METAL-ORGANIC COMPOUNDS

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2,2′-Ethylenebis(η^5-indenyl)TiCl$_2$

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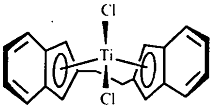
Abstract

The TiCl$_2$ moiety of 2,2′-ethylenebis(η^5-indenyl)titanium dichloride, [TiCl$_2$(C$_{20}$H$_{16}$)], spans the mirror plane in space group *Pnma*, forcing disorder of the bridged bisindenyl ligand. The Ti centre has a distorted tetrahedral geometry; the (η^5-centroid)—Ti—(η^5-centroid) angle is 128.6 (2)°. The indenes bend away from the TiCl$_2$ moiety, which twists 19.1 (2)° out of the cavity between the indenes.

Comment

Interest in chiral *ansa*-metallocene complexes stems from their catalytic activity in asymmetric hydrogenation and epoxidation, and their ability to act as precursors to homogeneous Ziegler-Natta polymerization catalysts (Ewen, 1986; Brintzinger, 1988). As part of our program aimed at synthesis of *ansa*-metallocenes (Sutton, Nantz & Parkin, 1993), we have determined the structure of 2,2′-ethylenebis(η^5-indenyl)titanium dichloride (I) (Fig. 1). Details of the chemistry of (I) and related compounds will appear elsewhere (Nantz, Hitchcock, Sutton & Smith, 1993).



(I)

The molecule spans the mirror plane of space group *Pnma*. This mirror plane forces the bisindenyl group, which wraps around the Ti atom, to disorder over two positions with statistically equal occupancies (Fig. 2). After location of the three heavy atoms by direct methods, a difference map revealed only a single, highly distorted indene-like fragment with many spurious electron-density peaks. Satisfactory refinement was made possible by forcing two half-occupancy indenes to conform to the known indene geometry (see *Experimental*).

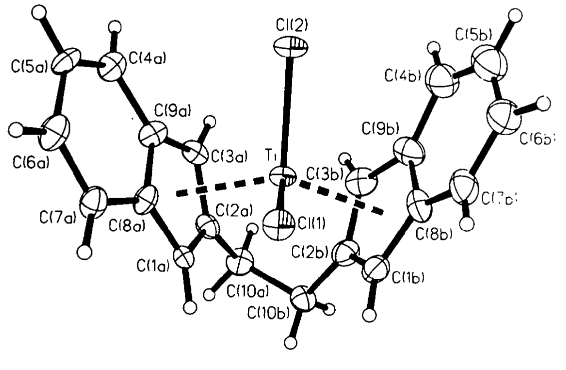


Fig. 1. Structure of (I) showing 50% probability displacement ellipsoids.

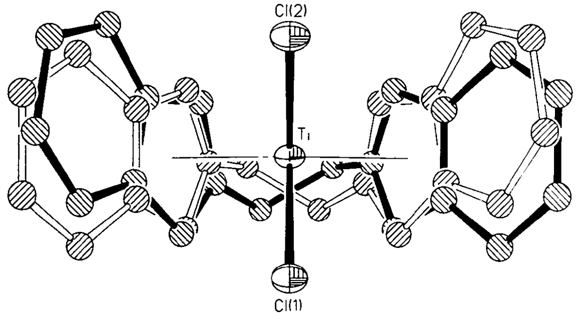


Fig. 2. The nature of the disorder observed at 120 K.

The Ti centre has a distorted tetrahedral geometry; the (η^5-centroid)—Ti—(η^5-centroid) angle is 128.6 (2)°. Ti—C distances are in the range 2.353 (6)-2.538 (6) Å. The shortest are to C1 adjacent to the ethylene bridge and the longest are to C9 opposite the tether, which has a dihedral angle of 43.9 (6)°. The indenes bow out of planarity away from the TiCl$_2$ moiety, which is twisted 19.1 (2)° out of the cavity formed by the indene groups.

At room temperature, (I) is probably a classical harmonic oscillator, flipping rapidly between conformations. Similar fluxional behaviour has been documented by other workers (Burger, Diebold, Gutman, Hund & Brintzinger, 1991). Variable-temperature NMR studies on a related system in solution have revealed evidence for suppression of such motion at low temperature. These studies were conducted as low as 183 K, with coalescence occurring at about 213 K (Burk, Colletti & Halterman, 1991). The crystals used in the present study were grown by slow diffusion of ether into a dichloromethane solution at room temperature, then flash cooled to 120 K for data collection. On the timescale of crystal growth processes, the overall molecular shape would be an average of the two conformations, which provides a likely explanation of how crystals of (I) could form in a space group that forces them to be disordered.

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Experimental

Crystal data

[$TiCl_2(C_{20}H_{16})$]
$M_r = 375.13$
Orthorhombic
Pnma
$a = 13.325$ (2) Å
$b = 17.260$ (2) Å
$c = 7.1140$ (10) Å
$V = 1636.1$ (4) Å^3
$Z = 4$
$D_x = 1.523$ Mg m^{-3}
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å

Cell parameters from 24 reflections
$\theta = 47$-$52°$
$\mu = 7.380$ mm^{-1}
$T = 120.0$ (10) K
0.15 × 0.12 × 0.03 mm
Hexagonal slab
Red
Crystal source: diffusion of ether into a dichloromethane solution

Data collection

Siemens *P*4-*RA* diffractometer
θ-2θ scans
Absorption correction: analytical
$T_{\min} = 0.360$, $T_{\max} = 0.802$
7480 measured reflections
1040 independent reflections
1018 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0359$ before absorption correction, 0.0238 after absorption correction
$\theta_{\max} = 54.30°$
$h = -14 \rightarrow 14$
$k = -18 \rightarrow 18$
$l = -7 \rightarrow 7$
2 standard reflections monitored every 198 reflections intensity variation: +3%

Refinement

Refinement on F^2
$R(F) = 0.0415$
$wR(F^2) = 0.0946$
$S = 1.191$
1040 reflections
200 parameters
Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.0300P)^2 + 5.7185P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\max} = 0.327$ e Å^{-3}
$\Delta\rho_{\min} = -0.595$ e Å^{-3}

Extinction correction: $F_c^* = kF_c[1 + 0.001F_c^2 \times \lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00029 (10)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8, 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ti	0.78685 (6)	3/4	0.15367 (12)	0.0168 (5)
Cl1	0.95404 (9)	3/4	0.0482 (2)	0.0234 (6)
Cl2	0.82411 (10)	3/4	0.4714 (2)	0.0271 (8)
C1*A*	0.7602 (5)	0.6500 (4)	−0.0665 (8)	0.019 (3)
C2*A*	0.6653 (4)	0.6689 (4)	0.0068 (9)	0.022 (3)
C3*A*	0.6656 (4)	0.6496 (4)	0.1986 (10)	0.022 (3)
C4*A*	0.7853 (6)	0.5644 (5)	0.3991 (10)	0.026 (3)
C5*A*	0.8744 (6)	0.5284 (5)	0.3941 (12)	0.024 (3)
C6*A*	0.9371 (5)	0.5292 (4)	0.2221 (12)	0.030 (3)
C7*A*	0.9078 (5)	0.5677 (5)	0.0666 (13)	0.025 (3)
C8*A*	0.8156 (5)	0.6105 (3)	0.0760 (9)	0.021 (3)
C9*A*	0.7562 (5)	0.6091 (4)	0.2385 (9)	0.022 (3)
C10*A*	0.5777 (5)	0.7053 (4)	−0.0950 (9)	0.028 (3)
C1*B*	0.7740 (6)	0.8529 (4)	−0.0620 (8)	0.027 (3)
C2*B*	0.6763 (4)	0.8239 (4)	−0.0372 (9)	0.028 (3)
C3*B*	0.6491 (4)	0.8369 (4)	0.1511 (11)	0.031 (3)
C4*B*	0.7348 (7)	0.9130 (5)	0.4234 (10)	0.043 (3)
C5*B*	0.8193 (8)	0.9532 (6)	0.4634 (12)	0.047 (4)
C6*B*	0.9005 (7)	0.9622 (6)	0.3284 (13)	0.039 (3)
C7*B*	0.8955 (6)	0.9279 (5)	0.1591 (13)	0.034 (3)
C8*B*	0.8032 (5)	0.8921 (4)	0.1048 (9)	0.028 (3)
C9*B*	0.7248 (5)	0.8828 (4)	0.2376 (9)	0.032 (3)
C10*B*	0.6134 (5)	0.7809 (4)	−0.1799 (10)	0.026 (3)

Table 2. *Selected geometric parameters* (Å, °)

Ti—Cl2	2.314 (2)	C1*A*—C8*A*	1.427 (6)
Ti—Cl1	2.351 (2)	C2*A*—C3*A*	1.405 (7)
Ti—C1*B*$^{\rm i}$	2.353 (6)	C2*A*—C10*A*	1.511 (6)
Ti—C1*A*$^{\rm i}$	2.358 (6)	C3*A*—C9*A*	1.423 (6)
Ti—C3*B*$^{\rm i}$	2.370 (6)	C4*A*—C5*A*	1.341 (8)
Ti—C2*B*$^{\rm i}$	2.375 (6)	C4*A*—C9*A*	1.432 (7)
Ti—C2*A*$^{\rm i}$	2.383 (6)	C5*A*—C6*A*	1.481 (13)
Ti—C3*A*$^{\rm i}$	2.391 (6)	C6*A*—C7*A*	1.348 (8)
Ti—C8*B*$^{\rm i}$	2.486 (6)	C7*A*—C8*A*	1.435 (6)
Ti—C8*A*$^{\rm i}$	2.500 (6)	C8*A*—C9*A*	1.401 (9)
Ti—C9*B*$^{\rm i}$	2.509 (6)	C10*A*—C10*B*	1.515 (6)
Ti—C9*A*$^{\rm i}$	2.538 (6)	C2*B*—C10*B*	1.512 (6)
C1*A*—C2*A*	1.406 (6)		
Cl2—Ti—Cl1	96.22 (6)	Cl2—Ti—C8*B*$^{\rm i}$	96.76 (15)
Cl2—Ti—C1*B*$^{\rm i}$	130.72 (15)	Cl1—Ti—C8*B*$^{\rm i}$	82.7 (2)
Cl1—Ti—C1*B*$^{\rm i}$	82.0 (2)	Cl2—Ti—C8*A*$^{\rm i}$	100.55 (14)
Cl2—Ti—C1*A*$^{\rm i}$	132.93 (14)	Cl1—Ti—C8*A*$^{\rm i}$	77.5 (2)
Cl1—Ti—C1*A*$^{\rm i}$	86.0 (2)	C8*B*$^{\rm i}$—Ti—C8*A*$^{\rm i}$	154.9 (2)
C1*B*$^{\rm i}$—Ti—C1*A*$^{\rm i}$	96.2 (2)	Cl2—Ti—C9*B*$^{\rm i}$	80.7 (2)
Cl2—Ti—C3*B*$^{\rm i}$	100.0 (2)	Cl1—Ti—C9*B*$^{\rm i}$	112.8 (2)
Cl1—Ti—C3*B*$^{\rm i}$	137.0 (2)	Cl2—Ti—C9*A*$^{\rm i}$	78.6 (2)
Cl2—Ti—C2*B*$^{\rm i}$	133.8 (2)	Cl1—Ti—C9*A*$^{\rm i}$	103.20 (15)
Cl1—Ti—C2*B*$^{\rm i}$	113.9 (2)	C9*B*$^{\rm i}$—Ti—C9*A*$^{\rm i}$	140.0 (2)
Cl2—Ti—C2*A*$^{\rm i}$	125.0 (2)	C3*A*—C2*A*—C10*A*	124.5 (5)
Cl1—Ti—C2*A*$^{\rm i}$	120.3 (2)	C1*A*—C2*A*—C10*A*	127.9 (5)
C2*B*$^{\rm i}$—Ti—C2*A*$^{\rm i}$	69.1 (2)	C2*A*—C10*A*—C10*B*	107.9 (5)
Cl2—Ti—C3*A*$^{\rm i}$	90.8 (2)	C1*B*—C2*B*—C10*B*	127.2 (5)
Cl1—Ti—C3*A*$^{\rm i}$	133.1 (2)	C3*B*—C2*B*—C10*B*	125.1 (6)
C3*B*$^{\rm i}$—Ti—C3*A*$^{\rm i}$	86.4 (2)	C2*B*—C10*B*—C10*A*	109.3 (6)

Symmetry code: (i) $x, \frac{3}{2} - y, z$.

The structure was refined on coordinates from a single molecule at half occupancy (Fig. 2). Similarity restraints were applied to equivalent interatomic distances and angles in each indene group, assuming a non-crystallographic mirror plane perpendicular to the indene plane joining C2 and the midpoint of C5—C6. Distances between Ti and pairs of chemically equivalent C atoms in the two π-bonding systems were given similarity restraints to prevent oscillation of the coordinates along the crystallographic *b* axis. Anisotropic displacement parameters were refined for all atoms. Rigid bond, similarity and approximate isotropicity restraints (*DELU*, *SIMU* and *ISOR* in *SHELXL*92, respectively; Sheldrick, 1993) were needed for the C-atom U_{ij} parameters to retain physically reasonable values. Data collection: *P*3/*PC Diffractometer program* (Siemens, 1989*a*). Cell refinement: *P*3/*PC Diffractometer program*. Data reduction: *XDISK* (Siemens, 1989*b*). Program(s) used to solve structure: *SHELXTL XS* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*92. Molecular graphics: *SHELXTL XP*. Software used to prepare material for publication: *SHELXL*92 and local programs.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71523 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1073]

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Tetra(*N*-methylimidazol)-kupfer(II)-bis(triiodid) $[Cu(C_4H_6N_2)_4](I_3)_2$*

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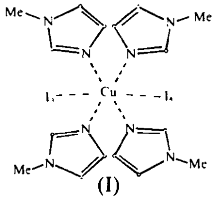
Abstract

The structure of the title compound, tetrakis(1-methylimidazole-N^3)copper(II) bis(triiodide), consists of square-planar coordinated $[Cu(C_4H_6N_2)_4]^{2+}$ cations and symmetric triiodide anions I_3^-, which form long contacts with the cations. In the neutral complex, four coplanar N atoms and two triiodide ions form the expected quasi-octahedral coordination around Cu.

Kommentar

Die Lageparameter sind in Tabelle 1 und die wichtigeren geometrischen Größen in Tabelle 2 aufgelistet. Die Bezeichnung der Atome geht aus Fig. 1 hervor. Die Kristallstruktur von Tetra(*N*-methylimidazol)-kupfer(II)-bis(triiodid) (I) wird aus dem isolierten, neutralen, koordinativ abgesättigten Komplex $[Cu(C_4H_6N_2)_4](I_3)_2$ der Punktsymmetrie 2 aufgebaut, der sich in das quadratisch planare Kation $[Cu(C_4H_6N_2)_4]^{2+}$ und die nahezu unverzerrten und schwach gewinkelten Triiodidionen I_3^- zerlegen läßt, welche die Koordination des Zentralatoms zu einer gestreckt oktaedrischen ergänzen. Diese quasioktaedrische Koordination vom Typ 4+2 ist für Komplexe des zweiwertigen Kupfers mit vier sterisch anspruchslosen Stickstoff- und zwei Iodliganden charakteristisch, wie der Vergleich mit den Strukturen der Verbindungen $[Cu(NH_3)_4I_4]$ (Dubler & Linowsky, 1975), $[Cu(NH_3)_4I_6]$ (Tebbe, 1982), $[Cu(NH_3)_4(TlI_4)_2]$ (Tebbe, 1989) und $[Cu(NH_3)_4(CuI_2)_2]$ (Hoyer & Hartl, 1991) zeigt. Hier führt die schwache koordinative Bindung zu keiner merklichen Verzerrung des Triiodidions. Die Geometrie des Liganden *N*-Methylimidazol entspricht ebenfalls der Erwartung, wie ein Vergleich mit den Standardgrößen (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987) und mit den Strukturen z.B. der Verbindungen $[Cu(imMe)_4][CuCl_3].H_2O$ (Clegg, Nicholson, Collison & Garner, 1988, und dort zitierte Literatur) und $[CuCl(imMe)(H_2NCH_2COO)]$ (Norman, Rose & Stenkamp, 1990) zeigt. Wegen der weitergehenden Substitution des Liganden, den unterschiedlichen Koordinationseigenschaften des Zentralatoms und nicht zuletzt wegen der Fehlordnung im Komplex und der merkwürdigen Verzerrung des Triiodidions (die Verkürzung des einen Schenkels ist der Verlängerung des anderen gleich) ist die Struktur der Verbindung $Pt(imMe_2)_4(I_3)_2$ (Korte, Krebs, van Kralingen, Marcelis & Reedijk, 1981) trotz ähnlicher Zusammensetzung für einen Vergleich weniger geeignet. Die Packung der neutralen Komplexe im Kristall folgt den bekannten Prinzipien (Kitaigorodskii, 1979). Gliedert man diese in kationische Bereiche $Cu(imMe)_4^{2+}$ und anionische Bereiche I_3^-, so deutet sich senkrecht zu [0 0 1] ein schichtartiger Aufbau der Kristallstruktur an. Die Triiodidionen I_3^- sind in solchen anionischen Schichten um $z = 0, \frac{1}{2}$ jeweils parallel ausgerichtet, ohne dabei bemerkenswerte Kontakte zu knüpfen. Diese wechseln sich mit den kationischen Schichten um $z = \frac{1}{4}, \frac{3}{4}$ ab, wobei aber die Liganden imMe in die Iodschicht hineinragen und die Triiodidionen voneinander trennen.



(I)

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* Untersuchungen an Polyhalogeniden. 13. Teil 12: Tebbe & Kavoosian (1993).