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A Titanium Alkoxide (Pinacolate) Complex Incorporating a 10-Membered Ring

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We have reported earlier[1] on the preparation of two pinacol compounds of Ti(IV) of empirical formula $CpTiCl(OCMe_2CMe_2O)$. The action of TlCp on $[TiCl_2(OCMe_2CMe_2O)]_x$ at low temperature and in nonpolar solvents gives a material shown by cryoscopic molecular weight measurement to be a monomer. Synthesis in polar solvents, or refluxing the monomer in benzene (eq 1), gives dimer I, whose ^1H

$$2CpTiCl(OCMe_2CMe_2O) \xrightarrow{\Delta} \underset{\text{I}}{[CpTiCl(OCMe_2CMe_2O)]_2} \quad (1)$$

NMR chemical shifts are distinguishable from those of the monomer. Since this reaction must involve an entropy decrease, we were interested in the detailed structure of I as a first step toward rationalizing the exergonic nature of eq 1. These results are reported here.

Experimental Section

The synthesis and characterization of $[CpTiCl(OCMe_2CMe_2O)]_2$ have been reported in detail.[1]

Structure Determinations. Crystal data and parameters of the data collection (at −172 °C, $5° \leq 2\theta \leq 55°$) are shown in Table I. No absorption correction was performed on the data. Sample handling (under N_2), data collection and processing, and structure solving (direct methods have been described.[2] The maximum variation of four standard reflections was 0.4σ over the time of data collection; there was no evidence for crystal decomposition. All atoms (including hydrogen) were refined by full-matrix methods, consistent with the crystallographic center of symmetry imposed on the dimer. Positional and thermal parameters are given in Table II, with bond lengths and angles in Table III. The molecular structure and atom labeling are shown in Figures 1–3. Anisotropic *U*'s and a table of calculated and observed structure factors are available as supplementary material.

Hydrogen atoms deviate by less than 3σ from the cyclopentadienyl carbon plane, always toward the metal. This trend is also evident in the structure of $[CpTiCl_2]_2O_2C_2Me_4$.[3] Within the ring, C–H separations average 0.91 Å, varying from 0.81 (3) to 0.96 (4) Å. Within the pinacolate group, the average C–H separation is 0.94 Å, ranging from 0.89 (4) to 1.01 (4) Å; the H–C–H angles average 108.2°, while the C–C–H angles average 110.7°. The refined hydrogen positions establish a staggered rotational conformation about the C–C bonds of the pinacolate group (Figure 1). Titanium lies 2.057 Å from the Cp least-squares plane, while Cl, O(3), and O(6) lie 2.967, 2.849, and 2.864 Å, respectively, from this same plane. A line from Ti to the ring midpoint makes an angle of 88.3° with the Cp ring plane.

Results and Discussion

Table I. Crystal Data for $[C_5H_5TiCl(O_2C_2Me_4)]_2$

formula	$C_{22}H_{34}O_4Cl_2Ti$
color	colorless
cryst dimens, mm	0.18 × 0.20 × 0.23
space group	*Pcab*
cell dimens (at −172 °C; 40 rflns)	
a, Å	13.364 (3)
b, Å	13.513 (3)
c, Å	13.773 (3)
molecules/cell	4
volume, Å^3	2487.10
calcd density, g/cm^3	1.413
wavelength, Å	0.71069
mol wt	529.2
linear abs coeff, cm^{-1}	8.760
no. of unique intens	2855
no. with $F > 0.0$	2551
no. with $F > \sigma(F)$	2303
no. with $F > 2.33\sigma(F)$	2025
final residuals	
$R(F)$	0.0526
$R_w(F)$	0.0406
goodness of fit for last cycle	0.978
max δ/σ for last cycle	0.05

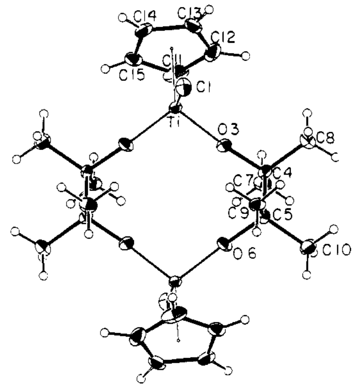

Figure 1. ORTEP drawing of $[CpTiCl(OCMe_2CMe_2O)]_2$, showing atom labeling. Unlabeled atoms are related to those shown by a center of symmetry.

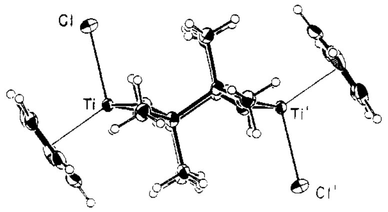

Figure 2. ORTEP side view of the 10-membered ring, showing axial/equatorial positioning of substituents.

In the solid state, centrosymmetric $[CpTiCl(O_2C_2Me_4)]_2$ is dimeric by virtue of forming a 10-membered ring. Because of the near-linearity of the Ti–O–C bonds, the ring conformation may be said to resemble chair cyclohexane. The crystallographic center of symmetry imposes a trans relationship on the substituents on different titanium atoms, and the bulkier η^5-C_5H_5 substituents occupy equatorial positions while the chlorines are axial (Figure 2). The detailed structure of the molecule is quite faithful to an idealized symmetry of C_{2h}, so that the eight methyl groups fall into only two classes, axial or equatorial in the 10-membered ring. This C_{2h} conformation is also the ground state of cyclodecane.[4] $(CpTiCl_2)_2O_2C_2Me_4$, a useful comparison compound (Table IV, which also contains data showing the weaker Ti–O binding in $Cp_2Ti(OEt)Cl$) also crystallizes with a crystallographic center of

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(1) Marsella, J. A.; Moloy, K. G.; Caulton, K. G. *J. Organomet. Chem.* **1980**, *201*, 389.

(2) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

(3) Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009.

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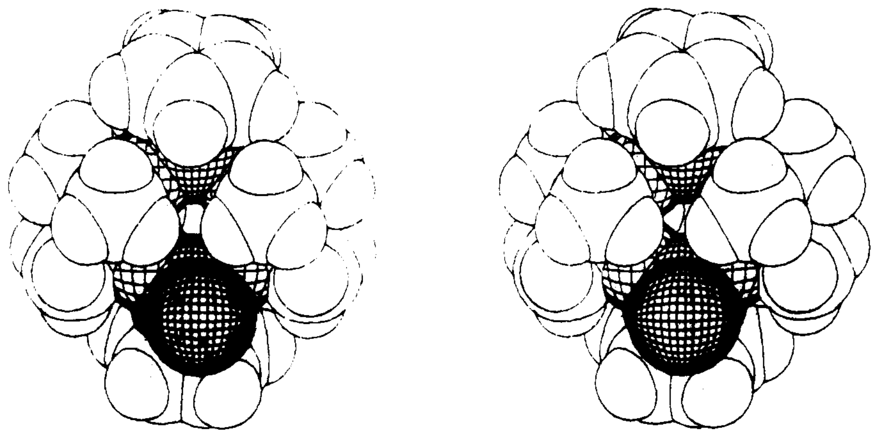


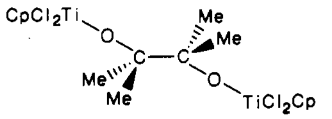
Figure 3. Stereo space-filling model drawings of [$CpTiCl(OCMe_2CMe_2O)]_2$ viewed approximately perpendicular to the ring.

Table II. Fractional Coordinates and Thermal Parameters[a,b] for $[C_5H_5TiCl(O_2C_2Me_4)]_2$

	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Ti	10028.2 (4)[b]	3175.9 (4)	4913.2 (3)	11
Cl	8819.9 (5)	2790.2 (6)	3767.0 (5)	17
O(3)	10762 (1)	4017 (1)	4237 (1)	13
C(4)	11483 (2)	4601 (2)	3738 (2)6	13
C(5)	10921 (2)	5556 (23)	3397 (2)	13
O(6)	10638 (1)	6083 (1)	4249 (1)	15
C(7)	12325 (2)	4824 (2)	4449 (2)	18
C(8)	11877 (3)	4000 (2)	2881 (2)	18
C(9)	9965 (3)	5312 (2)	2844 (2)	15
C(10)	11604 (3)	6223 (3)	2791 (3)	19
C(11)	11309 (3)	2451 (3)	5816 (3)	26
C(12)	11377 (3)	2042 (3)	4885 (3)	27
C(13)	10529 (3)	1488 (2)	4723 (2)	22
C(14)	9926 (3)	1534 (2)	5569 (2)	19
C(15)	10423 (3)	2113 (2)	6247 (2)	19
H(16)	12608 (28)	4218 (26)	4647 (25)	27 (8)
H(17)	12868 (29)	5214 (25)	4173 (26)	30 (8)
H(18)	12117 (23)	5183 (21)	5002 (21)	9 (6)
H(19)	12171 (25)	3411 (27)	3083 (24)	24 (7)
H(20)	11307 (26)	3822 (24)	2430 (23)	21 (7)
H(21)	12378 (24)	4362 (24)	2550 (22)	16 (7)
H(22)	9679 (20)	5881 (22)	2667 (19)	4 (5)
H(23)	10076 (24)	4922 (23)	2301 (26)	17 (7)
H(24)	9539 (29)	4930 (24)	3222 (26)	24 (8)
H(25)	12210 (27)	6332 (25)	3116 (25)	25 (8)
H(26)	11766 (29)	5875 (28)	2215 (29)	33 (9)
H(27)	11291 (24)	6812 (26)	2630 (23)	19 (7)
H(28)	11704 (25)	2810 (24)	6087 (23)	16 (7)
H(29)	11894 (27)	2146 (25)	4413 (25)	28 (8)
H(30)	10335 (27)	1175 (25)	4140 (26)	28 (8)
H(31)	9274 (24)	1263 (23)	5624 (22)	16 (7)
H(32)	10208 (25)	2291 (25)	6837 (24)	22 (7)

[a] The isotropic thermal parameter listed for atoms refined anisotropically is the isotropic equivalent. These appear without an esd. [b] Numbers in parentheses in this and all following tables refer to the error in the least significant digits.

symmetry, which gives it a rigorously staggered conformation about the central C–C bond of the bridging pinacolate unit (II).



II

Although it is not required to be so by the center of symmetry, the torsional angle O(3)–C(4)–C(5)–O(6) (65.5°) in I is very close to that of a staggered conformation.

Compound I shows one ^1H NMR Cp resonance and two methyl resonances. This is consistent with the trans relationship of the Cp rings, which leave the geminal methyl groups inequivalent even if there is rapid torsional motion about C–C and C–O bonds in the 10-membered ring.

Table III. Selected Bond Distances (Å) and Angles (deg) in $[CpTiCl(O_2C_2Me_4)]_2$

Ti–Cl	2.318 (1)	Ti–O(6)	1.768 (2)
Ti–O(3)	1.767 (2)		
Ti–C(11)	2.332 (3)	Ti–C(14)	2.400 (3)
Ti–C(12)	2.366 (3)	Ti–C(15)	2.392 (3)
Ti–C(13)	2.391 (3)		
O(3)–C(4)	1.423 (3)	O(6)–C(5)	1.425 (3)
C(4)–C(5)	1.565 (4)		
C(4)–C(7)	1.522 (4)	C(5)–C(9)	1.523 (4)
C(4)–C(8)	1.526 (4)	C(5)–C(10)	1.530 (4)
C(11)–C(12)	1.400 (5)	C(13)–C(14)	1.419 (5)
C(11)–C(15)	1.401 (5)	C(14)–C(15)	1.388 (5)
C(12)–C(13)	1.375 (5)		
Cl–Ti–O(3)	99.9 (1)	Ti–O(3)–C(4)	170.9 (2)
Cl–Ti–O(6)′	102.8 (1)	Ti–O(6)′–C(5)′	162.7 (2)
O(3)–Ti(1)–O(6)′	105.0 (1)		
O(3)–C(4)–C(5)	106.1 (2)	O(6)–C(5)–C(4)	107.0 (2)
O(3)–C(4)–C(7)	107.4 (2)	O(6)–C(5)–C(9)	107.3 (2)
O(3)–C(4)–C(8)	108.2 (2)	O(6)–C(5)–C(10)	108.2 (2)
C(5)–C(4)–C(7)	112.7 (2)	C(4)–C(5)–C(9)	112.0 (2)
C(5)–C(4)–C(8)	111.9 (2)	C(4)–C(5)–C(10)	111.3 (2)
C(7)–C(4)–C(8)	110.4 (3)	C(9)–C(5)–C(10)	110.8 (2)
C(12)–C(11)–C(15)	108.3 (3)	C(13)–C(14)–C(15)	107.7 (3)
C(11)–C(12)–C(13)	108.0 (3)	C(11)–C(15)–C(14)	107.7 (3)
C(12)–C(13)–C(14)	108.2 (3)		

Table IV. Summary of Corresponding Structural Parameters of Three Titanium(IV) Alkoxides

	$Cp_2Ti(OEt)Cl$	$[CpTiCl_2]_2O_2C_2Me_4$	$[CpTiCl(O_2C_2Me_4)]_2$
Ti–O–C, deg	133.2 (3)	166.2 (2)	170.9 (2) 162.7 (2)
Ti–O, Å	1.855 (2)	1.750 (2)	1.767 (2) 1.768 (2)
Ti–Cl, Å	2.405 (1)	2.276 (1)	2.318 (1)

The C–C and C–O distances in both $[CpTiCl_2]_2O_2C_2Me_4$ and I are respectively within 1σ of each other, indicating good agreement between bonds anticipated to be chemically very similar. This provides increased confidence in the following subtle differences. The Ti–C distances in I vary by 0.068 Å (16σ), a fact also reflected in the 88.3° angle between the five-carbon ring plane and a line from Ti to the ring midpoint. The pattern of bond lengths is correlated such that the longest Ti–C distances flank the shortest C–C distances. These trends, which have the mirror symmetry of the TiO_2Cl unit, correlate with the rotational conformation of the Cp ring: the shortest C–C distances are trans to the alkoxide ligands. Since this effect also appears in the structure of $[CpTiCl_2]_2O_2C_2Me_4$, the idea[1] that strong alkoxide π-donation weakens bonds trans to oxygen gains further weight. It is evident from a space-filling model (Figure 3) that the Cp ring rotational conformation is dictated by interleaving two Cp hydrogens between the geminal methyl groups on one quaternary carbon and a third Cp hydrogen between the two CMe_2 groups on different pinacolate ligands. We find the same to be true of $(CpTiCl_2)_2O_2C_2Me_4$ when space-filling models are examined. This leads to the general conclusion that these molecules, containing both Cp and tertiary alkoxide ligands, are rather crowded.

We commented earlier that the Ti–O–C angle of 166.2° in $[CpTiCl_2]_2O_2C_2Me_4$ (Table IV) was the largest then recorded. Compound I provides two additional values, one a very large 170.9 (2)°, reinforcing the idea of very strong π-donation from oxygen. Additional large angles have been reported recently at the alkoxide oxygen of tartrate attached to Ti(IV).[5] Note that near-linearity at oxygen aggravates nonbonded repulsions between pinacol methyl groups and the Cp rings in I compared to what they might have been had the 10-membered ring in I adopted the conformation of cyclodecane.[4]

Finally, we return to the question of the driving force for the dimerization portrayed in eq 1. Why does the 5-membered ring of the kinetic product, $CpTiCl(\eta^2\text{-}O_2C_2Me_4)$, rearrange spontaneously (albeit not instantaneously) to a 10-membered ring? We suggest that it involves unfavorable nonbonded repulsions between the Cp ring and the two syn methyl groups in the monomer. It is evident from Figure 3 that such interactions are incipient in I. Since the O–Ti–O angle will be quite constrained in $CpTiCl(\eta^2\text{-}O_2C_2Me_4)$, the degrees of freedom in this 5-membered ring will be limited and Cp/methyl interactions will be increased. Constraints within the 5-membered ring will also have the effect of decreasing the Ti–O–C angle;[6] to the extent that π-donation by oxygen contributes thermodynamic stability (a point established by the structure we report here), this represents a second factor that explains the thermodynamics of eq 1.

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Registry No. I, 76971-95-4; CpTiCl($OCMe_2CMe_2O$), 62422-44-0.

Supplementary Material Available: A listing of anisotropic thermal parameters (1 page); a listing of observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

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(6) Reasonable bond lengths and O–C–C angles lead to the prediction of a Ti–O–C angle between 112 and 117° in a five-membered TiOCCO ring.

Contribution from the Department of Chemistry,
University of Modena, Modena, Italy

Crystal Structure and Electronic and EPR Spectra of a Compound Containing a Symmetric Square-Planar $CuCl_4^{2-}$ Ion

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Square-planar $CuCl_4^{2-}$ ions are exceedingly rare, notwithstanding the large number of ions with this stoichiometry that have been reported in the literature.[1,2] In fact most of the $CuCl_4^{2-}$ anions have distorted tetrahedral geometries with trans Cl–Cu–Cl angles close to 130°. The way to obtain isolated square-planar ions is to stabilize them through hydrogen bonds, and indeed, the only nearly idealized square-planar complexes reported so far have been obtained with organic cations that can form stable hydrogen bonds with the $CuCl_4^{2-}$ ions. However, although planar, these compounds have the ions slightly asymmetric, with two different Cu–Cl bond distances. This is an unfortunate circumstance, because the square-planar $CuCl_4^{2-}$ ion is a very interesting reference for the spectral properties of the tetrachlorocuprate complexes, which have been often used as models for copper(II) metalloproteins.

Table I. Crystallographic Data and Summary of Intensity Data Collection

(A) Crystallographic Parameters

cryst syst: monoclinic
space group: $P2_1/c$ (C_{2h}^5, No. 14) uniquely determined on the basis of systematic absences
molecular formula: $C_{14}H_{14}Cl_4CuN_4S_2$
$a = 7.053$ (2) Å
$b = 9.747$ (2) Å
$c = 14.029$ (2) Å
$\beta = 98.48$ (2)°
$V = 953.89$ Å^3
$Z = 2$
$d_{calcd} = 1.77$ g/cm^3
mol wt = 507.78
$F(000) = 510.0$
$d_{obsd} = 1.75$ g/cm^3 (by flotation)

(B) Measurement of Diffraction Data

radiation (λ, Å): graphite-monochromated Mo Kα (0.71069)
reflcns measd: $\pm h,+k,+l$
scan type: ω–2θ
θ range: 2–27°
scan speed range: 2.1–5.5° min^{-1}
scan width: $(1.3 + 0.35 \tan \theta)$°
no. of std reflcns: 3 every 4 h (no significant changes)
no. of collcd reflcns: 2287
no. of obsd. reflcns: 1359 with $I > 3.0\sigma(I)$ (after merge, $R = 0.046$)
cryst size: 0.2 × 0.2 × 0.5 mm
abs coeff: 18.3 (abs cor applied: $0.99 < T_{factor} < 0.80$)

Table II. Final Positional Parameters

atom	*x/a*	*y/b*	*z/c*
Cu	0.0	0.0	0.0
Cl(1)	−0.1257 (3)	0.0429 (2)	0.1369 (1)
Cl(2)	−0.2239 (2)	0.1376 (2)	−0.0850 (1)
S	−0.1938 (3)	0.6256 (2)	0.1381 (1)
N(1)	−0.2154 (7)	0.4158 (5)	0.0271 (3)
N(2)	−0.1115 (8)	0.3620 (6)	0.1879 (4)
C(1)	−0.1694 (8)	0.4517 (6)	0.1198 (4)
C(2)	−0.2789 (8)	0.6497 (6)	0.0148 (4)
C(3)	−0.2768 (7)	0.5258 (6)	−0.0336 (4)
C(4)	−0.3335 (8)	0.5182 (7)	−0.1332 (4)
C(5)	−0.3924 (9)	0.6395 (8)	−0.1796 (5)
C(6)	−0.3981 (9)	0.7610 (8)	−0.1315 (5)
C(7)	−0.3417 (9)	0.7688 (7)	−0.0323 (5)

We have now isolated a nearly idealized square-planar $CuCl_4^{2-}$ complex with the organic cation 2-aminobenzothiazolium, which has four Cu–Cl bonds whose lengths are equal within experimental error, and we wish to report here the crystal structure and the electronic and EPR spectra.

Experimental Section

Complex Preparation. All chemicals were reagent grade and used as received. The complex was prepared by adding diethyl ether to a methanolic solution of 2-aminobenzothiazole (L) (2 mM), $CuCl_2 \cdot 2H_2O$ (1 mM) and HCl 37% (16 mM). After 24 h, single green crystals suitable for X-ray were collected by filtration, washed with methanol/HCl (v/v 90/10) and then diethyl ether, and dried in vacuo over silica gel. Anal. Calcd. for $C_{14}H_{14}CuN_4S_2Cl_4$: C, 33.12; H, 2.78; N, 11.03; S, 12.63. Found: C, 33.29; H, 2.77; N, 11.04; S, 12.58.

Spectral Measurements. The electronic spectrum of the solid compound was recorded as a mull transmission spectrum with a Cary 2300 Varian spectrophotometer. EPR spectra were recorded on a Varian E spectrometer on polycrystalline sample with diphenylpicrylhydrazyl (dpph, $g = 2.0036$) as the calibrating field marker.

X-ray Structure Determination. The intensity data were collected at room temperature on a CAD 4 Enraf-Nonius automatic diffractometer. The crystals were shaped as irregular prisms. Details on crystal data, intensity collection, and refinement are reported in Table I.

The structure was solved by conventional Patterson and Fourier methods and refined through full-matrix least-squares calculations, with $\sum w(|F_o| - |F_c|)^2$ being minimized. After isotropic refinement of nonhydrogen atoms, all the hydrogen atoms were located from difference Fourier maps; they were then treated as fixed contributors with assigned isotropic thermal parameters 1.0 Å^2 higher than those of the bonded

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