)
C(8)–Ti–C(10)	56.1(6)	C(9)–Ti–C(10)	34.2(6)
Ti–C(1)–C(2)	72.9(9)	Ti–C(1)–C(5)	72(1)
C(2)–C(1)–C(5)	106(2)	Ti–C(2)–C(1)	72.1(9)
Ti–C(2)–C(3)	74(1)	C(1)–C(2)–C(3)	106(2)
Ti–C(3)–C(2)	70.8(9)	Ti–C(3)–C(4)	72.3(9)
C(2)–C(3)–C(4)	107(2)	Ti–C(4)–C(3)	74(1)
Ti–C(4)–C(5)	71.4(9)	C(3)–C(4)–C(5)	109(2)
Ti–C(5)–C(1)	74(1)	Ti–C(5)–C(4)	76(1)
C(1)–C(5)–C(4)	111(2)	Ti–C(6)–C(7)	70(1)
Ti–C(6)–C(10)	73.4(9)	C(7)–C(6)–C(10)	107(2)

TABLE 3 (continued)

Angles			
Ti–C(6)–C(14)	139(1)	C(7)–C(6)–C(14)	131(2)
C(10)–C(6)–C(14)	118(2)	Ti–C(7)–C(6)	77(1)
Ti–C(7)–C(8)	71(1)	C(6)–C(7)–C(8)	109(2)
Ti–C(8)–C(7)	75(1)	Ti–C(8)–C(9)	74(1)
C(7)–C(8)–C(9)	108(2)	Ti–C(9)–C(8)	72(1)
Ti–C(9)–C(10)	77.3(9)	C(8)–C(9)–C(10)	107(2)
Ti–C(10)–C(6)	74(1)	Ti–C(10)–C(9)	68.5(9)
C(6)–C(10)–C(9)	108(2)	Ti–C(10)–C(11)	135(1)
C(6)–C(10)–C(11)	118(2)	C(9)–C(10)–C(11)	133(2)
C(10)–C(11)–C(12)	110(2)	C(11)–C(12)–C(13)	110(1)
C(11)–C(12)–C(15)	113(1)	C(13)–C(12)–C(15)	86(1)
C(12)–C(13)–C(14)	85(1)	C(6)–C(14)–C(13)	103(1)
C(6)–C(14)–C(15)	116(1)	C(13)–C(14)–C(15)	86(1)
C(12)–C(15)–C(14)	86(1)	C(12)–C(15)–C(16)	116(1)
C(14)–C(15)–C(16)	123(2)	C(12)–C(15)–C(17)	111(1)
C(14)–C(15)–C(17)	112(1)	C(16)–C(15)–C(17)	108(2)
Cent1–Ti–Cent2	132.0	Cent1–Ti–Cl(1)	106.0
Cent1–Ti–Cl(2)	106.7	Cent2–Ti–Cl(1)	106.2
Cent2–Ti–Cl(2)	106.6		

[a] Cent1 is the centroid of the C(1)–C(5) ring, Cent2 the C(6)–C(10) ring.

There was isolated 153 mg (23%) of **7** as brown-black crystals, m.p. 185–186.3°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.17 (t, $J = 2.9$ Hz, 1H); 5.12 (t, $J = 2.7$ Hz, 1H); 4.92 (t, $J = 2.4$Hz, 1H); 3.36 (dd, $J = 14.2$, 12.9 Hz, 1H); 2.75 (t, $J = 5.3$ Hz, 2H); 2.66 (dd, $J = 14.6$, 24 Hz, 1H); 2.45 (m, 2H); 2.08 (s, 15H); 1.36 (s, 3H); 0.50 (s, 3H). ^{13}C NMR (75 MHz, C_6D_6): 148.87, 139.99, 133.96, 115.90, 111.60, 107.55, 44.25, 42.36, 40.98, 31.89, 29.17, 26.40, 21.51, 13.33 ppm. MS: m/z ($M^+ - Cl$) calcd. 377.1515, obsd. 377.1475; $[\alpha]_D^{19}$ $-356°$ (c 0.1, toluene). Anal. Found: C, 63.39; H, 7.37.

$C_{22}H_{30}Cl_2Ti$ calcd.: C, 63.94; H, 7.32%.

*2.4. exo-4-(Trimethylsilyl)-(1S,8R)-9,9-dimethyltricyclo-[6.1.0.0^{2,6}]deca-2,5-diene (**10**)*

A cold (−78°C), magnetically stirred solution of chlorotrimethylsilane (3.06 ml, 24.13 mmol) in anhydrous THF (50 ml) was treated via cannula during 30 min with a solution of **9** (2.00 g, 12.03 mmol) in the same solvent (150 ml). The reaction mixture was stirred at −78°C for 1 h and allowed to warm to room temperature during 30 min. Ether (200 ml) was added and the salts were removed by washing with water (3 × 200 ml). The organic phase was dried and evaporated to leave a yellow oil (2.66 g, 85%) as an 89 : 11 mixture of **10** and its epimer. MPLC purification (silica gel, elution with petroleum ether) afforded pure **10** (2.0 g, 71%) as a colorless crystalline solid, m.p. 46–47°C. IR (CCl_4): 3065, 2930, 2875, 2845, 2755, 1880, 1680, 1645, 1570, 1470, 1435, 1390, 1370, 1358, 1251, 942, 910, 841, 750 cm^{-1}. ^{1}H NMR (300 MHz, C_6H_6): δ 6.08

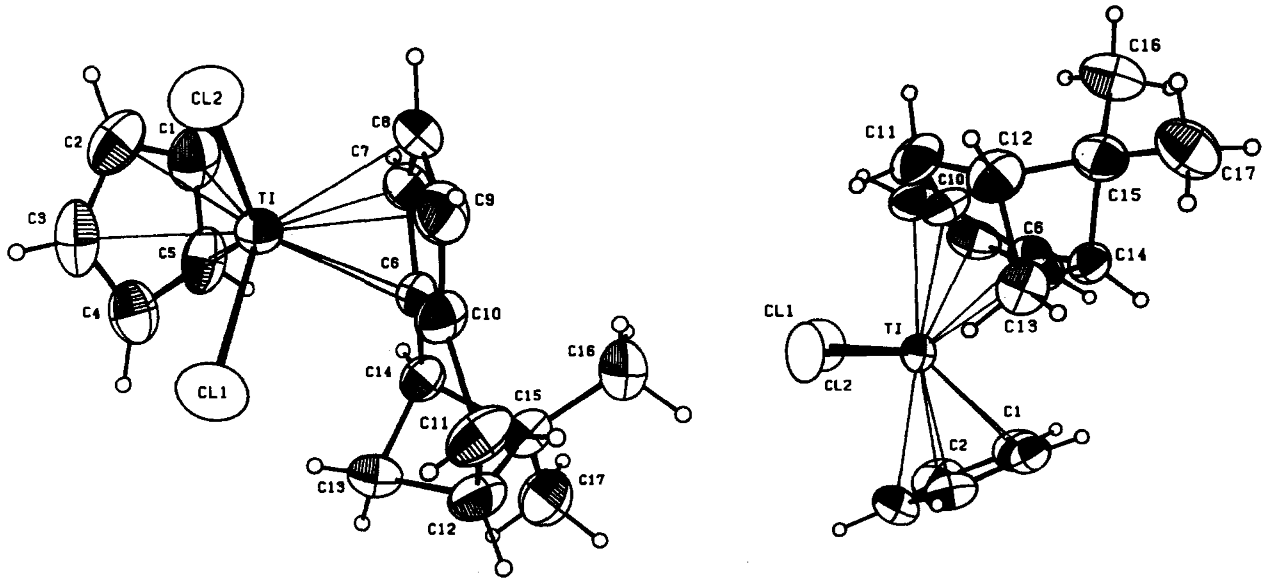

Fig. 1. Two views of the crystallographically determined molecular structure of **5** as drawn with 50% thermal ellipsoids.

(s, 1H); 5.95 (s, 1H); 3.18 (s, 1H); 2.76 (m, 4H); 2.57 (m, 1H); 2.02 (m, 1H); 1.27 (s, 3H); 1.26 (d, $J = 9.4$ Hz, 1H); 0.87 (s, 3H); −0.04 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): 151.35, 139.90, 125.81, 121.00, 49.44, 43.67, 41.89, 40.66, 33.10, 28.20, 26.53, 21.65, −2.03 ppm. MS: m/z (M^+) calcd. 232.1647, obsd. 232.1655; $[\alpha]_D^{19}$ −49.8° (c 0.25, $CHCl_3$). Anal. Found: C, 77.44; H, 10.41.

$C_{15}H_{24}Si$ calcd.: C, 77.51; H, 10.41%.

2.5. endo-(η^5-(1S,8R)-9,9-dimethyltricyclo-[6.1.1.0^{2,6}]-deca-2,5-dienyl)titanium trichloride (11)

Into a dry, air-free flask was placed **10** (1.50 g, 6.45 mmol) and toluene (5 ml). This solution was added during 30 min to a cold (−78°C), stirred solution of titanium tetrachloride (1.22 g, 6.45 mmol) in toluene. The brick-red reaction mixture was stirred at −78°C for 1 h and at room temperature for 1 h prior to filtration through Celite under argon to give an orange-

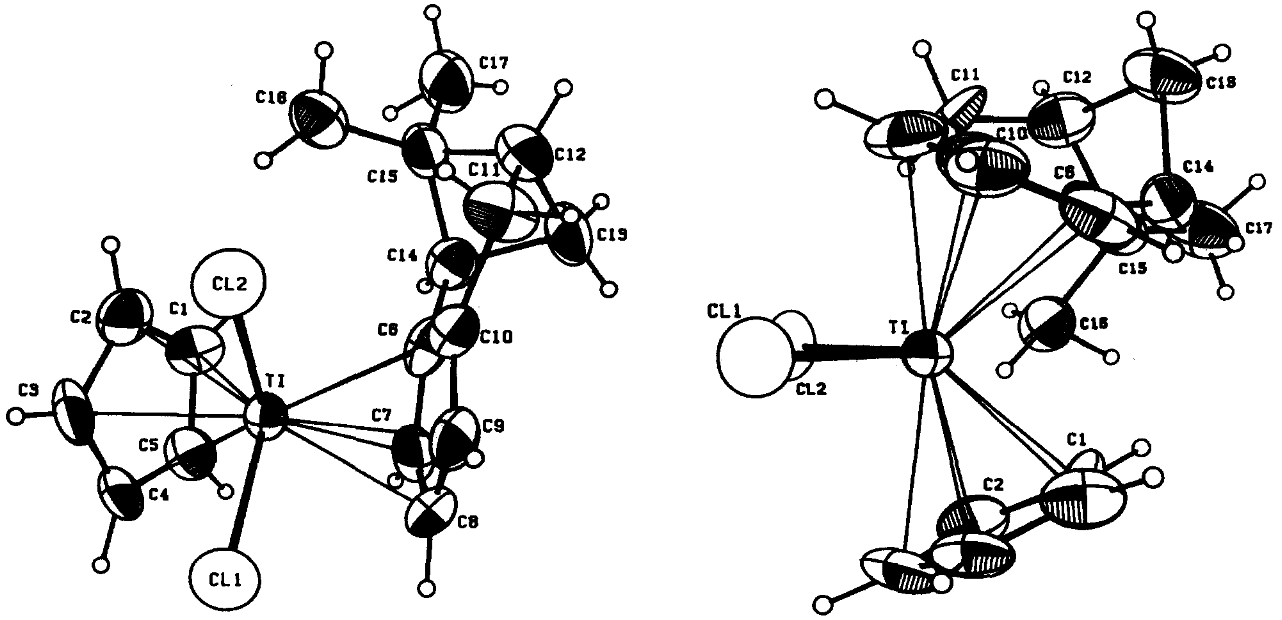

Fig. 2. Two views of the crystallographically determined molecular structure of **6** as drawn with 50% ellipsoids.

red solution, which was concentrated *in vacuo* to give **11** (1.26 g, 62%) as a brown-black solid, m.p. 92–94°C (after sublimation). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.12 (d, $J = 2.9$ Hz, 1H); 6.56 (br s, 1H); 6.47 (t, $J = 3.0$ Hz, 1H); 3.34 (dd, $J = 15.9$, 1.8 Hz, 1H); 3.32 (t, $J = 5.2$ Hz, 1H); 3.00 (dd, $J = 14.2$, 3.5 Hz, 1H); 2.77 (m, $J = 5.0$ Hz, 1H); 2.24 (br s, 1H); 1.34 (s, 3H); 0.94 (s, 3H); 0.78 (d, $J = 9.9$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 153.88, 139.17, 124.55, 122.43, 118.83, 46.28, 40.89, 40.34, 36.25, 27.61, 26.13, 21.42 ppm. MS: m/z ($M^+ - Cl$) calcd. 277.9922, obsd. 277.9917; $[\alpha]_D^{20}$ −125° (c 0.12, $CHCl_3$). Anal. Found: C, 46.32; H, 4.94. $C_{12}H_{15}Cl_3Ti$ calcd.: C, 45.98; H, 4.82%.

2.6. Reaction of 10 with N-phenylmaleimide

A solution of **10** (205 mg, 0.882 mmol) in hexane (5 ml) was treated with a solution of *N*-phenylmaleimide (152.7 mg, 0.882 mmol) in benzene (20 ml) and stirred at room temperature for 36 h. Solvent evaporation and chromatography on the residue on silica gel (elution with 5% ethyl acetate in petroleum ether) afforded pure **12** (262 mg, 82%) and pure **13** (59 mg, 16%).

For **12**: colorless solid, m.p. 175–176.7°C (from ether). IR ($CHCl_3$): 3009, 2960, 2935, 1767, 1706, 1500, 1380, 1267, 1210, 1184, 1101, 1020, 934, 892, 783, 672 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49–7.22 (m, 5H); 3.28 (s, 2H); 3.03 (dd, $J = 11.6$, 6.8 Hz, 2H); 2.49 (m, 2H); 2.40 (t, $J = 5.5$ Hz, 1H); 2.20 (d, $J = 2.4$ Hz, 1H); 2.15 (m, 1H); 1.31 (s, 3H); 1.10 (s, 1H); 0.61 (s, 3H); 0.19 (s, 1H); −0.02 (s, 9H). ^{13}C NMR (62.5 MHz, $CDCl_3$): 177.69, 177.50, 153.26, 138.02, 132.00, 129.20, 128.61, 126.40, 52.49, 51.11, 50.27, 50.09, 43.33, 42.38, 41.88, 41.47, 40.43, 32.28, 28.92, 26.55, 21.39, −0.46 ppm. MS m/z (M^+) calcd. 405.2124, obsd. 405.2128; $[\alpha]_D^{19}$ −23.0° (c 0.11, $CHCl_3$).

For **13**: colorless solid, m.p. 139–141°C (from ether). IR ($CHCl_3$); 3005, 2958, 2939, 2861, 1768, 1708, 1501, 1378, 1265, 1253, 1182, 870, 840, 692 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50–7.22 (m, 5H); 3.33 (br s, 2H); 3.00 (d, $J_{AB} = 6.8$ Hz, 1H); 2.89 (d, $J_{AB} = 6.8$ Hz, 1H); 2.50 (m, 2H); 2.37 (t, $J = 4.9$ Hz, 1H); 2.10 (t, $J = 3.8$ Hz, 1H); 1.55 (s, 1H); 1.31 (s, 3H); 1.00 (s, 1H); 0.92 (s, 3H); 0.54 (d, $J = 8.9$ Hz, 1H); 0.0 (s, 9H), ^{13}C NMR (75 MHz, $CDCl_3$): 177.33, 177.18, 151.99, 137.97, 132.03, 129.21, 129.15, 128.71, 128.63, 127.80, 126.45, 125.92, 53.47, 52.35, 51.06, 49.68, 41.73, 40.25, 39.61, 33.52, 29.41, 26.79, 21.97, −0.26 ppm. MS m/z (M^+) calcd. 405.2124, obsd. 405.2115; $[\alpha]_D^{19}$ −54.6° (c 0.26, $CHCl_3$).

2.7. X-Ray crystallographic analysis of 5

A red single crystal of **5** was mounted on a pin and transferred to the goniometer. The space group was determined to be the acentric $P2_12_12_1$ from the systematic absences. A summary of data collection is given in Table 1.

Least-squares refinement with isotropic thermal parameters led to $R = 0.096$. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å. The methyl hydrogen atoms were included as a rigid group with rotational freedom at the bonded carbon atoms (C–H = 0.95 Å, $B = 5.5$ Å^2). Absolute configuration

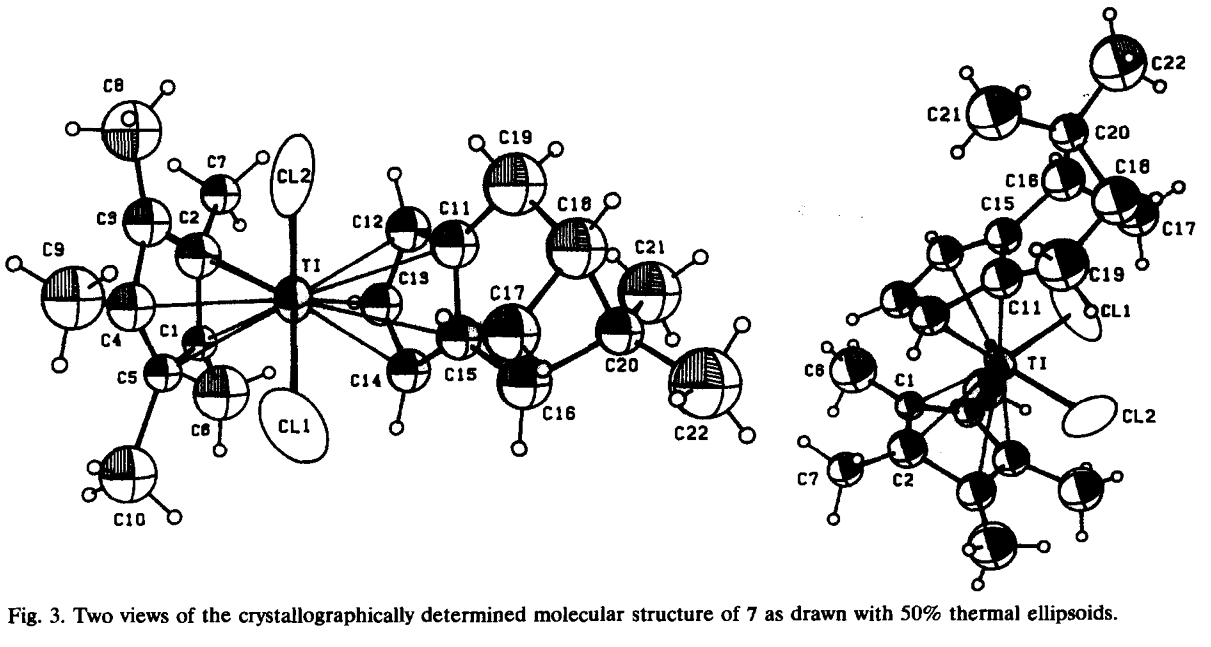

Fig. 3. Two views of the crystallographically determined molecular structure of 7 as drawn with 50% thermal ellipsoids.

TABLE 4. Bond distances (Å) and angles (°) for 7

Bond distances			
Ti–Cl(1)	2.310(6)	Ti–Cl(2)	2.352(6)
Ti–C(1)	2.40(2)	Ti–C(2)	2.42(2)
Ti–C(3)	2.52(2)	Ti–C(4)	2.39(1)
Ti–C(5)	2.35(2)	Ti–C(11)	2.51(2)
Ti–C(12)	2.42(2)	Ti–C(13)	2.31(1)
Ti–C(14)	2.32(2)	Ti–C(15)	2.51(2)
C(1)–C(2)	1.37(2)	C(1)–C(5)	1.32(2)
C(1)–C(6)	1.46(2)	C(2)–C(3)	1.54(2)
C(2)–C(7)	1.53(2)	C(3)–C(4)	1.44(2)
C(3)–C(8)	1.40(2)	C(4)–C(5)	1.35(2)
C(4)–C(9)	1.54(2)	C(5)–C(10)	1.62(2)
C(11)–C(12)	1.44(2)	C(11)–C(15)	1.37(2)
C(11)–C(19)	1.52(2)	C(12)–C(13)	1.36(2)
C(13)–C(14)	1.37(2)	C(14)–C(15)	1.39(2)
C(15)–C(16)	1.51(2)	C(16)–C(17)	1.53(2)
C(16)–C(20)	1.53(2)	C(17)–C(18)	1.56(2)
C(18)–C(19)	1.53(2)	C(18)–C(20)	1.57(2)
C(20)–C(21)	1.57(2)	C(20)–C(22)	1.50(2)
Ti–Cent1 [a]	2.10	Ti–Cent2	2.10
Angles			
Cl(1)–Ti–Cl(2)	97.0(2)	C(2)–C(1)–C(5)	109(2)
C(2)–C(1)–C(6)	126(2)	C(5)–C(1)–C(6)	124(2)
C(1)–C(2)–C(3)	108(2)	C(1)–C(2)–C(7)	132(2)
C(3)–C(2)–C(7)	119(2)	C(2)–C(3)–C(4)	100(1)
C(2)–C(3)–C(8)	123(2)	C(4)–C(3)–C(8)	137(2)
C(3)–C(4)–C(5)	110(1)	C(3)–C(4)–C(9)	113(2)
C(5)–C(4)–C(9)	137(2)	C(1)–C(5)–C(4)	113(1)
C(1)–C(5)–C(10)	125(2)	C(4)–C(5)–C(10)	119(1)
C(12)–C(11)–C(15)	104(2)	C(12)–C(11)–C(19)	135(2)
C(15)–C(11)–C(19)	120(2)	C(11)–C(12)–C(13)	111(1)
C(12)–C(13)–C(14)	106(1)	C(14)–C(14)–C(15)	109(1)
C(11)–C(15)–C(14)	109(2)	C(11)–C(15)–C(16)	117(2)
C(14)–C(15)–C(16)	133(1)	C(15)–C(16)–C(17)	108(1)
C(15)–C(16)–C(20)	108(1)	C(17)–C(16)–C(20)	86(1)
C(16)–C(17)–C(18)	88(1)	C(17)–C(18)–C(19)	110(1)
C(17)–C(18)–C(20)	84(1)	C(19)–C(18)–C(20)	111(1)
C(11)–C(19)–C(18)	110(1)	C(16)–C(20)–C(18)	87(1)
C(16)–C(20)–C(21)	121(1)	C(18)–C(20)–C(21)	111(1)
C(16)–C(20)–C(22)	113(1)	C(18)–C(20)–C(22)	111(1)
C(21)–C(20)–C(22)	111(1)	Cent1–Ti–Cent2	132.9
Cent1–Ti–Cl(1)	105.8	Cent1–Ti–Cl(2)	106.7
Cent2–Ti–Cl(1)	104.2	Cent2–Ti–Cl(2)	104.6

[a] Cent1 is the centroid of the C(1)–C(5) ring, Cent2 the C(11)–C(15) ring.

was determined by choice of optically pure starting material. Refinement of nonhydrogen atoms with anisotropic temperature factors led to the final values of $R = 0.0031$ and $R_w = 0.040$. The final values of the positional parameters are given in the Supplementary Material.

2.8. *X-Ray crystallographic analysis of 6*

A dark red single crystal of **6** was mounted on a pin and transferred to the goniometer. The space group was determined to be the acentric $P2_12_12_1$ from the systematic absences. A summary of data collection parameters is given in Table 1. The structural details of **6** were solved utilizing the fractional coordinates of the isostructural Zr analog [6c].

Least-squares refinement with isotropic thermal parameters led to $R = 0.087$. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. The methyl hydrogen atoms were included as a rigid group with rotational freedom at the bonded carbon atom (C–H = 0.95 Å, $B = 5.5$ Å^2). Absolute configuration was predetermined from optically pure starting materials. Refinement of nonhydrogen atoms with anisotropic temperature factors led to the final values of $R = 0.056$ and $R_w = 0.071$. The final values of the positional parameters are given in Supplementary Material.

2.9. *X-Ray crystallographic analysis of 7*

A single crystal of **7** was mounted on a pin and transferred to the goniometer. The space group was determined to be the acentric $P2_12_12_1$ from the systematic absences. A summary of data collection parameters is given in Table 1.

Refinement of this compound was severely hampered by pseudosymmetry relating most of the atoms. There were only about 10–12 very weak reflections which break the observed requirements for *Pnma* or $Pn2_1a$. Refinement can actually be carried out in *Pnma* leading to a similar R value (however, the bonding parameters are poor and disorder appears to be present). Only four atoms cannot (at least approximately) be related by the pseudomirror plane. Nonetheless, $P2_12_12_1$ is the correct space group and the refinement was carried out in it. The resulting correlations did have an effect on the bonding parameters and the e.s.d's, however, the refinement and the bonding parameters are reasonable for this compound.

Least-squares refinement with isotropic thermal parameters led to $R = 0.127$. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. The methyl hydrogen atoms were included as a rigid group with rotational freedom at the bonded carbon atom (C–H = 0.95 Å, $B = 5.5$ Å^2). Absolute configuration was determined by the choice of optically pure starting materials. Refinement of Ti, Cl(1), and Cl(2) with anisotropic temperature factors and of the remaining atoms with isotropic thermal parameters led to the final values of $R = 0.064$ and $R_w = 0.077$. The final values of the positional parameters are given in the Supplementary Material.

TABLE 5. Comparison of bonding parameters

Compound	**5**	**6**	**7**	**14**	**15**	Cp_2TiCl_2	$CpCp^*TiCl_2$
Ti–Cl(1)	2.389(5)	2.331(1)	2.310(6)	2.318(1)	2.286(3)	2.364(3)	2.3518(9)
Ti–Cl(2)	2.336(5)	2.366(1)	2.352(6)	2.380(1)	2.353(3)	–	–
Ti–Cent1 [a]	2.04	2.06	2.10	2.10	2.11	2.06	2.07
Ti–Cent2	2.09	2.08	2.10	2.11	2.12	–	2.10
Ti–Cp1							
Range	2.32(2)–2.40(2)	2.361(4)–2.402(5)	2.35(2)–2.52(2)			2.326(6)–2.394(8)	2.344(4)–2.428(3)
Average	2.36(3)	2.38(2)	2.42(2)			2.37	2.38(4)
Ti–Cp2							
Range	2.34(2)–2.49(2)	2.317(4)–2.479(4)	2.31(1)–2.51(2)	2.311(4)–2.624(3)	2.30(1)–2.63(1)		2.398–2.440(3)
Cl(1)–Ti–Cl(2)	92.0(2)	91.80(5)	97.0(3)	95.08(4)	99.2(1)	94.53(6)	94.44(5)
Cent1–Ti–Cent2	132.0	131.1	132.9	131.7	131.9	131.0	132.0
Cent1–Ti–Cl(1)	106.0	105.6	105.8	107.0	105.2	106.4	105.4
Cent1–Ti–Cl(2)	106.7	106.6	106.7	105.4	106.0	–	–
Cent2–Ti–Cl(1)	106.2	107.1	104.2	106.6	105.9	–	106.7
Cent2–Ti–Cl(2)	106.6	107.6	104.6	105.1	104.2	–	–

[a] Cent1 is the centroid of the C_5H_5 ring in **1** and **2** and the Cp^* ring in **3**. Cent2 is the centroid of the C_5 ring in the substituted ligand.

3. Supplementary material available

Tables of final fractional coordinates and thermal parameters for **5–7** (9 pages) are available from the authors.

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