# Structure of μ-Oxo-bis[trichloro-(2,2-diisobutyl-1,3-dimethoxypropane-O,O')titanium(IV)]

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## Abstract

$TiCl_4$ reacts with $(^iC_4H_9)_2C(CH_2OCH_3)_2$ in *n*-heptane forming the monomeric complex [$TiCl_4(C_{13}H_{28}O_2)$] which is converted into the oxygen-bridged dimeric structure [$TiCl_3(C_{13}H_{28}O_2)$]$_2$O in the presence of $H_2O$. In the dimeric structure the coordination of each Ti atom is octahedral. The angle between the bridging O atom and the Ti atoms is 163.4 (4)°.

## Comment

Modern heterogeneous Ziegler–Natta catalysts for the polymerization of propylene are composed of titanium tetrachloride on a magnesium dichloride support (Pino & Mulhaupt, 1980; Kashiwa, 1980; Barbe, Cecchin & Noristi, 1987; Miyatake, Mizunuma & Kakugo, 1990). The stereospecificity of the basic catalyst can be improved by internal donors such as dialkyl phthalates and external donors such as phenyl- and alkylalkoxysilanes. Generally, both internal and external donors are needed to obtain a catalyst with high stereospecificity and activity in α-olefin polymerization processes (Arzoumanidis & Karayannis, 1991; Burkhardt, Langer, Barist, Funk & Gaydos, 1988; Soga, Shiono & Doi, 1988; Chien, Hu & Vizzini, 1990; Sacchi, Tritto, Shan, Mendichi & Noristi, 1991; Härkönen, Seppälä & Väänänen, 1991; Terano, Kataoka & Hosaka, 1988; Clayden & Jones, 1990).

In this paper we describe the structure of a novel donor, 2,2-diisobutyl-1,3-dimethoxypropane, used as a heterogeneous Ziegler–Natta catalyst in propylene polymerization. This donor has also been reported recently in conjunction with the synthesis of a non-supported $TiCl_3$ catalyst (Giovanni, Borsotti, Schimperna & Barbassa, 1991).

The isospecific activity of the catalyst is very high, without external donors. This makes the catalyst unique among $TiCl_4/MgCl_2$-supported stereospecific catalysts (Iiskola, Pelkonen, Kakkonen, Pursiainen & Pakkanen, 1993). The reaction of the bidentate ligand 2,2-diisobutyl-1,3-dimethoxypropane (*L*) with $TiCl_4$ in heptane gives a quantitative yield of $TiCl_4L$ monomer, which was unambiguously identified on the basis of elemental analysis and $^{13}C$ NMR data. However, the crystal structure did not show the monomer, but a dimeric oxygen-bridged titanium complex (Fig. 1). Apparently, the moisture in the air diffused through the rubber septum of the vial during recrystallization of a small sample and caused dimerization of the original complex.

In each monomeric unit of the dimeric structure the O atoms and the Ti atom are coplanar within experimental error, the angle between these planes being 117.2 (1)°. The short Ti—O* distances [1.808 (7) and 1.796 (7) Å] are close to the value previously observed for [$Ti_2(\mu$-O)($\mu$-$O_2$CPh)$_2$Cl$_4$-(EtOAc)$_2$] [1.783 (7) Å (Alcock, Bartlett, Gordon, Illson & Wallbridge, 1986)]. The Ti(1)—O*—Ti(2) angle [163.4 (4)°] is more linear than in [$Ti_2(\mu$-O)-($\mu$-$O_2$CPh)$_2$Cl$_4$(EtOAc)$_2$] [137.2 (4)°] but it is similar to values found in oxo-bridged (cyclopentadienyl)-titanium compounds (157–180°) (Petersen, 1980). The non-bonded O(1)···O(2) and O(1*B*)···O(2*B*) distances [2.790 (8) and 2.794 (8) Å, respectively] are about 0.1 Å longer than in seven corresponding monomeric diester complexes of $TiCl_4$ [average 2.68 (3) Å] (Kakkonen, Pursiainen, Pakkanen, Ahlgrèn & Iiskola, 1993).
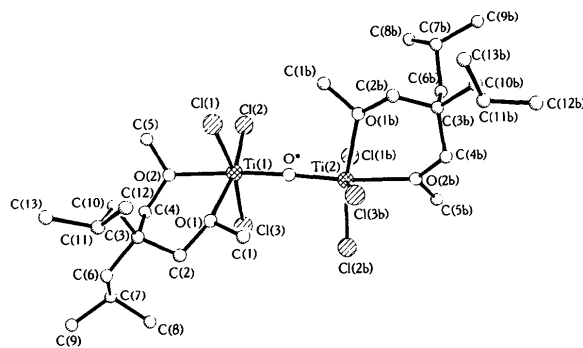


Fig. 1. View of [$TiCl_3(C_{13}H_{28}O_2)$]$_2$O.

## Experimental

*Crystal data*

| | |
|---|---|
| [$Ti_2Cl_6O(C_{13}H_{28}O_2)_2$] | Cell parameters from 25 |
| $M_r = 757.2$ | reflections |
| Orthorhombic | $\theta = 7$–$12.5°$ |

*Pbca*
$a = 18.98$ (3) Å
$b = 13.24$ (2) Å
$c = 30.18$ (5) Å
$V = 7583$ (12) Å$^3$
$Z = 8$
$D_x = 1.327$ Mg m$^{-3}$
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

$\mu = 0.873$ mm$^{-1}$
$T = 294$ K
Prism
$0.8 \times 0.6 \times 0.2$ mm
Yellow
Crystal source: from *n*-heptane/CH$_2$Cl$_2$

*Data collection*

Nicolet *R3m* diffractometer
$\omega$ scans
Absorption correction:
    none
7381 measured reflections
6633 independent reflections
2233 observed reflections
    $[I \geq 3\sigma(I)]$
$R_{int} = 0.0149$

$\theta_{max} = 25°$
$h = 0 \rightarrow 23$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 36$
1 standard reflection
    monitored every 99
    reflections
    intensity variation: 3%

*Refinement*

Refinement on $F$
Final $R = 0.049$
$wR = 0.052$
$S = 1.17$
2233 reflections
352 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.0005(F)^2]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.40$ e Å$^{-3}$
$\Delta\rho_{min} = -0.34$ e Å$^{-3}$
Atomic scattering factors
    from *International Tables*
    *for X-ray Crystallography*
    (1974, Vol. IV)

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

$U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| Ti(1) | 0.3876 (1) | 0.0007 (1) | 0.3734 (1) | 0.034 (1) |
| Ti(2) | 0.5119 (1) | 0.2028 (1) | 0.3726 (1) | 0.033 (1) |
| Cl(1) | 0.4499 (1) | −0.1204 (2) | 0.4120 (1) | 0.048 (1) |
| Cl(2) | 0.3323 (2) | 0.0645 (3) | 0.4332 (1) | 0.071 (1) |
| Cl(3) | 0.3257 (2) | 0.0931 (2) | 0.3222 (1) | 0.058 (1) |
| Cl(1B) | 0.4290 (1) | 0.2977 (2) | 0.4090 (1) | 0.051 (1) |
| Cl(2B) | 0.4803 (2) | 0.2549 (2) | 0.3043 (1) | 0.054 (1) |
| Cl(3B) | 0.6143 (1) | 0.1237 (2) | 0.3479 (1) | 0.051 (1) |
| O* | 0.4602 (3) | 0.0891 (4) | 0.3734 (2) | 0.031 (2) |
| O(1) | 0.4255 (3) | −0.0832 (5) | 0.3161 (2) | 0.031 (2) |
| O(2) | 0.3052 (3) | −0.1117 (5) | 0.3678 (2) | 0.035 (2) |
| C(1) | 0.4950 (5) | −0.0525 (8) | 0.3002 (3) | 0.058 (4) |
| C(2) | 0.3825 (5) | −0.1214 (8) | 0.2793 (3) | 0.036 (3) |
| C(3) | 0.3269 (5) | −0.1946 (8) | 0.2957 (3) | 0.031 (3) |
| C(4) | 0.2724 (5) | −0.1433 (7) | 0.3266 (3) | 0.035 (3) |
| C(5) | 0.2727 (6) | −0.1589 (9) | 0.4054 (3) | 0.061 (5) |
| C(6) | 0.2858 (5) | −0.2372 (7) | 0.2544 (3) | 0.039 (4) |
| C(7) | 0.2228 (5) | −0.1804 (10) | 0.2343 (3) | 0.053 (4) |
| C(8) | 0.2433 (7) | −0.0802 (10) | 0.2117 (4) | 0.082 (6) |
| C(9) | 0.1869 (6) | −0.2517 (11) | 0.2017 (3) | 0.087 (6) |
| C(10) | 0.3601 (5) | −0.2855 (7) | 0.3216 (3) | 0.037 (4) |
| C(11) | 0.4122 (5) | −0.3541 (8) | 0.2958 (3) | 0.041 (4) |
| C(12) | 0.4866 (6) | −0.3410 (8) | 0.3130 (4) | 0.062 (5) |
| C(13) | 0.3895 (7) | −0.4633 (8) | 0.2994 (4) | 0.072 (5) |
| O(1B) | 0.5561 (3) | 0.1793 (5) | 0.4383 (2) | 0.035 (2) |
| O(2B) | 0.5803 (3) | 0.3383 (5) | 0.3793 (2) | 0.037 (2) |
| C(1B) | 0.5214 (6) | 0.1084 (9) | 0.4666 (3) | 0.069 (5) |
| C(2B) | 0.6286 (5) | 0.1959 (8) | 0.4519 (3) | 0.040 (4) |
| C(3B) | 0.6500 (5) | 0.3058 (8) | 0.4470 (3) | 0.030 (5) |
| C(4B) | 0.6503 (5) | 0.3398 (8) | 0.3987 (3) | 0.041 (4) |
| C(5B) | 0.5577 (6) | 0.4361 (8) | 0.3639 (3) | 0.062 (5) |
| C(6B) | 0.5995 (5) | 0.3765 (7) | 0.4738 (3) | 0.040 (4) |
| C(7B) | 0.5930 (5) | 0.3602 (8) | 0.5239 (3) | 0.042 (4) |
| C(8B) | 0.5162 (6) | 0.3652 (9) | 0.5378 (3) | 0.068 (5) |
| C(9B) | 0.6345 (6) | 0.4363 (10) | 0.5504 (3) | 0.085 (6) |
| C(10B) | 0.7275 (5) | 0.3190 (8) | 0.4647 (3) | 0.047 (4) |
| C(11B) | 0.7874 (6) | 0.2647 (11) | 0.4400 (4) | 0.064 (5) |
| C(12B) | 0.8506 (7) | 0.3294 (12) | 0.4367 (6) | 0.133 (9) |
| C(13B) | 0.8101 (8) | 0.1734 (13) | 0.4674 (6) | 0.149 (10) |

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

| | | | |
|---|---|---|---|
| Ti(1)—Cl(1) | 2.306 (5) | Ti(1)—Cl(2) | 2.251 (5) |
| Ti(1)—Cl(3) | 2.295 (5) | Ti(1)—O* | 1.808 (7) |
| Ti(1)—O(1) | 2.179 (7) | Ti(1)—O(2) | 2.166 (7) |
| Ti(2)—Cl(1B) | 2.294 (5) | Ti(2)—Cl(2B) | 2.256 (5) |
| Ti(2)—Cl(3B) | 2.330 (5) | Ti(2)—O* | 1.796 (7) |
| Ti(2)—O(1B) | 2.174 (7) | Ti(2)—O(2B) | 2.224 (7) |
| O(1)—C(1) | 1.462 (12) | O(1)—C(2) | 1.466 (10) |
| O(2)—C(4) | 1.450 (10) | O(2)—C(5) | 1.437 (11) |
| O(1B)—C(1B) | 1.431 (13) | O(1B)—C(2B) | 1.451 (11) |
| O(2B)—C(4B) | 1.451 (11) | O(2B)—C(5B) | 1.441 (12) |
| Cl(1)—Ti(1)—Cl(2) | 95.5 (1) | Cl(1)—Ti(1)—Cl(3) | 166.5 (1) |
| Cl(2)—Ti(1)—Cl(3) | 95.8 (1) | Cl(1)—Ti(1)—O* | 93.4 (2) |
| Cl(2)—Ti(1)—O* | 96.5 (2) | Cl(3)—Ti(1)—O* | 92.7 (2) |
| Cl(1)—Ti(1)—O(1) | 82.9 (2) | Cl(2)—Ti(1)—O(1) | 169.0 (2) |
| Cl(3)—Ti(1)—O(1) | 84.6 (2) | O*—Ti(1)—O(1) | 94.5 (2) |
| Cl(1)—Ti(1)—O(2) | 86.1 (2) | Cl(2)—Ti(1)—O(2) | 89.1 (2) |
| Cl(3)—Ti(1)—O(2) | 86.7 (2) | O*—Ti(1)—O(2) | 174.4 (2) |
| O(1)—Ti(1)—O(2) | 79.9 (2) | Cl(1B)—Ti(2)—Cl(2B) | 95.1 (1) |
| Cl(1B)—Ti(2)—Cl(3B) | 166.3 (1) | Cl(2B)—Ti(2)—Cl(3B) | 93.7 (1) |
| Cl(1B)—Ti(2)—O* | 94.4 (2) | Cl(2B)—Ti(2)—O* | 97.1 (2) |
| Cl(3B)—Ti(2)—O* | 94.8 (2) | Cl(1B)—Ti(2)—O(1B) | 84.6 (2) |
| Cl(2B)—Ti(2)—O(1B) | 168.3 (2) | Cl(3B)—Ti(2)—O(1B) | 84.6 (2) |
| O*—Ti(2)—O(1B) | 94.5 (2) | Cl(1B)—Ti(2)—O(2B) | 85.1 (2) |
| Cl(2B)—Ti(2)—O(2B) | 89.5 (2) | Cl(3B)—Ti(2)—O(2B) | 84.5 (2) |
| O*—Ti(2)—O(2B) | 173.4 (2) | O(1B)—Ti(2)—O(2B) | 78.9 (2) |
| Ti(1)—O*—Ti(2) | 163.4 (4) | Ti(1)—O(1)—C(1) | 114.6 (5) |
| Ti(1)—O(1)—C(2) | 126.4 (5) | Ti(1)—O(2)—C(5) | 123.1 (5) |
| Ti(1)—O(2)—C(4) | 125.1 (5) | Ti(2)—O(1B)—C(1B) | 117.4 (5) |
| Ti(2)—O(1B)—C(2B) | 127.0 (5) | Ti(2)—O(2B)—C(5B) | 121.4 (6) |
| Ti(2)—O(2B)—C(4B) | 125.6 (5) | | |

A moisture sensitive crystal of the title compound was selected for data collection and mounted in a Hildenberg glass capillary, which was sealed under an N$_2$ atmosphere with viscous grease.

All crystallographic calculations were performed using the *SHELXTL-Plus* program package (Sheldrick, 1987). Ti- and Cl-atom positions were located by applying direct methods. C- and O-atom coordinates were determined from subsequent difference electron density calculations. Ti, Cl, C and O atoms were refined anisotropically. H atoms were placed in calculated positions with C—H = 0.96 Å and not refined.

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# Niobium 1,4-Diazabutadiene Derivatives. Structure of ($\eta^5$-Cp)NbCl$_2$($^t$BuNCH-CHN$^t$Bu)

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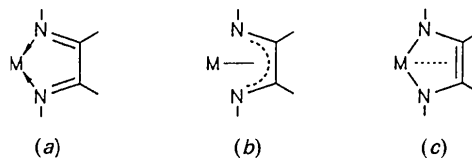
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## Abstract

Crystals of dichloro($\eta^5$-cyclopentadienyl)(N,N'-di-*tert*-butyl-1,2-ethanediimine-N,N')niobium were obtained by ligand exchange reaction between CpNbCl$_2$(PMe$_3$)$_3$ and $^t$BuN=CH—CH=N$^t$Bu. The structure shows pseudo-octahedral coordination

around the metal, with the chlorine ligands in *cis* positions relative to each other. The diimine ligand has an $\eta^2$-coordination mode with the five-membered metallacyclic ring adopting an envelope conformation. The long C—N distance together with the short C—C one imply electronic delocalization over the chelate. The conformation of the chelate leads to short Nb—C bonds and the $\sigma^2,\pi$-metallacyclopentene character of the diimine ligand reduces the electron deficiency of the metal.

## Comment

1,4-Diazabutadiene ligands, $R$N=CH—CH=N$R$ ($R$-dab), have been shown to exhibit a diverse coordination chemistry as a result of their steric and electronic flexibility (Vrieze & Van Koten, 1985; Van Koten & Vrieze, 1982). However, studies have mostly involved later transition metals and few reports concern early transition metals (Scholz, Dietrich, Schuman & Thiele, 1991; Scholz, Dlikan, Stöhl, Dietrich, Schuman & Thiele, 1990; Woitha, Behrens, Vergopoulos & Rehder, 1990). No reaction between a niobium or tantalum derivative and 1,4-diazabutadiene ligands has been reported to our knowledge. Since these ligands have been shown to be able to stabilize low formal oxidation states, we have investigated their behaviour towards niobium and tantalum species in various oxidation states. The reaction between ($\eta^5$-Cp)NbCl$_2$(PMe$_3$)$_3$ and di-*tert*-butylethanediimine offered ($\eta^5$-Cp)NbCl$_2$-($^t$BuNC$_2$H$_2$N$^t$Bu). Its structure was investigated by X-ray diffraction in order to determine precisely the coordination mode of the versatile nitrogen ligand, which may adopt a large variety of forms, although types (a) to (c) are the most likely for the compound under study.



*(a)*        *(b)*        *(c)*

($\eta^5$-Cp)NbCl$_2$($^t$BuNCHCHN$^t$Bu) has been obtained by the ligand-exchange reaction (photochemically activated) between CpNbCl$_2$(PMe$_3$)$_3$ (Zaki, Hubert-Pfalzgraf & Toupet, 1991) and di-*tert*-butylethanediimine. Crystals suitable for X-ray analysis were obtained from the reaction medium. The compound crystallizes as discrete molecules. The overall structure corresponds to a piano-stool geometry with the chlorine ligands in *cis* positions, as found, for example, for CpNbCl$_2$(dmpe) (dmpe = dimethylphosphinoethane) (Holloway & Melnik, 1986). The Nb—Cl bond lengths (2.516 Å av.) are in agreement with the data reported for other Nb$^{III}$