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Dichloro(η^5 -cyclopentadienyl){[1-(4-methoxyphenyl)cyclohexyl]- η^5 -cyclopentadienyl}titanium(IV)

JUN TIAN,* NING-HAI HU, QI SHEN
AND BAO-TONG HUANG

*Changchun Institute of Applied Chemistry,
Chinese Academy of Sciences, Changchun 130022,
People's Republic of China*

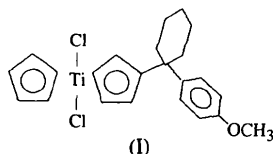
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Abstract

The title molecule, $[\text{TiCl}_2(\text{C}_5\text{H}_5)(\text{C}_{18}\text{H}_{21}\text{O})]$, has a pseudotetrahedral bent metallocene structure in which the cyclopentadienyl ring is symmetrically bonded to Ti [range of Ti—C distances 2.36 (1)–2.41 (1) Å], but the substituted cyclopentadienyl ring adopts asymmetrical bonding [Ti—C 2.33 (1)–2.48 (1) Å] due to the interaction of the large substituent with the Cl(2) atom. The angle C(11)—C(1)—C(21) is 111.1 (8)° with the large substituent occupying a *cis* position with respect to the substituted ring.

Comment

Cyclopentadiene-substituted metallocene derivatives of Group IV are of considerable interest as precursors of Ziegler–Natta polymerization catalysts because of their unusually high activities (Sinn, Kaminsky, Vollmer & Woldt, 1980; Sinn & Kaminsky, 1980) and specific stereoselectivity (Erker *et al.*, 1991). Recently, many bulky *tert*-alkyl-cyclopentadiene-substituted metallocenes have been synthesized and structurally characterized (Howie, McQuillan, Thompson & Lock, 1986; Erker *et al.*, 1989), but only a limited number of mono-substituted metallocenes have been reported (Gelmini, Puddephatt & Vittal, 1993; Ott, de Bore & Grubbs, 1984). In this paper, we present the structure of a new mono-substituted titanocene complex, (I).



The crystal consists of discrete molecules, since the shortest intermolecular contacts are H(15)···Cl(1) ($1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$) 2.707 and H(27a)···Cl(1) ($\frac{3}{2} - x, -y, \frac{1}{2} + z$) 2.941 Å.

The molecule has bent metallocene geometry, with the Ti center pseudotetrahedrally coordinated by two sym-

metrically bound chloride ligands, one cyclopentadienyl ring (Cp) and one mono-substituted cyclopentadienyl ring [η^5 -Cp(C₁₃H₁₇O)] (Cp'), where each cyclopentadienyl ring is considered to occupy a single coordination site. The Ti atom has a coordination number of 8. Both the cyclopentadienyl rings are planar, with the maximum displacements of the C atoms from the mean planes of 0.020 Å for the Cp ring and 0.002 Å for the Cp' ring.

The dihedral angle between the two rings, Cp and Cp', is 50.3 (8)°. The C(11)—C(1)—C(21) angle is 111.1 (8)°, while C(1) is almost in the plane of the benzyl ring [C(21)—C(26) 0.020 (8) Å] but deviates slightly from the substituted Cp' ring [0.258 (9) Å] due to the interaction of the large substituent with the Cl(2) atom. The Cl(1)—Ti—Cl(2) angle is 93.3 (1)°, which is a little smaller than those found in $(\text{RCp})_2\text{TiCl}_2$ complexes (Clearfield, Warner, Saldarriaga-Molina, Popal & Bernal, 1975; McKenzie, Sanner & Beraw, 1975) and that found in a 2-propenyl mono-substituted complex (Gelmini, Puddephatt & Vittal, 1993), also as a result of the interaction of the large substituent with the Cl(2) atom.

The Ti—Cl distances [mean 2.412 (3) Å] are normal and comparable to other published data (Clearfield *et al.*, 1975; McKenzie, Sanner & Beraw, 1975). The Ti—C distances associated with the Cp ring are in the narrow range of 2.36 (1)–2.41 (1) Å, whereas those associated with the Cp' ring cover a much wider range: 2.33 (1)–2.48 (1) Å. Thus, the Cp' ring is asymmetrically bonded to Ti and tilted in such a way that the Ti—C bond to the substituted C atom is the longest. There is one short Ti—C distance [Ti—C(14) 2.33 (1) Å], two medium [Ti—C(13) 2.39 (1) and Ti—C(15) 2.39 (1) Å] and two long distances [Ti—C(11) 2.48 (1) and Ti—C(12) 2.47 (1) Å]. The Ti—centroid distances are

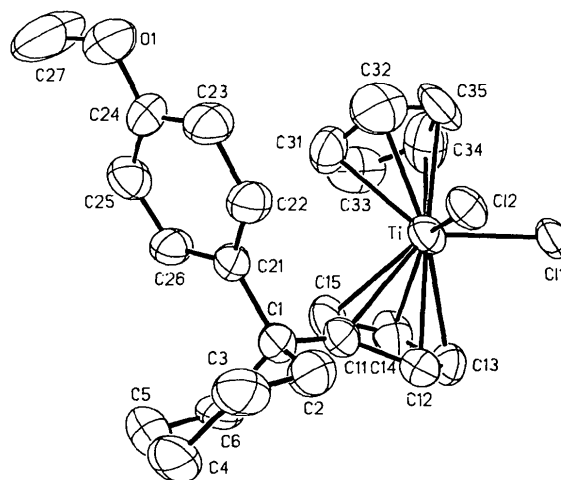


Fig. 1. View of $[\text{TiCl}_2(\eta^5\text{-Cp})\{\eta^5\text{-Cp}(\text{C}_{13}\text{H}_{17}\text{O})\}]$ showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels; H atoms are drawn as small circles of arbitrary radii.

2.38 (1) and 2.41 (1) Å for Cp and Cp', respectively. Similar 'Ti slippage' has also been observed in (η^5 -MeC₅H₄)₂TiCl₂ (Peterson & Dahl, 1975), (η^5 -vinyl-C₅H₄)₂TiCl₂ (Ogasa *et al.*, 1991) and (η^5 -C₅H₅)[η^5 -2-(C₃H₅)C₅H₄]TiCl₂ (Gelmini, Puddephatt & Vittal, 1993). The distortion is towards an η^4 bonding mode of the Cp' ring, which could be the result of interaction between the large [1-(4-methoxyphenyl)cyclohexyl]-cyclopentadienyl substituent and the two Cl atoms.

The C—C distances in Cp and Cp' range 1.30 (2)–1.40 (2) Å, mean 1.35 (2) Å, and 1.39 (1)–1.46 (2) Å, 1.43 (2) Å, respectively.

Experimental

Crystal data

[TiCl₂(C₅H₅)(C₁₈H₂₁O)]

$M_r = 437.24$

Orthorhombic

$P2_12_12_1$

$a = 9.680$ (5) Å

$b = 12.846$ (5) Å

$c = 16.944$ (6) Å

$V = 2107$ (1) Å³

$Z = 4$

$D_x = 1.377$ Mg m⁻³

Data collection

Nicolet R3m/E diffractometer

ω scans (width 1.2°, rate 5.8° min⁻¹)

Absorption correction: none

1927 measured reflections

1904 independent reflections

1406 observed reflections

[$F_o > 3\sigma(F_o)$]

Refinement

Refinement on F

$R = 0.066$

$wR = 0.086$

$S = 1.09$

1406 reflections

244 parameters

H-atom parameters not refined

Mo $K\alpha$ radiation

$\lambda = 0.71069$ Å

Cell parameters from 21 reflections

$\theta = 3.2$ – 11.7°

$\mu = 0.68$ mm⁻¹

$T = 293$ K

Flat slice

$0.46 \times 0.44 \times 0.20$ mm

Dark red

$R_{int} = 0.020$

$\theta_{max} = 24^\circ$

$h = 0 \rightarrow 11$

$k = 0 \rightarrow 14$

$l = 0 \rightarrow 19$

2 standard reflections

monitored every 98

reflections

intensity decay: <1.3%

$w = 1/[\sigma^2(F_o)$

$+ 0.0036(F_o)^2]$

$(\Delta/\sigma)_{max} = 0.03$

$\Delta\rho_{max} = 0.48$ e Å⁻³

$\Delta\rho_{min} = -0.32$ e Å⁻³

Extinction correction: none

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

C(1)	0.868 (1)	-0.1178 (7)	0.1421 (5)	0.050 (3)
C(2)	0.944 (1)	-0.0301 (8)	0.0906 (6)	0.062 (4)
C(3)	1.098 (1)	-0.049 (1)	0.0811 (6)	0.073 (5)
C(4)	1.123 (1)	-0.163 (1)	0.0457 (7)	0.094 (6)
C(5)	1.050 (1)	-0.2477 (9)	0.0886 (7)	0.069 (4)
C(6)	0.898 (1)	-0.2259 (8)	0.0975 (6)	0.065 (4)
C(11)	0.714 (1)	-0.1029 (7)	0.1419 (5)	0.051 (3)
C(12)	0.632 (1)	-0.0354 (8)	0.0911 (6)	0.061 (4)
C(13)	0.493 (1)	-0.0608 (8)	0.0983 (7)	0.053 (4)
C(14)	0.481 (1)	-0.1454 (9)	0.1537 (8)	0.068 (4)
C(15)	0.622 (1)	-0.1700 (7)	0.1797 (7)	0.060 (4)
C(21)	0.925 (1)	-0.1216 (7)	0.2274 (6)	0.047 (3)
C(22)	0.978 (1)	-0.0351 (8)	0.2636 (6)	0.058 (4)
C(23)	1.026 (1)	-0.0364 (8)	0.3422 (7)	0.065 (4)
C(24)	1.030 (1)	-0.1303 (9)	0.3831 (6)	0.072 (5)
C(25)	0.982 (1)	-0.2207 (8)	0.3459 (7)	0.063 (4)
C(26)	0.932 (1)	-0.2129 (7)	0.2700 (6)	0.057 (4)
C(27)	1.095 (3)	-0.223 (1)	0.496 (1)	0.16 (1)
O(1)	1.083 (1)	-0.1257 (6)	0.4565 (4)	0.097 (4)
C(31)	0.638 (1)	-0.0793 (9)	0.3451 (6)	0.073 (4)
C(32)	0.636 (2)	0.0203 (9)	0.3598 (8)	0.097 (6)
C(33)	0.504 (1)	-0.1146 (9)	0.3379 (8)	0.091 (6)
C(34)	0.422 (1)	-0.026 (1)	0.346 (1)	0.095 (6)
C(35)	0.506 (2)	0.0543 (9)	0.3573 (8)	0.107 (8)

Table 2. Selected geometric parameters (Å, °)

Ti—Cl(1)	2.419 (3)	Ti—Cl(2)	2.404 (3)
Ti—C(11)	2.48 (1)	Ti—C(12)	2.47 (1)
Ti—C(13)	2.39 (1)	Ti—C(14)	2.33 (1)
Ti—C(15)	2.39 (1)	Ti—C(31)	2.36 (1)
Ti—C(32)	2.39 (1)	Ti—C(33)	2.41 (1)
Ti—C(34)	2.40 (2)	Ti—C(35)	2.36 (1)
C(1)—C(2)	1.60 (1)	C(1)—C(6)	1.61 (1)
C(1)—C(11)	1.50 (1)	C(1)—C(21)	1.55 (1)
C(2)—C(3)	1.52 (2)	C(3)—C(4)	1.60 (2)
C(4)—C(5)	1.49 (2)	C(5)—C(6)	1.51 (2)
C(11)—C(12)	1.45 (1)	C(11)—C(15)	1.39 (1)
C(12)—C(13)	1.40 (2)	C(13)—C(14)	1.44 (2)
C(14)—C(15)	1.46 (2)	C(21)—C(22)	1.37 (1)
C(21)—C(26)	1.38 (1)	C(22)—C(23)	1.41 (1)
C(23)—C(24)	1.39 (2)	C(24)—C(25)	1.40 (2)
C(25)—C(26)	1.38 (1)	O(1)—C(24)	1.34 (1)
O(1)—C(27)	1.42 (1)	C(31)—C(32)	1.30 (2)
C(31)—C(33)	1.38 (2)	C(32)—C(35)	1.34 (2)
C(33)—C(34)	1.40 (2)	C(34)—C(35)	1.32 (2)
Cl(1)—Ti—Cl(2)	93.3 (1)	Cl(1)—Ti—C(11)	131.1 (2)
Cl(2)—Ti—C(11)	86.9 (2)	Cl(1)—Ti—C(13)	76.3 (3)
Cl(2)—Ti—C(13)	106.2 (3)	Cl(1)—Ti—C(31)	133.3 (3)
Cl(2)—Ti—C(31)	102.9 (3)	Cl(1)—Ti—C(34)	79.0 (4)
Cl(2)—Ti—C(34)	122.4 (4)	C(11)—Ti—C(14)	57.6 (4)
Cl(13)—Ti—C(15)	58.3 (4)	C(31)—Ti—C(34)	55.2 (5)
C(32)—Ti—C(35)	32.8 (6)	C(11)—Ti—C(31)	93.7 (4)
C(11)—Ti—C(33)	105.8 (4)	C(35)—Ti—C(11)	146.3 (5)
C(35)—Ti—C(14)	132.9 (5)	Ti—C(11)—C(1)	132.9 (7)
C(1)—C(11)—C(12)	127.9 (9)	C(11)—C(1)—C(21)	111.1 (8)
C(2)—C(1)—C(11)	111.2 (8)	C(6)—C(1)—C(11)	106.7 (8)
C(1)—C(21)—C(22)	121.7 (8)	C(24)—O(1)—C(27)	115.6 (11)
C(12)—C(11)—C(15)	107.1 (9)	C(12)—C(13)—C(14)	107.9 (9)
C(32)—C(31)—C(33)	109.2 (12)	C(33)—C(34)—C(35)	107.4 (13)
C(2)—C(1)—C(6)	105.6 (8)	C(3)—C(4)—C(5)	114.5 (10)
C(21)—C(22)—C(23)	122.4 (9)	C(24)—C(25)—C(26)	118.5 (9)

The structure was solved by direct methods and refined by block-diagonal least squares. All non-H atoms were refined anisotropically. The H atoms were introduced at theoretical positions and fixed with isotropic displacement parameters ($U_{iso} = 0.06$ Å²) in the final cycles of refinement.

All calculations were performed using the *SHELXTL* (Sheldrick, 1983) crystallographic software package.

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Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Ti	0.5550 (2)	-0.0025 (1)	0.2278 (1)	0.051 (1)
Cl(1)	0.3512 (3)	0.0984 (2)	0.1966 (2)	0.054 (1)
Cl(2)	0.7080 (3)	0.1430 (2)	0.2094 (1)	0.048 (1)

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1007). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(Benzobicyclooctatriene)tetracarbonylchromium

JENNIFER L. BLAKE, DONALD J. COOK,
PHILIP J. SQUATTRITO AND BOB A. HOWELL

*Department of Chemistry, Central Michigan University,
Mount Pleasant, Michigan 48859, USA*

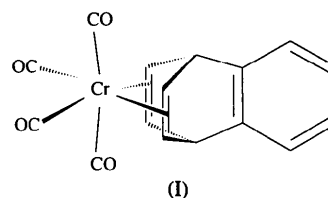
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Abstract

(2,3-Benzobicyclo[2.2.2]octa-2,5,7-triene)tetracarbonylchromium, $[\text{Cr}(\text{C}_{12}\text{H}_{10})(\text{CO})_4]$, is a complex of chromium(0) in which the organic ligand is coordinated to the Cr atom through the two free double bonds in a *cis* chelating arrangement. Four terminal carbonyl ligands complete the coordination sphere of the metal. The geometry about the Cr atom is a modestly distorted octahedron formed by the four carbonyl groups and the centroids of the two coordinated double bonds.

Comment

The field of organochromium chemistry has been dominated by the study of (arene)chromium compounds. Of particular interest have been (arene)carbonylchromium compounds which exhibit greater stability with respect to oxidative and thermodynamic decomposition than bis(benzene)chromium. The title compound, (I), was isolated as part of a study of (alkenylarene)chromium compounds. While there exist many examples of (arene)chromium compounds, relatively few complexes with π -bonded alkene ligands are known. Of the (alkene)carbonylchromium complexes that have been reported, most involve alkene moieties that are part of a chelated ligand, such as norbornadiene (Bennett, Pratt & Wilkinson, 1961) and butadiene (von Gustorf, Jaenicke & Polansky, 1972). Theoretical studies have concluded that unconjugated dienes of this type coordinate favourably to the $\text{Cr}(\text{CO})_4$ fragment (Elián & Hoffmann, 1975).



As shown in Fig. 1, the benzobicyclooctatriene ligand bonds to the Cr atom as a chelating diene with the two vertical double bonds occupying *cis* positions in the octahedral coordination sphere. That each alkene moiety is acting as a two-electron π donor is supported by the C5—C6 and C7—C8 distances, which are very close to those of a free double bond. The four carbonyl ligands are bound in almost linear fashion at the remaining vertices of the octahedron. The axial carbonyl groups are bent away from the chelate to give a C14—Cr—C13 angle of $163.4(3)^\circ$, while the two in the equatorial plane are spread slightly apart so that the C15—Cr—C16 angle is $95.4(3)^\circ$. The axial Cr—C bonds are slightly longer than the equatorial Cr—C bonds. The metrical details of the complex (Table 2) are consistent with those

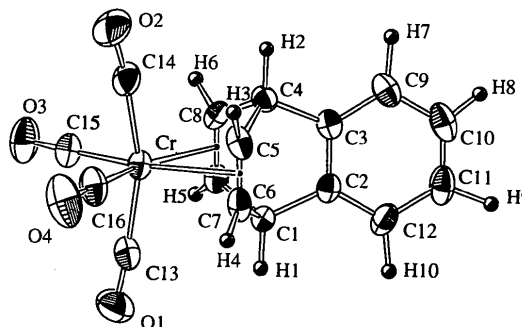


Fig. 1. ORTEP diagram (Johnson, 1976) of the title compound showing the atomic labeling scheme. The displacement ellipsoids of the non-H atoms are shown at the 35% probability level.