

## References

- Beurskens, P. T. (1984). *DIRDIF. Direct Methods for Difference Structures – an Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors*. Technical Report 1984/1. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.
- Charalambous, J., Haines, L. I. B., Harris, N. J., Henrick, K. & Taylor, F. B. (1984). *J. Chem. Res. (M)*, **220**, 2101–2109.
- Elerman, Y., Atakol, O., Svoboda, I. & Geselle, M. (1995). *Acta Cryst. C51*, 1520–1522.
- Helm, D. van der, Merritt, L. L. & Degeilh, R. (1965). *Acta Cryst.* **18**, 355–362.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst. A24*, 351–359.
- Okabe, N. & Tamaki, K. (1995). *Acta Cryst. C51*, 2004–2005.
- Okabe, N., Tamaki, K., Suga, T. & Kohyama, Y. (1995). *Acta Cryst. C51*, 1295–1297.
- Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.

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### Bis( $\eta^5$ -cyclopentadienyl)bis(formato-O)-titanium

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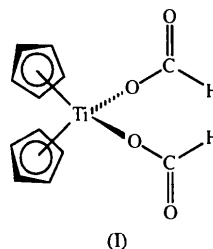
## Abstract

The title compound, [Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CHO<sub>2</sub>)<sub>2</sub>], has a 'bent metallocene' structure type typically found for Cp<sub>2</sub>MX<sub>2</sub> complexes. The Ti—O—C bond angles are larger than in related titanocene alkoxy complexes, suggesting enhanced  $\pi$  character in the Ti—O bonds of the title compound; however, the Ti—O bond lengths are longer than those in related alkoxy compounds.

## Comment

In spite of their importance as probable intermediates in metal-catalyzed carbon dioxide hydrogenation reactions (Jessop, Ikariya & Noyori, 1995), relatively few  $\eta^1$ -formato complexes have been structurally characterized

(see Fong, Fox & Cooper, 1987, and references therein; Hermann, Alt & Thewalt, 1990; Wöhrle & Thewalt, 1994). The title compound, (I), has been characterized in order to compare its properties with those of other formato complexes and with those of related bis(acyloxy) derivatives.



Considering the vectors from titanium to the centroids of the cyclopentadienyl rings, together with the bonds to the two O atoms of the formato ligands, the geometry about titanium can be described as distorted tetrahedral. The Ti—O bond lengths, 1.951 (2) and 1.952 (2) Å, indicate some  $\pi$  character in these bonds since both are less than 2 Å, but the electron-withdrawing nature of the formato groups reduces this character in comparison with that of an alkoxy complex. Thus, Cp<sub>2</sub>Ti(OCH<sub>2</sub>CH<sub>3</sub>)Cl shows a Ti—O bond length of 1.855 (2) Å (Huffman, Moloy, Marsella & Caulton, 1980) and Cp<sub>2</sub>Ti(OCH<sub>3</sub>)Cl shows a Ti—O bond length of 1.839 (2) Å (Gibson, Ding, Mashuta & Richardson, 1996). The Ti—O—C bond angles have also been taken as further indicators of  $\pi$  character in the Ti—O bonds of alkoxy complexes; the shorter Ti—O bond lengths are attended by larger Ti—O—C angles [133.2 (2) and 141.4 (3)°, respectively]. With acyloxy derivatives, however, this relationship is not maintained. The Ti—O—C bond angles in (I) are 143.3 (2) and

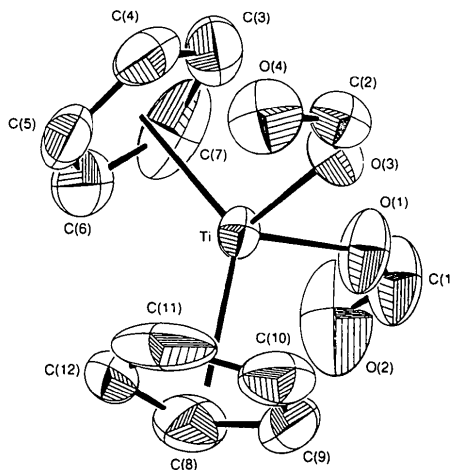


Fig. 1. ORTEPII (Johnson, 1976) plot of the title complex showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

145.2 (1)° and are larger than those in the alkoxy complexes. Also, Cp<sub>2</sub>Ti(OCOFCF<sub>3</sub>)<sub>2</sub> (Herman *et al.*, 1990) shows Ti—O bond lengths which are slightly longer [1.979 (5) and 1.970 (6) Å] than those of (I) because of the strongly electron-withdrawing CF<sub>3</sub> groups, but shows large and unequal Ti—O—C angles of 142.8 (5) and 149.2 (2)°. Furthermore, Cp<sub>2</sub>Ti(OCOPh)<sub>2</sub> (Hoffman, Chester & Fay, 1983) shows slightly shorter Ti—O bond lengths [1.927 (7) and 1.930 (5) Å] than (I), but shows much larger Ti—O—C angles of 147.9 (7) and 148.6 (4)°. Thus, larger Ti—O—C bond angles in the alkoxy complexes are not a direct reflection of enhanced  $\pi$  character in the Ti—O bonds. By comparison, the 18 e complex *trans*-[Mo(dmpe)<sub>2</sub>(OCHO)<sub>2</sub>] [dmpe = 1,2-bis(dimethylphosphino)ethane] shows a normal Mo—O bond length of 2.102 (4) Å and an Mo—O—C bond angle of 136.7 (5)° (Fong *et al.*, 1987).

## Experimental

Synthesis was carried out by the reaction of Cp<sub>2</sub>TiMe<sub>2</sub> with formic acid (1:2 molar ratio) in CH<sub>2</sub>Cl<sub>2</sub> solution during 1 h at 298 K. Evaporation of solvent afforded the pure product which was then recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/toluene; m.p. 445 K.

### Crystal data

[Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CHO)<sub>2</sub>]<sub>2</sub>

$M_r = 268.12$

Monoclinic

$P2_1/c$

$a = 8.210 (2) \text{ \AA}$

$b = 12.076 (5) \text{ \AA}$

$c = 11.949 (3) \text{ \AA}$

$\beta = 99.71 (2)^\circ$

$V = 1167.7 (6) \text{ \AA}^3$

$Z = 4$

$D_x = 1.525 \text{ Mg m}^{-3}$

$D_m$  not measured

Mo  $K\alpha$  radiation

$\lambda = 0.7107 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 15\text{--}18^\circ$

$\mu = 0.732 \text{ mm}^{-1}$

$T = 295 (2) \text{ K}$

Block

$0.50 \times 0.42 \times 0.33 \text{ mm}$

Orange

### Data collection

CAD-4 diffractometer

$\omega/2\theta$  scans

Absorption correction:

$\psi$  scans (North, Phillips & Mathews, 1968)

$T_{\min} = 0.95$ ,  $T_{\max} = 1.00$

2856 measured reflections

2689 independent reflections

1933 observed reflections

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

$R_{\text{int}} = 0.017$

$\theta_{\text{max}} = 26.94^\circ$

$h = 0 \rightarrow 10$

$k = 0 \rightarrow 15$

$l = -15 \rightarrow 15$

3 standard reflections

frequency: 60 min

intensity decay: <2%

### Refinement

Refinement on  $F$

$R = 0.038$

$wR = 0.038$

$S = 1.88$

1933 reflections

$\Delta\rho_{\text{max}} = 0.27 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$

Extinction correction:

Zachariasen (1967) type

2, Gaussian isotropic

203 parameters

H atoms refined with

isotropic displacement

parameters

$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\text{max}} = 0.024$

Extinction coefficient:

$3.1 (2) \times 10^{-6}$

Atomic scattering factors

from *International Tables*

for X-ray Crystallography

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

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

	x	y	z	$U_{\text{eq}}$
Ti	0.18682 (5)	0.05394 (4)	0.22452 (4)	0.0331 (1)
O(1)	-0.0493 (2)	0.0223 (2)	0.2077 (2)	0.0630 (7)
O(2)	-0.2162 (3)	0.1435 (2)	0.2675 (3)	0.117 (1)
O(3)	0.2186 (2)	-0.0764 (2)	0.1343 (2)	0.0462 (5)
O(4)	0.4748 (3)	-0.1259 (2)	0.1242 (2)	0.0717 (8)
C(1)	-0.1892 (4)	0.0590 (3)	0.2233 (4)	0.072 (1)
C(2)	0.3288 (4)	-0.1403 (3)	0.1059 (3)	0.0485 (9)
C(3)	0.1280 (5)	0.1450 (3)	0.0467 (3)	0.071 (1)
C(4)	0.2953 (5)	0.1366 (3)	0.0732 (3)	0.064 (1)
C(5)	0.3500 (5)	0.1966 (3)	0.1681 (3)	0.064 (1)
C(6)	0.2167 (7)	0.2452 (3)	0.2025 (4)	0.078 (2)
C(7)	0.0777 (6)	0.2139 (4)	0.1265 (6)	0.091 (2)
C(8)	0.1998 (7)	0.0830 (4)	0.4206 (3)	0.080 (1)
C(9)	0.1684 (6)	-0.0274 (3)	0.4042 (3)	0.069 (1)
C(10)	0.2950 (6)	-0.0763 (4)	0.3685 (3)	0.070 (1)
C(11)	0.4131 (6)	0.0066 (7)	0.3623 (4)	0.101 (2)
C(12)	0.3527 (8)	0.1042 (4)	0.3972 (3)	0.091 (2)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

$M(1)$  and  $M(2)$  are the centroids of the planes containing C(3)—C(7) and C(8)—C(12), respectively. C—H bond distances for these groups were found in the range 0.78–0.99 Å; C—H bond distances for formate were found in the range 0.85–0.90 Å.

Ti—O(1)	1.952 (2)	O(3)—C(2)	1.279 (3)
Ti—O(3)	1.951 (2)	O(4)—C(2)	1.194 (4)
O(1)—C(1)	1.275 (4)	Ti— $M(1)$	2.049
O(2)—C(1)	1.188 (4)	Ti— $M(2)$	2.059
O(1)—Ti—O(3)	90.56 (8)	O(1)—Ti— $M(1)$	107.2
Ti—O(1)—C(1)	145.2 (2)	O(1)—Ti— $M(2)$	106.4
Ti—O(3)—C(2)	143.3 (2)	O(3)—Ti— $M(1)$	105.8
$M(1)$ —Ti— $M(2)$	132.0	O(3)—Ti— $M(2)$	107.0

Atomic scattering factors were taken from Cromer & Waber (1974); corrections for anomalous-dispersion effects were made.

Data collection: *Diffractometer Control Software* (Enraf-Nonius, 1988). Cell refinement: *Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993). Program(s) used to solve structure: *PATY* in *DIRDIF92* (Beurskens *et al.*, 1992). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with a packing diagram, have been deposited with the IUCr (Reference: BK1212). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, University of Nijmegen, The Netherlands.
- Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2A, pp. 72–98. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- Enraf–Nonius (1988). *Diffraction Control Software*. Enraf–Nonius, Delft, The Netherlands.
- Fong, L. K., Fox, J. R. & Cooper, N. J. (1987). *Organometallics*, **6**, 223–231.
- Gibson, D. H., Ding, Y., Mashuta, M. S. & Richardson, J. F. (1996). *Acta Cryst. C52*, 559–560.
- Hermann, G. S., Alt, H. G. & Thewalt, U. (1990). *J. Organomet. Chem.* **399**, 83–92.
- Hoffman, D. M., Chester, N. D. & Fay, R. C. (1983). *Organometallics*, **2**, 48–52.
- Huffman, J. C., Moloy, K. G., Marsella, J. A. & Caulton, K. G. (1980). *J. Am. Chem. Soc.* **102**, 3009–3014.
- Jessop, P. G., Ikariya, T. & Noyori, R. (1995). *Chem. Rev.* **95**, 259–272.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1993). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.6. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Wöhrle, T. & Thewalt, U. (1994). *J. Organomet. Chem.* **468**, C1–C3.
- Zachariassen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

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## A Diphenylamido–Bromide Complex of Niobium: Dibromo[tris(diphenylamido)]-niobium(V) Tetrahydrofuran Solvate

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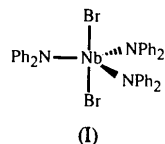
## Abstract

NbBr<sub>5</sub> reacts with three equivalents of Me<sub>3</sub>SiNPh<sub>2</sub> in ether to give the title compound, [NbBr<sub>2</sub>(C<sub>12</sub>H<sub>10</sub>N)<sub>3</sub>].·C<sub>4</sub>H<sub>8</sub>O. Nb(NPh<sub>2</sub>)<sub>3</sub>Br<sub>2</sub> has trigonal bipyramidal geometry with axial bromide ligands.

## Comment

Several diethylamido–chloride and –fluoride complexes of niobium have been prepared from NbX<sub>5</sub> and trimethylsilyldiethylamine, including Nb(NEt<sub>2</sub>)<sub>3</sub>Cl<sub>2</sub>, [Nb(NEt<sub>2</sub>)<sub>2</sub>Cl<sub>3</sub>]<sub>2</sub>, Nb(NEt<sub>2</sub>)F<sub>4</sub> and Nb(NEt<sub>2</sub>)<sub>2</sub>F<sub>3</sub> (Chao,

Polson & Wigley, 1990; Fugglè, Sharp & Winfield, 1972; Fowles & Pleass, 1957). We were interested in preparing similar amido–bromide derivatives to obtain a selection of complexes available for reduction studies (Hoffman & Rangarajan, 1993; Bott, Hoffman & Rangarajan, 1995). In this paper we describe the preparation and structure of Nb(NPh<sub>2</sub>)<sub>3</sub>Br<sub>2</sub>, (I).



NbBr<sub>5</sub> reacts with three equivalents of Me<sub>3</sub>SiNPh<sub>2</sub> or LiNPh<sub>2</sub> in ether to give Nb(NPh<sub>2</sub>)<sub>3</sub>Br<sub>2</sub>. The compound crystallizes from thf/CH<sub>3</sub>CN as dark red needles, but it is difficult to isolate cleanly from one or two persistent unidentified contaminants. The preparation based on Me<sub>3</sub>SiNPh<sub>2</sub> more consistently gives clean crystalline material than the one using LiNPh<sub>2</sub>. Proton NMR spectra for Nb(NPh<sub>2</sub>)<sub>3</sub>Br<sub>2</sub> show only resonances arising from one kind of phenyl group, consistent with the solid-state structure.

Nb(NPh<sub>2</sub>)<sub>3</sub>Br<sub>2</sub> crystallizes with one molecule of thf in the lattice. The Nb(NPh<sub>2</sub>)<sub>3</sub>Br<sub>2</sub> molecules are trigonal bipyramidal with axial bromide ligands (Fig. 1). A crystallographic threefold axis passes through the Nb and Br atoms. The amido ligand NC<sub>2</sub> ‘blades’ deviate by less than 4° from the trigonal plane defined by the three N atoms. In this configuration the amido N *pπ*-donor orbitals can interact only with niobium *d<sub>xz,yz</sub>* and not at all with *d<sub>xy,x2-y2</sub>*. This is expected since *d<sub>xy</sub>* and *d<sub>x2-y2</sub>* are involved in Nb–N σ bonding and would be too high in energy for an effective interaction with the *pπ* orbitals of nitrogen.

The Nb–N bond lengths [1.935 (8) Å] are similar to those in Nb(NMe<sub>2</sub>)<sub>5</sub> [1.977 (17)–2.044 (14) Å]

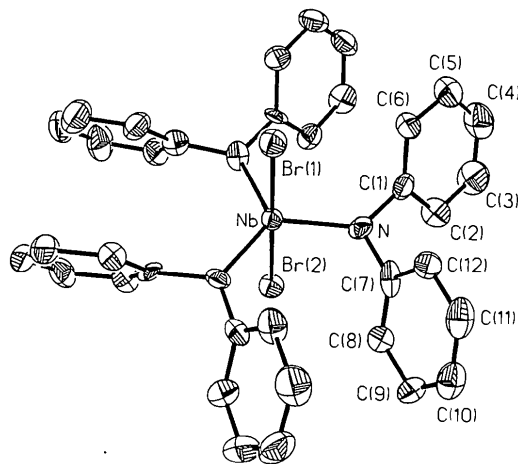


Fig. 1. View of Nb(NPh<sub>2</sub>)<sub>3</sub>Br<sub>2</sub> showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 40% probability level.