Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Dichlorido(*N*,*N*′-dibenzylideneethane-1,2-diamine-κ^2N,N')[(2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(diphenylmethanolato)-κ^2O,O']titanium(IV)

Chien-An Chen, Liang-Ying Chiang and Han-Mou Gau*

Department of Chemistry, National Chung Hsing University, Taichung 402, Taiwan
Correspondence e-mail: hmgau@dragon.nchu.edu.tw

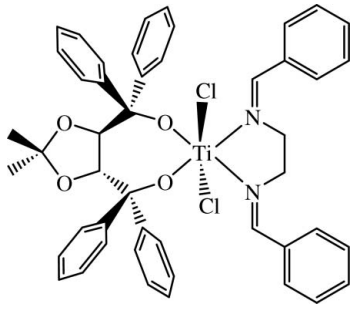
Received 17 October 2007; accepted 24 October 2007

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.036; wR factor = 0.085; data-to-parameter ratio = 16.8.

The title compound, $[TiCl_2(C_{31}H_{28}O_4)(C_{16}H_{16}N_2)]$, is a titanium(IV) complex of the bidentate 2,2-dimethyl-$\alpha,\alpha,\alpha',\alpha'$-tetraphenyl-1,3-dioxolane-4,5-dimethanolate (TADDOLate) ligand containing also two chloride ions and a bidentate neutral *N*,*N*′-dibenzylideneethane-1,2-diamine ligand. The molecular structure has a distorted octahedral geometry around the titanium metal center. The Ti—N bond lengths of 2.246 (2) and 2.2476 (17) Å are long, indicating weak bonding between the titanium(IV) metal center and the imine N atoms. Though the two chloride ligands are *trans* to each other, they bend away from the Ti–TADDOLate bonds with a Cl—Ti—Cl angle of 163.96 (3)°.

Related literature

For general background, see: Chen *et al.* (2007); Gau *et al.* (1996); Narasaka *et al.* (1989); Seebach *et al.* (1992); Shao & Gau (1998); Weber & Seebach (1994). For related structures, see: Hintermann & Togni (2000); Gothelf *et al.* (1995); Shao *et al.* (2001); Sheen & Gau (2004).



Experimental

Crystal data

$[TiCl_2(C_{31}H_{28}O_4)(C_{16}H_{16}N_2)]$
M_r = 819.64
Orthorhombic, $P2_12_12_1$
a = 9.9044 (9) Å
b = 18.8261 (17) Å
c = 23.238 (2) Å
V = 4332.9 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.37 mm^{-1}
T = 293 (2) K
0.70 × 0.59 × 0.21 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.672, T_{max} = 1.000
(expected range = 0.622–0.926)
24512 measured reflections
8479 independent reflections
6464 reflections with $I > 2\sigma(I)$
R_{int} = 0.042

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.085
S = 0.95
8479 reflections
505 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Absolute structure: Flack (1983), 3731 Friedel pairs
Flack parameter: −0.03 (2)

Table 1
Selected geometric parameters (Å, °).

Ti—O4	1.7797 (16)	Ti—N2	2.2476 (17)
Ti—O1	1.7855 (14)	Ti—Cl1	2.3459 (7)
Ti—N1	2.246 (2)	Ti—Cl2	2.3710 (7)
O4—Ti—O1	98.73 (7)	Cl1—Ti—Cl2	163.96 (3)
N1—Ti—N2	73.90 (7)		

Data collection: *SMART* (Siemens 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

This work was supported by grants from the National Science Council of Taiwan (grant No. NSC 96-2113-M-005-007-MY3).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2384).

References

Bruker (2000). *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chen, C.-A., Wu, K.-H. & Gau, H.-M. (2007). *Acta Cryst.* E**63**, m2665–m2666.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Gau, H.-M., Lee, C.-S., Lin, C.-C., Jiang, M.-K., Ho, Y.-C. & Kuo, C.-N. (1996). *J. Am. Chem. Soc.* **118**, 2936–2941.
Gothelf, K. V., Hazell, R. G. & Jørgensen, K. A. (1995). *J. Am. Chem. Soc.* **117**, 4435–4436.
Hintermann, L. & Togni, A. (2000). *Angew. Chem. Int. Ed.* **39**, 4359–4362.
Narasaka, K., Iwasawa, N., Inoue, M., Yamada, T., Nakashima, M. & Sugimori, J. (1989). *J. Am. Chem. Soc.* **111**, 5340–5345.
Seebach, D., Plattner, D. A., Beck, A. K., Wang, Y. M., Hunziker, D. & Petter, W. (1992). *Helv. Chim. Acta* **75**, 2171–2209.
Shao, M.-Y. & Gau, H.-M. (1998). *Organometallics* **17**, 4822–4827.
Shao, M.-Y., Sheen, W.-S. & Gau, H.-M. (2001). *Inorg. Chim. Acta* **314**, 105–110.

  doi:10.1107/S1600536807052725

Sheen, W.-S. & Gau, H.-M. (2004). *Inorg. Chim. Acta* **357**, 2279–2284.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Siemens (1996). *SMART* (Version 5) and *SAINT* (Version 4). Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Weber, B. & Seebach, D. (1994). *Tetrahedron* **50**, 7473–7484.

supplementary materials

Acta Cryst. (2007). E**63**, m2842-m2843 [**doi:10.1107/S1600536807052725**]

Dichlorido(*N*,*N*'-dibenzylideneethane-1,2-diamine-κ^2N,*N*')[(2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(diphenylmethanolato)-κ^2O,*O*']titanium(IV)

C.-A. Chen, L.-Y. Chiang and H.-M. Gau

Comment

Titanium(IV) complexes of 2,2-dimethyl-α,α,α',α'-tetraaryl-1,3-dioxolane- 4,5-dimethanolates (TADDOLs) have been reported to be excellent catalysts in a variety of asymmetric reactions such as ethylation (Shao & Gau, 1998), arylation (Weber & Seebach, 1994), *Diels-Alder* (Narasaka *et al.*, 1989), and fluorination reactions (Hintermann & Togni, 2000). In these studies, molecular structures of both four-coordinate Ti(TADDOLate)$_2$ (Seebach *et al.*, 1992) and six-coordinate Ti(TADDOLate)Cl$_2$*L*$_2$ (Gothelf *et al.*, 1995) complexes were reported. For six-coordinate complexes, the two chloride ligands are invariably *trans* to each other and *L*$_2$ could be two neutral monodentate ligands, such as tetrahydrofuran (Shao *et al.*, 2001) or acetonitrile (Hintermann & Togni, 2000). *L*$_2$ could also be a neutral bidentate like bipyridine or a 1,10-phenathroline. Recently, the molecular structure of an aluminium(III)-TADDOLate complex has been reported (Chen *et al.*, 2007).

The molecular structure of (**I**) has a distorted octahedral geometry about the titanium(IV) metal center with Ti—O(TADDOLate) bond lengths of 1.7797 (16)and 1.7855 (14) Å which are nearly identical to those in Ti(TADDOLate)Cl$_2$(CH$_3$CN)$_2$ (II) (Hintermann & Togni, 2000) and Ti(TADDOLate)Cl$_2$(bipyridine) (III) (Sheen & Gau, 2004). However, these Ti—O bond lengths are slightly longer than those of 1.752 (5) and 1.765 (5)Å in Ti(TADDOLate)Cl$_2$(MeOCH$_2$CH$_2$OMe) (Hintermann & Togni, 2000). The weakest Ti—*N*(imine) bonds are *trans* to the strongest Ti—O bonds (Gau *et al.*, 1996) where the bond lengths are found to be 2.246 (2) and 2.2476 (17) Å. These are slightly shorter than the Ti—N distances to the monodentate CH$_3$CN ligands in (II), 2.264 (4) and 2.283 (4) Å but are somewhat longer than those of 2.229 (5) and 2.232 (5) Å in the bidentate bipyridine complex (III). The N—Ti—N bond angle in the five-membered chelate ring 73.90 (7)° is close to that of 72.0 (2)° in (III). However, this angle is ~10° smaller than the 83.24 (14)° observed in (II) with two monodentate nitrogen donors. In terms of Ti—Cl bond lengths and O—Ti—O angles, relatively small variations are observed in these structures. The Ti—Cl bonds bend away from the Ti—O bonds with a Cl—Ti—Cl angle of 163.96 (3)°.

Experimental

To a solution of Ti(TADDOLate)Cl$_2$(AcOEt)$_2$ (1.55 g, 2.00 mmol) (Shao & Gau, 1998) in 5 ml CH$_2$Cl$_2$ at 298 K, *N*,*N*'-dibenzylideneethane-1,2-diamine (0.470 g, 2.00 mmol) in 5 ml CH$_2$Cl$_2$ was added. The solution was stirred for 12 h and the sovlent was removed. The resulted yellow solid was dissolved in 5 ml CH$_2$Cl$_2$ followed by a slow addition of 5 ml hexane. The two-layered solution was allowed to stand for 12 h at 298 K to give colorless crystals (0.917 g, 55.0%). ^{1}H NMR (300 MHz, CDCl$_3$): δ9.00 (s, 2H, N=C*H*), 7.77–7.12 (m, 30H, *Ph*), 5.60 (s, 2H, OC*H*), 4.13 (m, 4H, NC*H*$_2$), 0.56 (s, 6H, C*H*$_3$) p.p.m.. ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ166.77, 144.90, 143.70, 131.66, 131.52, 130.33, 129.78, 128.73, 128.18, 127.52, 127.45, 127.32, 127.03, 126.95, 111.35, 99.99, 80.26, 51.70, 27.38 p.p.m..

Refinement

All H atoms were treated as riding, with C—H = 0.93–0.98 Å, and with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C). Higher U_{eq} values are observed for C6, C7, C17, C18, C36, C37, C38, C39, C44 and C45 due to vibrations of peripheral methyl or phenyl groups away from the Ti metal center.

Figures

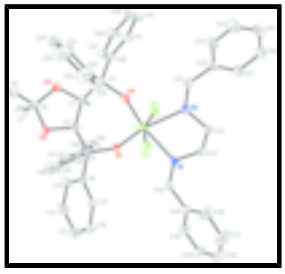


Fig. 1. The molecular structure of (I), with atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level. All except tertiary H atoms have been omitted for clarity.

Dichlorido(*N*,*N*'-dibenzylideneethane-1,2-diamine-κ^2*N*,*N*')[(2,2- dimethyl-1,3-dioxolane-4,5-diyl)bis(diphenylmethanolato)-κ^2*O*,*O*']titanium(IV)

Crystal data

$[TiCl_2(C_{31}H_{28}O_4)(C_{16}H_{16}N_2)]$	F_{000} = 1712
M_r = 819.64	D_x = 1.256 Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P 2ac 2ab	Cell parameters from 7794 reflections
a = 9.9044 (9) Å	θ = 2.3–26.0º
b = 18.8261 (17) Å	μ = 0.37 mm^{-1}
c = 23.238 (2) Å	T = 293 (2) K
V = 4332.9 (7) Å^3	Block, colorless
Z = 4	0.70 × 0.59 × 0.21 mm

Data collection

Bruker SMART 1000 CCD diffractometer	8479 independent reflections
Radiation source: fine-focus sealed tube	6464 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.042
T = 293(2) K	θ_{max} = 26.0º
φ and ω scans	θ_{min} = 2.1º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	h = −10→12
T_{min} = 0.672, T_{max} = 1.000	k = −23→23
24512 measured reflections	l = −28→23

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.036$	$w = 1/[\sigma^2(F_o^2) + (0.0439P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.085$	$(\Delta/\sigma)_{max} = 0.001$
$S = 0.95$	$\Delta\rho_{max} = 0.25$ e Å^{-3}
8479 reflections	$\Delta\rho_{min} = -0.23$ e Å^{-3}
505 parameters	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 3731 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: −0.03 (2)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ti	0.01130 (4)	0.890362 (18)	0.017317 (17)	0.03442 (10)
Cl1	−0.19289 (6)	0.87499 (4)	−0.03230 (3)	0.05223 (17)
Cl2	0.22879 (6)	0.87341 (3)	0.05768 (3)	0.05237 (17)
O1	0.04561 (15)	0.97815 (7)	−0.00782 (7)	0.0376 (4)
O2	−0.10731 (18)	1.13265 (8)	0.05941 (7)	0.0518 (4)
O3	−0.0431 (2)	1.08799 (9)	0.14664 (7)	0.0556 (5)
O4	−0.06491 (15)	0.91234 (8)	0.08435 (7)	0.0378 (4)
N1	0.09409 (19)	0.83911 (10)	−0.06252 (9)	0.0423 (5)
N2	−0.00005 (18)	0.77257 (9)	0.03233 (9)	0.0390 (4)
C1	0.0141 (2)	1.05209 (10)	−0.00378 (10)	0.0382 (5)
C2	−0.0782 (2)	1.05946 (11)	0.04940 (10)	0.0372 (5)
H2A	−0.1630	1.0343	0.0419	0.045*
C3	−0.0195 (2)	1.03286 (11)	0.10639 (10)	0.0380 (5)
H3A	0.0781	1.0262	0.1020	0.046*
C4	−0.0835 (2)	0.96249 (12)	0.12945 (10)	0.0371 (5)
C5	−0.0873 (4)	1.15128 (14)	0.11801 (12)	0.0625 (8)
C6	−0.2193 (5)	1.1747 (2)	0.14401 (18)	0.1215 (18)

H6A	−0.2845	1.1372	0.1403	0.182*
H6B	−0.2512	1.2162	0.1243	0.182*
H6C	−0.2062	1.1854	0.1840	0.182*
C7	0.0228 (5)	1.20642 (17)	0.12197 (15)	0.1091 (16)
H7A	0.1036	1.1884	0.1045	0.164*
H7B	0.0400	1.2172	0.1617	0.164*
H7C	−0.0053	1.2488	0.1023	0.164*
C8	−0.0567 (3)	1.07213 (12)	−0.06015 (11)	0.0445 (6)
C9	0.0162 (4)	1.06813 (15)	−0.11071 (11)	0.0632 (8)
H9A	0.1066	1.0549	−0.1095	0.076*
C10	−0.0427 (5)	1.0834 (2)	−0.16289 (14)	0.0867 (11)
H10A	0.0078	1.0800	−0.1965	0.104*
C11	−0.1747 (5)	1.1035 (2)	−0.16552 (15)	0.0887 (11)
H11A	−0.2146	1.1133	−0.2009	0.106*
C12	−0.2486 (4)	1.10906 (18)	−0.11572 (15)	0.0794 (10)
H12A	−0.3381	1.1239	−0.1173	0.095*
C13	−0.1903 (3)	1.09274 (14)	−0.06321 (12)	0.0586 (7)
H13A	−0.2415	1.0957	−0.0298	0.070*
C14	0.1464 (3)	1.09407 (12)	0.00229 (11)	0.0460 (6)
C15	0.1502 (3)	1.16627 (14)	−0.01034 (14)	0.0635 (8)
H15A	0.0730	1.1891	−0.0236	0.076*
C16	0.2688 (4)	1.20430 (17)	−0.00315 (17)	0.0898 (12)
H16A	0.2707	1.2525	−0.0118	0.108*
C17	0.3823 (4)	1.1718 (2)	0.0165 (2)	0.1116 (16)
H17A	0.4611	1.1979	0.0214	0.134*
C18	0.3811 (3)	1.10086 (19)	0.0291 (2)	0.1041 (15)
H18A	0.4592	1.0787	0.0422	0.125*
C19	0.2627 (3)	1.06186 (15)	0.02209 (16)	0.0702 (9)
H19A	0.2620	1.0137	0.0309	0.084*
C20	−0.2338 (2)	0.97070 (13)	0.14184 (11)	0.0437 (6)
C21	−0.3293 (3)	0.94547 (16)	0.10358 (14)	0.0606 (8)
H21A	−0.3018	0.9228	0.0700	0.073*
C22	−0.4658 (3)	0.9538 (2)	0.11499 (17)	0.0855 (11)
H22A	−0.5296	0.9361	0.0893	0.103*
C23	−0.5063 (4)	0.9878 (2)	0.16382 (19)	0.0984 (13)
H23A	−0.5979	0.9936	0.1711	0.118*
C24	−0.4135 (4)	1.0133 (2)	0.20214 (17)	0.0826 (11)
H24A	−0.4418	1.0371	0.2351	0.099*
C25	−0.2781 (3)	1.00354 (17)	0.19176 (13)	0.0613 (8)
H25A	−0.2152	1.0192	0.2186	0.074*
C26	−0.0096 (3)	0.93361 (12)	0.18191 (10)	0.0430 (6)
C27	0.1065 (3)	0.96223 (18)	0.20453 (13)	0.0652 (8)
H27A	0.1421	1.0035	0.1887	0.078*
C28	0.1710 (4)	0.9303 (2)	0.25059 (16)	0.0865 (11)
H28A	0.2483	0.9509	0.2659	0.104*
C29	0.1224 (4)	0.8686 (2)	0.27395 (16)	0.0933 (12)
H29A	0.1682	0.8462	0.3038	0.112*
C30	0.0059 (4)	0.84082 (18)	0.25278 (15)	0.0860 (10)
H30A	−0.0298	0.7998	0.2691	0.103*

C31	−0.0595 (3)	0.87281 (16)	0.20752 (13)	0.0633 (8)
H31A	−0.1393	0.8530	0.1938	0.076*
C32	0.1284 (3)	0.76385 (13)	−0.05528 (13)	0.0516 (7)
H32A	0.2164	0.7595	−0.0373	0.062*
H32B	0.1321	0.7408	−0.0926	0.062*
C33	0.0228 (2)	0.72842 (11)	−0.01819 (11)	0.0456 (6)
H33A	−0.0605	0.7230	−0.0397	0.055*
H33B	0.0536	0.6817	−0.0066	0.055*
C34	0.0898 (3)	0.86842 (14)	−0.11157 (12)	0.0544 (7)
H34A	0.0754	0.9172	−0.1109	0.065*
C35	0.1041 (3)	0.83741 (17)	−0.16978 (13)	0.0639 (8)
C36	0.0207 (5)	0.7833 (2)	−0.18752 (18)	0.1132 (15)
H36A	−0.0416	0.7635	−0.1623	0.136*
C37	0.0307 (7)	0.7587 (3)	−0.2438 (2)	0.149 (2)
H37A	−0.0269	0.7230	−0.2564	0.179*
C38	0.1227 (8)	0.7859 (3)	−0.2800 (2)	0.145 (2)
H38A	0.1303	0.7679	−0.3171	0.174*
C39	0.2044 (7)	0.8395 (3)	−0.2628 (2)	0.1272 (18)
H39A	0.2678	0.8586	−0.2879	0.153*
C40	0.1926 (5)	0.8654 (2)	−0.20779 (15)	0.0912 (12)
H40A	0.2469	0.9032	−0.1964	0.109*
C41	−0.0077 (3)	0.74781 (12)	0.08336 (12)	0.0497 (6)
H41A	−0.0180	0.7821	0.1118	0.060*
C42	−0.0030 (3)	0.67446 (13)	0.10504 (12)	0.0559 (7)
C43	0.0597 (5)	0.6663 (2)	0.15814 (16)	0.0970 (12)
H43A	0.0924	0.7060	0.1775	0.116*
C44	0.0734 (6)	0.6011 (3)	0.1818 (2)	0.1319 (19)
H44A	0.1147	0.5964	0.2176	0.158*
C45	0.0277 (6)	0.5429 (2)	0.1541 (2)	0.1213 (18)
H45A	0.0416	0.4981	0.1700	0.146*
C46	−0.0396 (4)	0.54923 (17)	0.10223 (18)	0.0899 (12)
H46A	−0.0740	0.5091	0.0841	0.108*
C47	−0.0557 (3)	0.61513 (14)	0.07746 (13)	0.0614 (7)
H47A	−0.1013	0.6199	0.0427	0.074*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ti	0.0350 (2)	0.02628 (18)	0.0420 (2)	−0.00081 (16)	−0.00169 (19)	0.00011 (18)
Cl1	0.0408 (3)	0.0585 (4)	0.0573 (4)	−0.0036 (3)	−0.0117 (3)	−0.0018 (3)
Cl2	0.0378 (3)	0.0460 (3)	0.0734 (5)	0.0010 (3)	−0.0125 (3)	−0.0005 (3)
O1	0.0435 (8)	0.0278 (7)	0.0415 (9)	−0.0019 (6)	0.0009 (7)	0.0017 (7)
O2	0.0807 (12)	0.0317 (9)	0.0430 (10)	0.0127 (8)	−0.0082 (9)	−0.0038 (8)
O3	0.0897 (14)	0.0405 (9)	0.0366 (9)	0.0029 (9)	−0.0097 (10)	−0.0058 (8)
O4	0.0397 (8)	0.0322 (8)	0.0414 (9)	0.0012 (6)	0.0002 (7)	0.0008 (7)
N1	0.0446 (11)	0.0327 (10)	0.0495 (13)	−0.0039 (8)	0.0038 (10)	−0.0033 (10)
N2	0.0373 (10)	0.0319 (9)	0.0477 (12)	−0.0014 (9)	−0.0028 (10)	0.0020 (8)
C1	0.0501 (13)	0.0247 (10)	0.0398 (13)	−0.0003 (10)	−0.0036 (12)	0.0011 (9)

C2	0.0463 (13)	0.0255 (11)	0.0396 (14)	0.0036 (10)	−0.0077 (11)	−0.0001 (10)
C3	0.0454 (14)	0.0331 (11)	0.0355 (13)	−0.0031 (10)	−0.0037 (12)	−0.0016 (9)
C4	0.0404 (13)	0.0362 (12)	0.0348 (13)	0.0003 (10)	−0.0023 (11)	0.0027 (10)
C5	0.110 (2)	0.0364 (15)	0.0408 (16)	0.0089 (15)	0.0019 (16)	−0.0042 (13)
C6	0.183 (4)	0.102 (3)	0.080 (3)	0.080 (3)	0.048 (3)	0.017 (2)
C7	0.205 (5)	0.0591 (19)	0.063 (2)	−0.045 (3)	−0.028 (3)	−0.0087 (16)
C8	0.0658 (17)	0.0300 (12)	0.0376 (14)	0.0014 (11)	−0.0076 (13)	0.0013 (11)
C9	0.084 (2)	0.0637 (17)	0.0421 (16)	0.0067 (17)	−0.0015 (17)	−0.0005 (13)
C10	0.122 (3)	0.097 (3)	0.0403 (18)	0.005 (2)	−0.003 (2)	0.0060 (17)
C11	0.131 (3)	0.085 (3)	0.050 (2)	0.001 (2)	−0.035 (2)	0.0054 (19)
C12	0.090 (2)	0.080 (2)	0.068 (2)	0.0131 (19)	−0.033 (2)	0.008 (2)
C13	0.0700 (19)	0.0585 (17)	0.0475 (17)	0.0083 (14)	−0.0117 (15)	0.0039 (14)
C14	0.0562 (15)	0.0346 (13)	0.0471 (15)	−0.0092 (11)	−0.0033 (12)	0.0060 (11)
C15	0.085 (2)	0.0376 (14)	0.068 (2)	−0.0114 (13)	−0.0020 (17)	0.0054 (14)
C16	0.115 (3)	0.0517 (19)	0.103 (3)	−0.040 (2)	0.006 (3)	0.0117 (19)
C17	0.096 (3)	0.088 (3)	0.151 (4)	−0.059 (2)	−0.024 (3)	0.021 (3)
C18	0.068 (2)	0.082 (2)	0.162 (4)	−0.0383 (18)	−0.029 (2)	0.038 (3)
C19	0.0597 (17)	0.0520 (16)	0.099 (3)	−0.0181 (14)	−0.0094 (19)	0.0205 (18)
C20	0.0413 (13)	0.0447 (14)	0.0451 (16)	0.0037 (11)	0.0010 (12)	0.0046 (12)
C21	0.0425 (15)	0.074 (2)	0.065 (2)	−0.0023 (14)	−0.0021 (15)	−0.0006 (16)
C22	0.0391 (18)	0.122 (3)	0.095 (3)	−0.0071 (17)	0.0012 (18)	−0.002 (2)
C23	0.0468 (19)	0.141 (4)	0.108 (3)	0.020 (2)	0.023 (2)	0.022 (3)
C24	0.070 (2)	0.102 (3)	0.075 (2)	0.020 (2)	0.028 (2)	0.002 (2)
C25	0.0572 (18)	0.077 (2)	0.0495 (17)	0.0089 (15)	0.0052 (15)	−0.0011 (16)
C26	0.0468 (14)	0.0466 (13)	0.0357 (13)	0.0078 (12)	0.0028 (13)	0.0047 (11)
C27	0.0593 (18)	0.079 (2)	0.0575 (19)	−0.0028 (16)	−0.0138 (16)	0.0208 (17)
C28	0.069 (2)	0.116 (3)	0.074 (2)	0.006 (2)	−0.0251 (19)	0.027 (2)
C29	0.107 (3)	0.108 (3)	0.065 (2)	0.031 (3)	−0.016 (2)	0.031 (2)
C30	0.108 (3)	0.080 (2)	0.070 (2)	0.008 (2)	0.002 (2)	0.0425 (19)
C31	0.0731 (19)	0.0586 (18)	0.0583 (18)	−0.0017 (15)	0.0010 (15)	0.0180 (15)
C32	0.0552 (15)	0.0364 (13)	0.0631 (18)	0.0042 (11)	0.0051 (14)	−0.0063 (13)
C33	0.0485 (14)	0.0309 (11)	0.0573 (16)	−0.0029 (10)	0.0022 (14)	−0.0023 (11)
C34	0.0719 (18)	0.0418 (14)	0.0494 (16)	0.0023 (13)	−0.0019 (14)	−0.0019 (13)
C35	0.087 (2)	0.0554 (17)	0.0497 (18)	0.0106 (16)	−0.0036 (17)	−0.0048 (15)
C36	0.134 (4)	0.121 (3)	0.085 (3)	−0.029 (3)	−0.002 (3)	−0.040 (3)
C37	0.206 (6)	0.146 (5)	0.095 (4)	−0.036 (5)	−0.007 (4)	−0.054 (4)
C38	0.238 (7)	0.130 (5)	0.067 (3)	0.032 (5)	−0.002 (4)	−0.037 (3)
C39	0.210 (6)	0.107 (3)	0.065 (3)	0.014 (4)	0.040 (3)	−0.005 (3)
C40	0.139 (3)	0.077 (2)	0.057 (2)	0.001 (2)	0.022 (2)	0.0007 (19)
C41	0.0539 (16)	0.0373 (13)	0.0578 (17)	0.0028 (12)	−0.0058 (15)	−0.0011 (12)
C42	0.0623 (16)	0.0463 (14)	0.0591 (17)	0.0063 (14)	0.0016 (16)	0.0147 (13)
C43	0.143 (3)	0.071 (2)	0.077 (3)	0.012 (2)	−0.027 (3)	0.018 (2)
C44	0.199 (5)	0.103 (4)	0.094 (3)	0.045 (4)	−0.035 (3)	0.037 (3)
C45	0.185 (5)	0.071 (3)	0.108 (4)	0.049 (3)	0.017 (4)	0.043 (3)
C46	0.123 (3)	0.0464 (18)	0.101 (3)	0.0019 (19)	0.036 (3)	0.0079 (19)
C47	0.0687 (17)	0.0444 (15)	0.0712 (19)	0.0004 (14)	0.0115 (15)	0.0087 (15)

Geometric parameters (Å, °)

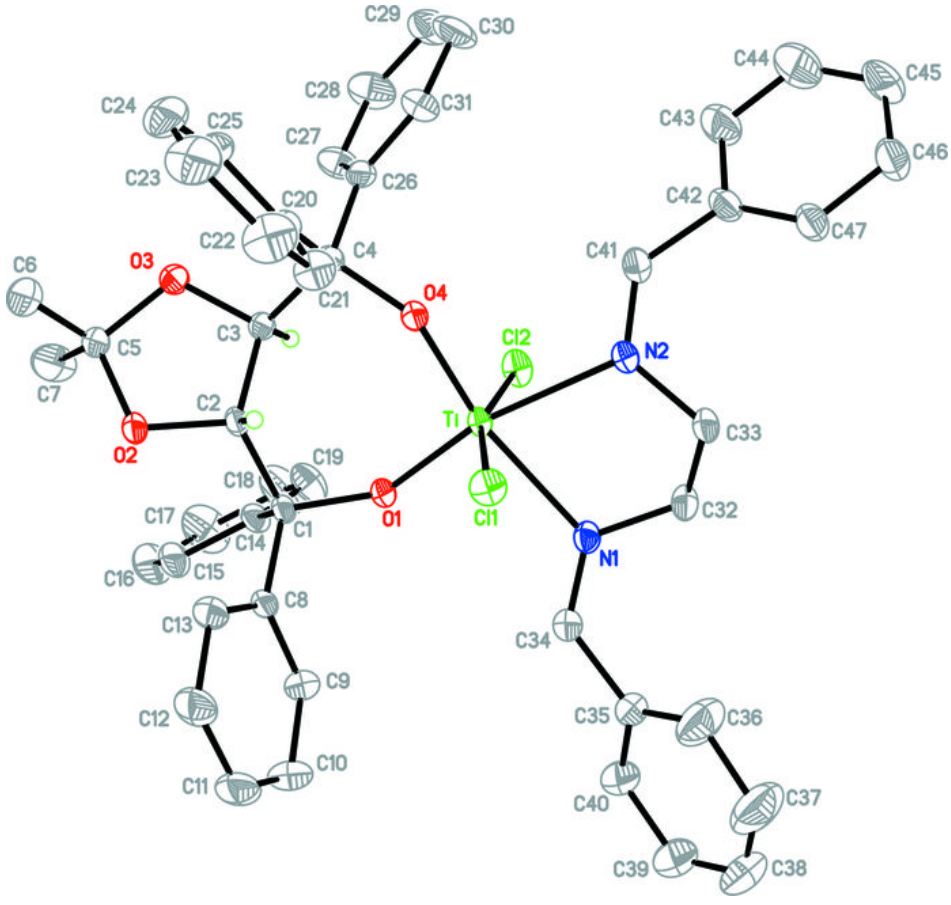
Ti—O4	1.7797 (16)	C19—H19A	0.9300
Ti—O1	1.7855 (14)	C20—C21	1.382 (4)
Ti—N1	2.246 (2)	C20—C25	1.386 (4)
Ti—N2	2.2476 (17)	C21—C22	1.387 (4)
Ti—Cl1	2.3459 (7)	C21—H21A	0.9300
Ti—Cl2	2.3710 (7)	C22—C23	1.363 (5)
O1—C1	1.430 (2)	C22—H22A	0.9300
O2—C5	1.420 (3)	C23—C24	1.367 (5)
O2—C2	1.427 (3)	C23—H23A	0.9300
O3—C3	1.417 (3)	C24—C25	1.375 (5)
O3—C5	1.433 (3)	C24—H24A	0.9300
O4—C4	1.422 (3)	C25—H25A	0.9300
N1—C34	1.267 (3)	C26—C27	1.374 (4)
N1—C32	1.467 (3)	C26—C31	1.382 (4)
N2—C41	1.276 (3)	C27—C28	1.384 (4)
N2—C33	1.456 (3)	C27—H27A	0.9300
C1—C8	1.533 (3)	C28—C29	1.368 (5)
C1—C14	1.537 (3)	C28—H28A	0.9300
C1—C2	1.543 (3)	C29—C30	1.359 (5)
C2—C3	1.531 (3)	C29—H29A	0.9300
C2—H2A	0.9800	C30—C31	1.374 (4)
C3—C4	1.563 (3)	C30—H30A	0.9300
C3—H3A	0.9800	C31—H31A	0.9300
C4—C26	1.522 (3)	C32—C33	1.510 (3)
C4—C20	1.525 (3)	C32—H32A	0.9700
C5—C6	1.505 (5)	C32—H32B	0.9700
C5—C7	1.508 (5)	C33—H33A	0.9700
C6—H6A	0.9600	C33—H33B	0.9700
C6—H6B	0.9600	C34—C35	1.480 (4)
C6—H6C	0.9600	C34—H34A	0.9300
C7—H7A	0.9600	C35—C40	1.351 (5)
C7—H7B	0.9600	C35—C36	1.374 (5)
C7—H7C	0.9600	C36—C37	1.390 (6)
C8—C13	1.381 (4)	C36—H36A	0.9300
C8—C9	1.381 (4)	C37—C38	1.341 (7)
C9—C10	1.376 (4)	C37—H37A	0.9300
C9—H9A	0.9300	C38—C39	1.354 (8)
C10—C11	1.362 (5)	C38—H38A	0.9300
C10—H10A	0.9300	C39—C40	1.372 (6)
C11—C12	1.373 (5)	C39—H39A	0.9300
C11—H11A	0.9300	C40—H40A	0.9300
C12—C13	1.384 (4)	C41—C42	1.471 (3)
C12—H12A	0.9300	C41—H41A	0.9300
C13—H13A	0.9300	C42—C47	1.390 (4)
C14—C19	1.381 (4)	C42—C43	1.390 (4)
C14—C15	1.391 (4)	C43—C44	1.352 (5)

C15—C16	1.386 (4)	C43—H43A	0.9300
C15—H15A	0.9300	C44—C45	1.351 (6)
C16—C17	1.359 (5)	C44—H44A	0.9300
C16—H16A	0.9300	C45—C46	1.382 (6)
C17—C18	1.367 (5)	C45—H45A	0.9300
C17—H17A	0.9300	C46—C47	1.377 (4)
C18—C19	1.393 (4)	C46—H46A	0.9300
C18—H18A	0.9300	C47—H47A	0.9300
O4—Ti—O1	98.73 (7)	C17—C18—C19	119.8 (3)
O4—Ti—N1	167.86 (7)	C17—C18—H18A	120.1
O1—Ti—N1	93.32 (7)	C19—C18—H18A	120.1
O4—Ti—N2	94.15 (7)	C14—C19—C18	120.7 (3)
O1—Ti—N2	166.79 (7)	C14—C19—H19A	119.7
N1—Ti—N2	73.90 (7)	C18—C19—H19A	119.7
O4—Ti—Cl1	95.35 (6)	C21—C20—C25	118.4 (2)
O1—Ti—Cl1	96.75 (5)	C21—C20—C4	120.8 (2)
N1—Ti—Cl1	81.71 (5)	C25—C20—C4	120.8 (2)
N2—Ti—Cl1	84.92 (5)	C20—C21—C22	120.4 (3)
O4—Ti—Cl2	94.04 (6)	C20—C21—H21A	119.8
O1—Ti—Cl2	94.65 (5)	C22—C21—H21A	119.8
N1—Ti—Cl2	86.40 (6)	C23—C22—C21	119.9 (4)
N2—Ti—Cl2	81.44 (5)	C23—C22—H22A	120.0
Cl1—Ti—Cl2	163.96 (3)	C21—C22—H22A	120.0
C1—O1—Ti	146.95 (14)	C22—C23—C24	120.6 (3)
C5—O2—C2	111.52 (18)	C22—C23—H23A	119.7
C3—O3—C5	110.67 (17)	C24—C23—H23A	119.7
C4—O4—Ti	148.64 (14)	C23—C24—C25	119.6 (3)
C34—N1—C32	122.1 (2)	C23—C24—H24A	120.2
C34—N1—Ti	122.94 (17)	C25—C24—H24A	120.2
C32—N1—Ti	113.87 (17)	C24—C25—C20	121.0 (3)
C41—N2—C33	123.35 (19)	C24—C25—H25A	119.5
C41—N2—Ti	120.50 (16)	C20—C25—H25A	119.5
C33—N2—Ti	115.48 (14)	C27—C26—C31	117.4 (2)
O1—C1—C8	106.47 (17)	C27—C26—C4	124.6 (2)
O1—C1—C14	108.70 (18)	C31—C26—C4	117.9 (2)
C8—C1—C14	109.99 (19)	C26—C27—C28	120.7 (3)
O1—C1—C2	105.63 (16)	C26—C27—H27A	119.6
C8—C1—C2	113.03 (19)	C28—C27—H27A	119.6
C14—C1—C2	112.66 (19)	C29—C28—C27	120.9 (4)
O2—C2—C3	104.57 (18)	C29—C28—H28A	119.6
O2—C2—C1	109.70 (18)	C27—C28—H28A	119.6
C3—C2—C1	116.00 (19)	C30—C29—C28	118.8 (3)
O2—C2—H2A	108.8	C30—C29—H29A	120.6
C3—C2—H2A	108.8	C28—C29—H29A	120.6
C1—C2—H2A	108.8	C29—C30—C31	120.6 (3)
O3—C3—C2	105.59 (17)	C29—C30—H30A	119.7
O3—C3—C4	109.11 (18)	C31—C30—H30A	119.7
C2—C3—C4	114.82 (18)	C30—C31—C26	121.6 (3)
O3—C3—H3A	109.1	C30—C31—H31A	119.2

C2—C3—H3A	109.1	C26—C31—H31A	119.2
C4—C3—H3A	109.1	N1—C32—C33	109.4 (2)
O4—C4—C26	106.91 (18)	N1—C32—H32A	109.8
O4—C4—C20	109.42 (19)	C33—C32—H32A	109.8
C26—C4—C20	110.8 (2)	N1—C32—H32B	109.8
O4—C4—C3	104.92 (17)	C33—C32—H32B	109.8
C26—C4—C3	112.47 (19)	H32A—C32—H32B	108.2
C20—C4—C3	112.02 (19)	N2—C33—C32	108.40 (18)
O2—C5—O3	106.40 (19)	N2—C33—H33A	110.0
O2—C5—C6	109.6 (3)	C32—C33—H33A	110.0
O3—C5—C6	108.8 (3)	N2—C33—H33B	110.0
O2—C5—C7	109.2 (3)	C32—C33—H33B	110.0
O3—C5—C7	108.9 (3)	H33A—C33—H33B	108.4
C6—C5—C7	113.7 (3)	N1—C34—C35	130.3 (3)
C5—C6—H6A	109.5	N1—C34—H34A	114.8
C5—C6—H6B	109.5	C35—C34—H34A	114.8
H6A—C6—H6B	109.5	C40—C35—C36	118.9 (3)
C5—C6—H6C	109.5	C40—C35—C34	120.4 (3)
H6A—C6—H6C	109.5	C36—C35—C34	120.6 (3)
H6B—C6—H6C	109.5	C35—C36—C37	119.1 (5)
C5—C7—H7A	109.5	C35—C36—H36A	120.5
C5—C7—H7B	109.5	C37—C36—H36A	120.5
H7A—C7—H7B	109.5	C38—C37—C36	120.7 (5)
C5—C7—H7C	109.5	C38—C37—H37A	119.6
H7A—C7—H7C	109.5	C36—C37—H37A	119.6
H7B—C7—H7C	109.5	C37—C38—C39	120.4 (5)
C13—C8—C9	118.2 (3)	C37—C38—H38A	119.8
C13—C8—C1	123.5 (2)	C39—C38—H38A	119.8
C9—C8—C1	118.3 (2)	C38—C39—C40	119.2 (5)
C10—C9—C8	121.1 (3)	C38—C39—H39A	120.4
C10—C9—H9A	119.4	C40—C39—H39A	120.4
C8—C9—H9A	119.4	C35—C40—C39	121.7 (4)
C11—C10—C9	120.3 (4)	C35—C40—H40A	119.1
C11—C10—H10A	119.9	C39—C40—H40A	119.1
C9—C10—H10A	119.9	N2—C41—C42	131.2 (2)
C10—C11—C12	119.7 (3)	N2—C41—H41A	114.4
C10—C11—H11A	120.2	C42—C41—H41A	114.4
C12—C11—H11A	120.2	C47—C42—C43	119.3 (3)
C11—C12—C13	120.3 (3)	C47—C42—C41	125.8 (3)
C11—C12—H12A	119.9	C43—C42—C41	114.9 (3)
C13—C12—H12A	119.9	C44—C43—C42	120.4 (4)
C8—C13—C12	120.5 (3)	C44—C43—H43A	119.8
C8—C13—H13A	119.8	C42—C43—H43A	119.8
C12—C13—H13A	119.8	C45—C44—C43	120.6 (4)
C19—C14—C15	118.5 (2)	C45—C44—H44A	119.7
C19—C14—C1	121.1 (2)	C43—C44—H44A	119.7
C15—C14—C1	120.4 (2)	C44—C45—C46	120.5 (3)
C16—C15—C14	120.2 (3)	C44—C45—H45A	119.8
C16—C15—H15A	119.9	C46—C45—H45A	119.8

C14—C15—H15A	119.9	C47—C46—C45	119.9 (4)
C17—C16—C15	120.6 (3)	C47—C46—H46A	120.1
C17—C16—H16A	119.7	C45—C46—H46A	120.1
C15—C16—H16A	119.7	C46—C47—C42	119.2 (3)
C16—C17—C18	120.4 (3)	C46—C47—H47A	120.4
C16—C17—H17A	119.8	C42—C47—H47A	120.4
C18—C17—H17A	119.8		

Fig. 1


C29
C30
C28
C31
C24
C25
C27
C23
C26
C20
C22
C4
C6
O3
C21
O4
C3
C5
Cl2
N2
C7
C2
Ti
C33
O2
C19
C18
O1
Cl1
C32
C17
C1
C14
N1
C16
C15
C8
C13
C34
C9
C12
C35
C36
C10
C11
C40
C37
C39
C38
C44
C45
C43
C46
C42
C47
C41