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*Acta Cryst.* (1993). **C49**, 30–33

## Structure of Dichloro( $\eta^5$ -cyclopentadienyl)(2-propenyl- $\eta^5$ -cyclopentadienyl)titanium(IV)

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(Received 25 November 1991; accepted 14 April 1992)

**Abstract.**  $[\text{TiCl}_2(\text{C}_5\text{H}_5)(\text{C}_8\text{H}_9)]$ ,  $M_r = 289.06$ , monoclinic,  $P2_1/c$ ,  $a = 8.276$  (1),  $b = 12.032$  (2),  $c = 12.987$  (2) Å,  $\beta = 97.11$  (1)°,  $V = 1283.3$  (7) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.45$  (5),  $D_x = 1.496$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 1.05$  mm<sup>-1</sup>,  $F(000) = 592$ ,  $T = 298$  K, final  $R = 0.0422$  and  $wR = 0.0504$  for 1710 observed reflections with  $I > 2.5\sigma(I)$ . The cyclopentadienyl ring is symmetrically bonded to Ti [range of Ti—C distances 2.364 (7)–2.384 (8) Å] but the 2-propenylcyclopentadienyl ring is asymmetrically bonded [Ti—C 2.345 (4)–2.478 (4) Å]. There is rotational disorder in the cyclopentadienyl ring with a 60:40 occupancy ratio.

**Introduction.** Alkenylcyclopentadienylmetal complexes are of interest as precursors to organometallic polymers, but there have been few structural studies of such complexes (Ogasa *et al.*, 1991). The title complex is of interest since it can act as a precursor to titanium carbide by pyrolysis of its vinyl polymer.

**Experimental.** The title compound was synthesized by reaction of 2-propenylcyclopentadienyllithium (22.6 mmol) with  $[\text{TiCl}_3(\eta^5\text{-C}_5\text{H}_5)]$  (22.6 mmol) in tetrahydrofuran (20 mL) at 193 K under a dry nitrogen atmosphere, then warmed to room temperature and allowed to react for 4 h. It was purified by chromatography on silica gel with benzene eluent and isolated in 60% yield. A suitable single crystal was obtained from tetrahydrofuran solution by slow cooling to 238 K. Then density was determined by flotation in aqueous  $\text{ZnCl}_2$  solution; a dark red crystal (0.33 × 0.33 × 0.16 mm) was mounted on a glass fibre.

Measurements were made using an Enraf–Nonius CAD-4F diffractometer. Unit-cell dimensions were obtained from 20 high-angle reflections ( $25.4 < 2\theta < 35.4^\circ$ ). Intensity data were collected with graphite-monochromated Mo  $K\alpha$  radiation at 298 K in the  $\theta$ – $2\theta$  mode, with variable scan speed (1.37–2.75° min<sup>-1</sup>) and scan width of  $(0.9 + 0.35\tan\theta)^\circ$  with additional 25% extensions at both ends for backgrounds and a maximum time per datum of

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60 s. A total of 2660 reflections in the  $2\theta$  range  $0-50^\circ$  ( $0 \leq h \leq 9$ ,  $-14 \leq k \leq 1$ ,  $-15 \leq l \leq 15$ ) were measured (Enraf-Nonius, 1984). Four standard reflections (400,  $0\bar{2}0$ , 002 and  $00\bar{2}$ ) were monitored every 120 min of X-ray exposure time and showed 0.2% decay over the total period of 65.9 h. Corrections were made for Lorentz, polarization and background radiation but not for decay. An empirical absorption correction was applied using  $360^\circ \psi$  scans of seven reflections in the  $\theta$  range  $5.7-14.7^\circ$  (North, Phillips & Mathews, 1968). The maximum and minimum transmission factors were 99.95 and 89.46%. Symmetry-equivalent data were averaged [ $R(F) = 0.009$ ] giving 2251 unique reflections. A  $p$  factor of 0.05 was applied to the data (Busing & Levy, 1957). Systematic absences ( $h0l$ ,  $l = 2n + 1$ ;  $0k0$ ,  $k = 2n + 1$ ) indicated space group  $P2_1/c$  (*International Tables for Crystallography*, 1983, Vol. A). Data were processed using the *Enraf-Nonius Structure Determination Package* (Enraf-Nonius, 1985) running on a DEC PDP11/23+ computer. The structure was solved by *SHELXS86* (Sheldrick, 1986) running on a SUN3/50 workstation, and was refined by full-matrix least-squares techniques on  $F$  using *SHELX76* (Sheldrick, 1976) software. All H atoms were located in a subsequent Fourier synthesis. Scattering factors for neutral non-H atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, p. 99) and the scattering factors for the H atoms were taken from Stewart, Davidson & Simpson (1965). The real component of anomalous scattering was included for all non-H atoms (Cromer & Liberman, 1970). The Ti and two Cl atoms were assigned anisotropic thermal parameters. The refinement converged at agreement factors  $R = 0.090$  and  $wR = 0.137$ . A difference Fourier map revealed clear evidence for disorder of the cyclopentadienyl (Cp) ring, at peak heights ranging from 2.4 to  $1.23 \text{ e } \text{\AA}^{-3}$ . The disorder model for this Cp ring was included and the occupancy factor was refined (with  $U$  constant) to 60 and 40%. Each C atom of the disordered Cp ring was assigned an individual isotropic thermal parameter and refined in the subsequent least-squares cycles. The rest of the C atoms were assigned anisotropic thermal parameters. On the other hand, all the C atoms were refined anisotropically in another model ignoring the disorder problem. The refinement converged to  $R = 0.0397$  and  $wR = 0.0500$ . However, owing to unrealistically large thermal parameters and unreasonable C—C bond distances [in the range  $1.307(9)-1.400(11) \text{ \AA}$ ] in the 'disordered' Cp ring, this model was not considered further. All the H atoms were included in their idealized positions (C—H =  $0.95 \text{ \AA}$ ) and common isotropic temperature factors (fixed at  $U = 0.12 \text{ \AA}^2$ ) were assigned to the H atoms in the Cp rings and the 2-propenyl group. The final refinement on  $F$ , employing 142 parameters and

Table 1. Atomic coordinates ( $\times 10^4$ ) and isotropic or equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ )

Disordered Cp atoms C(1)–C(5) with occupancy factors of 0.6, and C(1')–C(5') with occupancy factors of 0.4, were refined isotropically. Remaining atoms have equivalent isotropic thermal parameters with  $U_{\text{eq}} = (1/3)\sum_i U_{ij} a_i^* a_j^* a_i a_j$ .

	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$
Ti	7572.7 (8)	2109.7 (5)	1959.4 (5)	29.8 (2)
Cl(1)	7594 (1)	3640 (1)	3094 (1)	43.2 (3)
Cl(2)	7502 (1)	758 (1)	3282 (1)	48.5 (3)
C(1)	5884 (9)	2550 (10)	408 (6)	37 (2)
C(2)	5788 (9)	1389 (9)	557 (7)	36 (2)
C(3)	5051 (11)	1192 (8)	1439 (9)	46 (2)
C(4)	4685 (9)	2240 (12)	1875 (6)	43 (2)
C(5)	5207 (12)	3099 (7)	1234 (10)	49 (2)
C(1')	5550 (16)	3002 (11)	761 (13)	43 (3)
C(2')	5853 (13)	1973 (17)	368 (9)	40 (3)
C(3')	5403 (19)	1103 (12)	1024 (16)	59 (4)
C(4')	4700 (12)	1665 (13)	1813 (8)	30 (2)
C(5')	4785 (14)	2797 (13)	1653 (11)	37 (2)
C(6)	10074 (5)	1113 (3)	1841 (3)	41 (1)
C(7)	9351 (5)	1395 (4)	852 (3)	48 (1)
C(8)	9382 (5)	2559 (4)	761 (3)	48 (1)
C(9)	10116 (5)	2991 (4)	1700 (3)	42 (1)
C(10)	10574 (4)	2101 (3)	2389 (3)	35 (1)
C(11)	11447 (5)	2165 (4)	3447 (3)	42 (1)
C(12)	11855 (6)	1133 (4)	3998 (4)	63 (2)
C(13)	11909 (5)	3189 (4)	3860 (4)	61 (2)

1710 observations with  $I > 2.5\sigma(I)$ , converged at  $R = 0.0422$  and  $wR = 0.0504$  using a weighting scheme of the form  $w = k/[\sigma^2(F) + gF^2]$  where  $g = 0.0001$ ; a secondary-extinction parameter 0.0012 (5) and maximum shift  $-0.0267$  on  $y$  of C(1) were used. In the final difference Fourier synthesis there were five peaks with electron density in the range  $0.471-0.406 \text{ e } \text{\AA}^{-3}$ ; of these, four peaks were associated with the disordered Cp ring.

**Discussion.** Table 1 lists the final coordinates and thermal parameters for all non-H atoms and Table 2 gives the bond distances and angles for all atoms. A perspective view of the molecule including the atom-numbering scheme is presented in Fig. 1. The crystal consists of discrete molecules, since the shortest intermolecular contact is  $\text{Cl}(1)\cdots\text{H}(2')$  ( $x, 0.5 - y, z - 0.5$ ),  $2.528 \text{ \AA}$ . The closest intramolecular non-bonded interactions are  $\text{Cl}(1)\cdots\text{H}(5')$   $2.826$  and  $\text{Cl}(2)\cdots\text{H}(4')$   $2.872 \text{ \AA}$ .

The Ti—Cl bond distances [mean  $2.364(11) \text{ \AA}$ ] are normal and comparable to other published data (Ogasa *et al.*, 1991; Peterson & Dahl, 1975). The Ti—C distances associated with the  $\text{C}_5\text{H}_5$  ring (with occupancy factor 60%; Cp) are in the narrow range  $2.364(7)-2.384(8) \text{ \AA}$ , whereas those associated with the 2-propenylcyclopentadienyl ring [atoms C(6)–

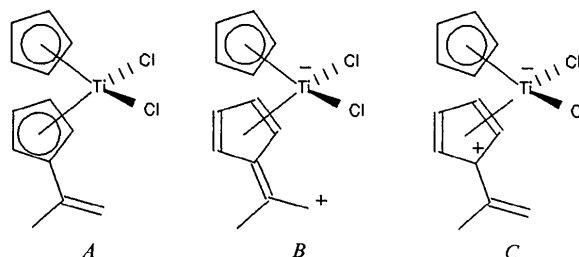
\* Lists of H-atom parameters, anisotropic thermal parameters, root-mean-square amplitudes of vibrations, weighted least-squares planes and structure amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55385 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD0086]

Table 2. Intramolecular bond distances (Å) and angles (°)

Ti—C(1)	2.356 (1)	Ti—C(2)	2.372 (1)
Ti—C(1)	2.365 (7)	Ti—C(2)	2.364 (7)
Ti—C(3)	2.384 (8)	Ti—C(4)	2.384 (7)
Ti—C(5)	2.384 (8)	Ti—C(6)	2.414 (4)
Ti—C(7)	2.345 (4)	Ti—C(8)	2.352 (4)
Ti—C(9)	2.418 (4)	Ti—C(10)	2.478 (4)
Ti—C(1')	2.394 (11)	Ti—C(2')	2.366 (11)
Ti—C(3')	2.372 (14)	Ti—C(4')	2.421 (9)
Ti—C(5')	2.436 (10)	C(1)—C(2)	1.414 (11)
C(2)—C(3)	1.384 (12)	C(3)—C(4)	1.430 (12)
C(4)—C(5)	1.427 (13)	C(5)—C(1)	1.432 (12)
C(6)—C(7)	1.390 (6)	C(6)—C(10)	1.421 (5)
C(7)—C(8)	1.405 (7)	C(8)—C(9)	1.395 (6)
C(9)—C(10)	1.417 (5)	C(10)—C(11)	1.474 (5)
C(11)—C(12)	1.452 (6)	C(11)—C(13)	1.378 (6)
C(1')—C(2')	1.375 (19)	C(1')—C(5')	1.409 (17)
C(2')—C(3')	1.428 (20)	C(3')—C(4')	1.411 (19)
C(4')—C(5')	1.381 (17)	C(1)—C(1')	0.784 (14)
C(1)—C(2')	0.696 (14)	C(2)—C(2')	0.748 (13)
C(2)—C(3')	0.798 (16)	C(3)—C(3')	0.652 (16)
C(3)—C(4')	0.823 (11)	C(4)—C(4')	0.697 (12)
C(4)—C(5')	0.738 (12)	C(5)—C(5')	0.772 (12)
C(5)—C(1')	0.718 (13)		
Cl(2)—Ti—Cl(1)	94.71 (4)	C(1)—Ti—Cl(1)	108.4 (3)
C(1)—Ti—Cl(2)	134.8 (2)	C(2)—Ti—Cl(1)	136.4 (2)
C(2)—Ti—Cl(2)	103.7 (3)	C(3)—Ti—Cl(1)	118.5 (3)
C(3)—Ti—Cl(2)	77.8 (2)	C(4)—Ti—Cl(1)	84.7 (3)
C(4)—Ti—Cl(2)	87.9 (3)	C(5)—Ti—Cl(1)	78.4 (2)
C(5)—Ti—Cl(2)	122.4 (3)	C(6)—Ti—Cl(1)	119.3 (1)
C(6)—Ti—Cl(2)	78.5 (1)	C(7)—Ti—Cl(1)	136.0 (1)
C(7)—Ti—Cl(2)	105.3 (1)	C(8)—Ti—Cl(1)	106.1 (1)
C(8)—Ti—Cl(2)	135.6 (1)	C(9)—Ti—Cl(1)	78.6 (1)
C(9)—Ti—Cl(2)	120.1 (1)	C(10)—Ti—Cl(1)	86.1 (1)
C(10)—Ti—Cl(2)	87.1 (1)	C(1')—Ti—Cl(1)	90.4 (4)
C(1')—Ti—Cl(2)	134.4 (3)	C(2')—Ti—Cl(1)	123.9 (4)
C(2')—Ti—Cl(2)	121.3 (5)	C(3')—Ti—Cl(1)	131.7 (4)
C(3')—Ti—Cl(2)	86.3 (5)	C(4')—Ti—Cl(1)	98.8 (4)
C(4')—Ti—Cl(2)	78.1 (3)	C(5')—Ti—Cl(1)	76.7 (3)
C(5')—Ti—Cl(2)	104.1 (4)	C(2)—Ti—C(1)	34.8 (3)
C(3)—Ti—C(2)	33.9 (3)	C(4)—Ti—C(3)	34.9 (3)
C(5)—Ti—C(1)	35.1 (3)	C(5)—Ti—C(4)	34.8 (3)
C(7)—Ti—C(6)	34.2 (2)	C(10)—Ti—C(6)	33.9 (1)
C(8)—Ti—C(7)	35.3 (2)	C(9)—Ti—C(8)	34.2 (2)
C(10)—Ti—C(9)	33.5 (1)	C(2')—Ti—C(1')	33.6 (5)
C(3')—Ti—C(2')	35.1 (5)	C(4')—Ti—C(3')	34.2 (4)
C(5')—Ti—C(1')	33.9 (4)	C(5')—Ti—C(4')	33.0 (4)
C(1')—Ti—C(1)	18.9 (3)	C(1')—Ti—C(5')	17.3 (3)
C(2')—Ti—C(1)	16.9 (3)	C(2')—Ti—C(2)	18.2 (3)
C(3')—Ti—C(2)	19.4 (4)	C(3')—Ti—C(3)	15.8 (4)
C(4')—Ti—C(3)	19.7 (3)	C(4')—Ti—C(4)	16.7 (3)
C(5')—Ti—C(4)	17.6 (3)	C(5')—Ti—C(5)	18.4 (3)
C(5)—C(1)—C(2)	108.7 (7)	C(3)—C(2)—C(1)	108.7 (7)
C(4)—C(3)—C(2)	108.3 (7)	C(5)—C(4)—C(3)	108.3 (7)
C(4)—C(5)—C(1)	106.1 (7)	C(5')—C(1')—C(2')	105.6 (10)
C(3')—C(2)—C(1')	111.4 (11)	C(4')—C(3')—C(2')	104.1 (11)
C(5')—C(4')—C(3')	109.3 (10)	C(4')—C(5')—C(1')	109.4 (10)
C(10)—C(6)—C(7)	108.9 (4)	C(8)—C(7)—C(6)	108.1 (4)
C(9)—C(8)—C(7)	108.0 (4)	C(10)—C(9)—C(8)	108.9 (4)
C(9)—C(10)—C(6)	106.1 (3)	C(11)—C(10)—C(6)	126.2 (3)
C(11)—C(10)—C(9)	127.7 (4)	C(12)—C(11)—C(10)	118.2 (4)
C(13)—C(11)—C(10)	119.3 (4)	C(13)—C(11)—C(12)	122.5 (4)

C(10); Cp'] cover a much wider range, 2.345 (4)–2.478 (4) Å. Thus, the Cp' ring is asymmetrically bonded to Ti and tilted in such a way that the Ti—C bond to the C atom with the isopropenyl substituent is longest. There are two short Ti—C(7), Ti—C(8) [2.345 (4) and 2.352 (4) Å] distances, two medium Ti—C(6), Ti—C(9) [2.414 (4) and 2.418 (4) Å] distances, and a long Ti—C(10) [2.478 (4) Å] distance. The Ti—centroid distances are 2.047 (Cp) and 2.079 Å (Cp'). Similar 'Ti slippage' has been observed in ( $\eta^3$ -C<sub>5</sub>H<sub>4</sub>-vinyl)<sub>2</sub>TiCl<sub>2</sub> (Ogasa *et al.*, 1991) and ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-Me)<sub>2</sub>TiCl<sub>2</sub> (Peterson & Dahl, 1975). The distortion is towards an  $\eta^4$  mode of

binding of the Cp' ring, which could be a result of electronic effects of the propenyl substituent or of interaction of the isopropenyl group with the two Cl atoms. The C—C distances in the Cp and Cp' rings are in the ranges 1.384 (12)–1.432 (12) Å, mean 1.417 (20) Å, and 1.390 (6)–1.421 (5) Å, mean 1.406 (13) Å, respectively.



The dimensions of the Cp' ring described above are consistent with there being a small contribution from the resonance forms *B* and *C* as well as the expected major form *A*. This could rationalize not only the long distance Ti—C(10) but also the pattern of C—C distances within the ring [long distances C(10)—C(6) and C(10)—C(9)] and the near coplanarity of the atoms C(6)—C(13). The Cp and Cp' rings are planar. However, the plane of the 2-propenyl group is twisted slightly with respect to that of the five-membered ring by 3 (2)°. The dihedral angle between the two rings, Cp and Cp', is 126.9 (2)°. The Ti—C distances in the minor component of the disordered cyclopentadienyl ring are in the range 2.366 (11)–2.435 (10) Å. The mean C—C distance of 1.401 (22) Å is normal in this ring. The two rotationally disordered Cp rings (with occupancy factors 60 and 40%) are related to each other by an angle of 37 (2)°.

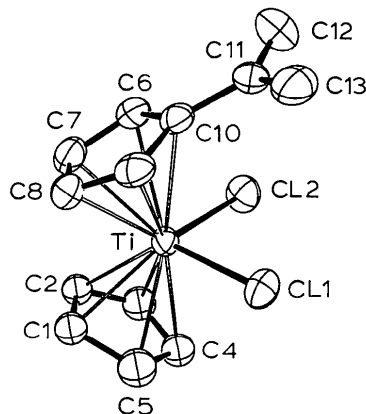


Fig. 1. A perspective view of the compound showing 50% thermal ellipsoids. Only one of the disordered positions of the Cp ring (with occupancy of 60%) is illustrated.

We thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work. JJV would like to thank Professor N. C. Payne of this department for X-ray and computing facilities.

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*Acta Cryst.* (1993). **C49**, 33–36

## Structure of *trans*-Dibromo(ethoxo)oxobis(triphenylphosphine)rhenium(V)

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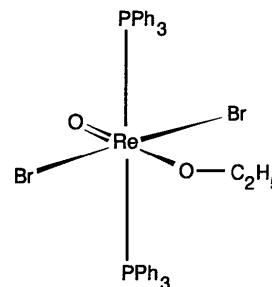
(Received 20 December 1991; accepted 28 April 1992)

**Abstract.** (OC-6-13)-Dibromo(ethoxo)oxobis(triphenylphosphine)rhenium(V),  $[\text{ReBr}_2\text{O}(\text{OC}_2\text{H}_5)\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]$ ,  $M_r = 931.66$ , monoclinic,  $C2/c$ ,  $a = 12.284$  (7),  $b = 14.509$  (4),  $c = 19.308$  (7) Å,  $\beta = 93.33$  (4)°,  $V = 3435$  (3) Å<sup>3</sup>,  $D_m(293 \text{ K}) = 1.82$ ,  $D_x = 1.801 \text{ Mg m}^{-3}$ ,  $Z = 4$ ,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu(\text{Mo } K\alpha) = 6.03 \text{ mm}^{-1}$ ,  $F(000) = 1816$ ,  $T = 293 \text{ K}$ , final  $R = 0.024$  for 1515 unique observed reflections. The crystal contains approximately octahedral molecules of the *trans*-dibromo-*trans*-bis(phosphine) isomer. The linear O—Re—O unit lies on a twofold axis and the ethyl group of the ethoxo ligand is disordered over two orientations.

**Introduction.** In the course of an ongoing study of metal–metal-bonded systems containing aromatic N-heterocyclic bridging ligands (Allaire & Beauchamp, 1989), synthetic routes to  $\text{Re}^{\text{III}}$  dimers *via*  $\text{Re}^{\text{V}}$  oxo complexes are being developed. The reactivity of  $[\text{ReX}_3\text{O}(\text{PR}_3)_2]$  and  $[\text{ReX}_2\text{O}(\text{OR})(\text{PR}_3)_2]$  with pyridines is well documented (Johnson, Taha & Wilkinson, 1964; Lock & Turner, 1977, 1978*a,b*; Brewer & Gray, 1989) and can be extrapolated to include more complex N-containing ligands. The title compound was considered to be a potential precursor for oxo complexes of controlled stereochemistry with N-containing heterocycles. Since the structure of the starting materials is of primary importance, X-ray

work was carried out to see if the bromo compound occurs in the same isomeric form as the chloro and iodo analogues (Graziani, Casellato, Rossi & Marchi, 1985; Ciani, D'Alfonso, Romiti, Sironi & Freni, 1983).

**Experimental.** Compound synthesized by the method of Johnson, Lock & Wilkinson (1964). Violet pseudo-hexagonal prisms obtained by recrystallization from an ethanol/benzene mixture. Crystal size [mm (pair of faces)]: 0.28 (111,  $\bar{1}\bar{1}\bar{1}$ )  $\times$  0.08 (101,  $\bar{1}0\bar{1}$ )  $\times$  0.28 (111,  $\bar{1}\bar{1}\bar{1}$ ).  $D_x$  measured by flotation in benzene/1,2-dibromoethane.



Data collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo  $K\alpha$  radiation. Reduced cell ( $a_r = b_r = 9.50$ ,  $c_r = 19.30$  Å,  $\alpha_r = \beta_r = 92.0$ ,  $\gamma_r = 99.4^\circ$ ) determined from 25 centred reflections ( $20.0 \leq 2\theta \leq 25.0^\circ$ ), checked with

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