Molecular Structure of $(\eta^5\text{-}C_5H_5)_2Ti(OC_2H_5)Cl$ and $[(\eta^5\text{-}C_5H_5)Cl_2Ti]_2O_2C_2(CH_3)_4$. A Structural Basis for Deoxygenation Using Titanium

John C. Huffman, Kenneth G. Moloy, John A. Marsella, and Kenneth G. Caulton*

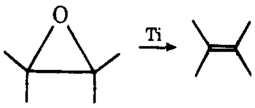
Contribution No. 3380 from the Molecular Structure Center and Department of Chemistry, Indiana University, Bloomington, Indiana 47405. *Received September 4, 1979*

Abstract: The crystal structures of $(\eta^5\text{-}C_5H_5)_2Ti(OC_2H_5)Cl$ (I) and $[(\eta^5\text{-}C_5H_5)Cl_2Ti]_2O_2C_2(CH_3)_4$ (II) have been determined at low temperature. A comparison of the structural parameters of these with each other and with those of Cp_2TiCl_2 provides structural evidence for π donation by both chloride and alkoxide ligands; alkoxide exceeds chloride in π-donor ability, and it is proposed that $Cp_2Ti(OC_2H_5)Cl$ achieves an effective 18 valence electron configuration via three-electron donation by the alkoxy ligand. As a result of the high Lewis acidity (unsaturation) of the $CpTi^{3+}$ fragment, compound II exhibits the shortest Ti-OR bond (1.750 Å) and the most obtuse angle at oxygen (166.2°) yet observed.

Introduction

In our report[1] concerning the hydrogenation (with H_2) of the CO ligand in $Cp_2Ti(CO)_2$, we proposed that intermediates containing titanium-oxygen bonds might be significant in eliciting unusual reactivity from CO. We referred at that time to the hard acid ("oxophilic") character of titanium. It is, of course, this property, in addition to their low oxidation state, which is responsible for the effectiveness of reduced heterogeneous forms of titanium as they are currently applied for deoxygenation in organic synthesis.[2] For example, the transformations represented in eq 1-3 have been effected by various

$$2R_2CO \xrightarrow{Ti} R_2C{=}CR_2 \qquad (1)$$



(2)

$$2ROH \xrightarrow{Ti} R{-}R \qquad (3)$$

low-valent titanium preparations. It is evident from the (unbalanced) equation which summarizes the titanium-based methanation (eq 4) that this reaction shares the "deoxygenation" feature characteristic of eq 1-3.

$$(C_5H_5)_2Ti(CO)_2 + H_2 \longrightarrow (C_5H_5)_6Ti_6(\mu_3\text{-}O)_8 + CH_4 +$$ 

(4)

In 1973, Coutts, Wailes, and Martin[3] reported on the products of reaction of several ketones and aldehydes with the trivalent complex $[CpTiCl_2]_n$. They concluded, on the basis of spectroscopic and molecular-weight measurements, that the single reducing equivalent possessed by Ti(III) led to alkoxide products which were dimeric by virtue of C-C single bond formation (reductive coupling of ketones to vicinal diolates):

$$2/n[CpTiCl_2]_n + 2R_2CO \rightarrow CpCl_2Ti\text{-}OCR_2CR_2O\text{-}TiCl_2Cp \qquad (5)$$

The products of this reaction are of interest for two reasons. First, they may potentially provide quantitative data on the oxophilicity of titanium of relevance to the Fischer-Tropsch activity of this element. In addition, they are potential intermediates in eq 1.

We report here the results of our attempt to provide structural evidence for strong (multiple) bonding between titanium and alkoxide oxygen in well-defined soluble molecular species. Specifically, we report the structure of a product of empirical formula $CpTiCl_2(OCMe_2)$ which may be obtained as described by Coutts, Wailes, and Martin. In addition, in order to provide some calibration of Ti-O bond lengths, we report the results of a structural study of $Cp_2TiCl(OEt)$. Later publications will define the chemical reactivity of these and related species.

Experimental Section

General. These reactions were carried out under an atmosphere of prepurified nitrogen either in glassware that had previously been flamed under vacuum or in a Vacuum Atmospheres glovebox. Ethanol was distilled from magnesium turnings and a small amount of iodine. Triethylamine was dried over Na or BaO and vacuum distilled. Benzene, THF, and Et_2O were vacuum transferred from a solution of sodium benzophenone ketyl; hexane was dried with Na/K alloy. Pinacol was sublimed at 25 °C under vacuum.

Syntheses. 1. $(C_5H_5)_2TiCl(OC_2H_5)$. Bis(cyclopentadienyl)chloroethoxotitanium(IV) was prepared using the method of Nesmeyanov;[4] a solution of 0.50 mL of ethanol (8.6 mmol) and 0.60 mL of triethylamine (4.3 mmol) in 10 mL of benzene was added to a vigorously stirred mixture of 1.0 g of Cp_2TiCl_2 (4.0 mmol) in 90 mL of benzene at 50 °C. The mixture was stirred at 50-60 °C for 2 h, after which time the solution was a light orange-yellow. After cooling to room temperature, triethylammonium chloride was filtered off and solvent was stripped from the filtrate to yield 0.60 g of a golden powder (mp 80-90 °C with some infusible material). A saturated toluene solution of this material was cooled for 24 h to yield bright orange crystals (mp 91-92.5 °C uncorrected) which were used in the crystallographic investigation. NMR ($CDCl_3$): δ 6.24 (s, 10 H), 4.41 (q, 2 H), 1.02 (t, 3 H).

2. $[(C_5H_5)Cl_2Ti]_2O_2C_2(CH_3)_2$. $CpTiCl_3$ (4.0 g, 18 mmol) was dissolved in 100 mL of THF containing 3.2 mL of triethylamine (23 mmol, 20% excess). Solid pinacol (1.12 g, 9.5 mmol, 5% excess) was then added slowly with vigorous stirring, giving immediate precipitation of a colorless solid. Stirring was halted after 2 h and the white triethylamine hydrochloride was filtered away. The solvent was then removed under vacuum until precipitation of a yellow solid began, after which ca. 50 mL of hexane was added dropwise, producing a large quantity of a bright yellow solid. This solid was filtered and dried under vacuum yielding 3.7 g of $[CpCl_2Ti]_2O_2C_2(CH_3)_4$ (85%). ^1H NMR ($CDCl_3$): δ 6.81 (10 H) and 1.60 (12 H). The IR spectrum agreed with that previously reported.[3] Crystals for the structure determination were grown by slow diffusion of diethyl ether into a saturated THF solution of the dimer. The synthesis of this compound from $CpTiCl_2$ and acetone[3] is not as reliable as that reported here.

Crystallographic. 1. $(C_5H_5)_2Ti(OC_2H_5)Cl$. Crystal data and parameters of the data collection (at −125 °C, $4° < 2\theta < 50°$) are shown in Table I. No absorption correction was performed on the data. The structure was solved using LSAM and Fourier techniques. Full-matrix least-squares refinement was carried out for all atoms; hydrogen atoms were refined with isotropic temperature factors. An examination of the observed and calculated structure factors gave no evidence for the effects of extinction. Fractional coordinates and equivalent isotropic

0002-7863/80/1502-3009$01.00/0

Table I. Crystal Data for $(C_5H_5)_2Ti(OC_2H_5)Cl$ and $[(C_5H_5)Cl_2Ti]_2O_2C_2(CH_3)_4$

mol formula	$C_{12}H_{15}ClOTi$	$C_{14}H_{22}Cl_4OTi_2$
color	yellow	yellow
crystal dimensions, mm	0.25 × 0.32 × 0.35	0.164 × 0.051 × 0.078
space group	$P2_1/n$	$P2_1/c$
cell dimensions		
a, Å	8.003(2)[a]	9.066(3)[b]
b, Å	17.708(6)	6.798(2)
c, Å	7.997(2)	16.613(5)
β, deg	90.66(2)	94.60(3)
molecules/cell	4	2
cell vol, $Å^3$	1133.24	1020.57
calcd density, g/cm^3	1.516	1.575
wavelength	0.710 69	0.710 69
mol wt	258.6	483.96
linear absorption coefficient, cm^{-1}	9.538	13.1
no. of unique intensities collected	2012	1806
no. with $F > 0.0$	1937	1769
no. with $F > \sigma(F)$	1926	1745
no. with $F > 2.33\sigma(F)$	1900	1622
final residuals		
$R(F)$	0.0505	0.034
$R_w(F)$	0.0685	0.049
goodness of fit for the last cycle	2.15	1.21
max Δ/σ for last cycle	0.03	0.12

[a] At −125 °C; 26 reflections. [b] At −138 °C; 20 reflections.

thermal parameters are presented in Table II, with bond lengths and angles shown in Tables III and IV. Table V contains least-squares lines, planes, and associated angles. Anisotropic B's and a table of calculated and observed structure factors are available as supplementary material. The structure is shown in Figure 1.

The five cyclopentadienyl carbons in each ring deviate by less than 4σ from their respective least-squares planes. While C-C distances within each ring vary by 6σ, such variations do not correlate with inequalities in Ti-C distances. The average C-C distances in each of the two rings are identical within experimental error. Hydrogen atoms deviate by less than 1σ from the associated five-carbon plane. Within the rings, the C-H separations[5] average 0.92 Å, varying from 0.82 to 1.05 Å. Within the ethyl group, the average C-H distance is 0.93 Å, ranging from 0.89 to 0.99 Å; the HCH angles average 112.8°, while the angles OCH and CCH average 107.4°. The refined hydrogen positions establish a staggered rotational conformation about the C-O and C-C bonds of the ethoxy group (Figure 1).

Intermolecular contacts are mainly between hydrogens; the shortest is 2.47 Å. Below 3 Å, there are only a few hydrogen contacts to heavier atoms, the shortest being 2.61 Å from H(3) to O(1) related by $1 - x$, $1 - y$, $1 - z$. Intramolecular contacts between rings exceed 2.36 (H···H), 2.69 (C···H), and 2.93 Å (C···C).

2. $[CpTiCl_2]_2O_2C_2(CH_3)_4$. Crystal data and characteristics of the data collection are summarized in Table I. Intensities ($4° \leq 2\theta \leq 50°$ at −138 °C) were processed as usual (including correction for absorption) and the structure was solved by direct methods and confirmed by Patterson techniques. All atoms, including hydrogens, were located and refined.

Fractional coordinates, bond lengths, and angles are given in Tables VI-VIII. The molecular structure is shown in Figures 2 and 3. Additional data are available as supplementary material. Ring C-H distances[5] average 0.88 Å, and range from 0.78 (4) to 0.95 (3) Å. Methyl group C-H distances are systematically longer (the average value is 0.98 Å), ranging from 0.93 (3) to 1.02 (4) Å. The average HCH angle within methyl groups is 108° with individual values ranging from 104 (3) to 114 (3)°. The methyl group CCH angles average 111°, and range from 106 (2) to 116 (3)°. Within the ring, C-C distances span a range of 6σ and average 1.403 Å. Titanium lies 2.018 Å from the least-squares plane of the five ring carbons, while Cl(1), Cl(2), and O(1) lie 2.999, 2.988, and 2.816 Å, respectively, from this same plane. The two Ti-Cl distances differ by 9σ, possibly as a result of the asymmetric rotational conformation of the Cp ring (i.e., no mirror plane relates Cl(1) and Cl(2), Figure 3).

Table II. Fractional Coordinates and Thermal Parameters for $Cp_2Ti(OC_2H_5)Cl$

atom	10^4x	10^4y	10^4z	$10B_{iso}$[a]
Ti(1)	7536.8(6)	3733.2(3)	4262.2(6)	9
Cl(1)	4677.4(8)	3417.6(4)	3625.3(9)	17
O(1)	7517(2)	4566(1)	2854(2)	13
C(1)	8296(4)	3628(2)	7160(4)	17
C(2)	6569(4)	3683(2)	7081(4)	15
C(3)	6158(4)	4415(2)	6484(3)	16
C(4)	7647(4)	4796(2)	6200(4)	19
C(5)	8973(4)	4306(2)	6557(4)	19
C(6)	9739(4)	3329(2)	2442(4)	19
C(7)	8281(4)	2967(2)	1904(4)	18
C(8)	7764(4)	2469(2)	3167(4)	17
C(9)	8887(4)	2527(2)	4505(4)	18
C(10	10114(4)	3070(2)	4068(4)	18
C(11)	7292(5)	4652(2)	1108(4)	19
C(12)	7429(4)	5469(2)	604(4)	21
H(1)	8870(57)	3262(27)	7448(58)	34(10)
H(2)	5915(39)	3287(19)	7452(38)	8(6)
H(3)	5068(46)	4616(21)	6329(46)	20(7)
H(4)	7802(46)	5294(27)	5762(48)	28(9)
H(5)	9924(46)	4458(19)	6372(43)	13(6)
H(6)	10375(41)	3734(19)	1726(43)	12(7)
H(7)	7758(40)	3067(20)	998(45)	12(6)
H(8)	6778(48)	2173(22)	3135(49)	24(8)
H(9)	8878(40)	2255(19)	5514(45)	13(6)
H(10)	10980(49)	3210(22)	4746(50)	22(7)
H(11)	8080(48)	4386(23)	609(47)	18(7)
H(12)	6175(62)	4525(30)	861(65)	45(11)
H(13)	6669(52)	5743(23)	1138(53)	24(8)
H(14)	8630(61)	5552(27)	846(63)	44(11)
H(15)	7244(45)	5556(25)	−572(52)	24(8)

[a] The isotropic thermal parameter listed for those atoms refined anisotropically is the isotropic equivalent. These appear without an esd.

Table III. Bond Distances in $Cp_2Ti(OC_2H_5)Cl$

		distance, Å				distance, Å
Ti(1)	Cl(1)	2.405(1)				
Ti(1)	O(1)	1.855(2)				
O(1)	C(11)	1.415(4)				
Ti(1)	M(1)[a]	2.092				
Ti(1)	M(2)[a]	2.082				
Ti(1)	C(1)	2.396(3)		Ti(1)	C(6)	2.407(3)
Ti(1)	C(2)	2.393(3)		Ti(1)	C(7)	2.404(3)
Ti(1)	C(3)	2.424(3)		Ti(1)	C(8)	2.411(3)
Ti(1)	C(4)	2.439(3)		Ti(1)	C(9)	2.401(3)
Ti(1)	C(5)	2.381(3)		Ti(1)	C(10)	2.380(3)
		2.407	av			2.401
C(1)	C(2)	1.387(5)		C(6)	C(7)	1.395(5)
C(1)	C(5)	1.405(5)		C(6)	C(10)	1.408(5)
C(2)	C(3)	1.419(5)		C(7)	C(8)	1.406(5)
C(3)	C(4)	1.390(5)		C(8)	C(9)	1.393(4)
C(4)	C(5)	1.397(5)		C(9)	C(10)	1.421(5)
		1.400	av			1.405

[a] M(1) denotes the midpoint of the plane containing C(1) through C(5). M(2) is midpoint of atoms C(6) to C(10).

Results

Description of the Structure of $Cp_2Ti(OC_2H_5)Cl$. The molecular structure is the "open clamshell" typically found for Cp_2MXY species (Figure 1). The rotational relationship between the Cp rings lies between staggered and eclipsed, being significantly closer to the latter. The ethyl portion of the ethoxide group lies completely out of the TiOCl plane, being directed toward one Cp ring; this causes no significant lengthening of the average Ti-C or C-C distances of that ring, however. A predictable consequence of the clamshell config-

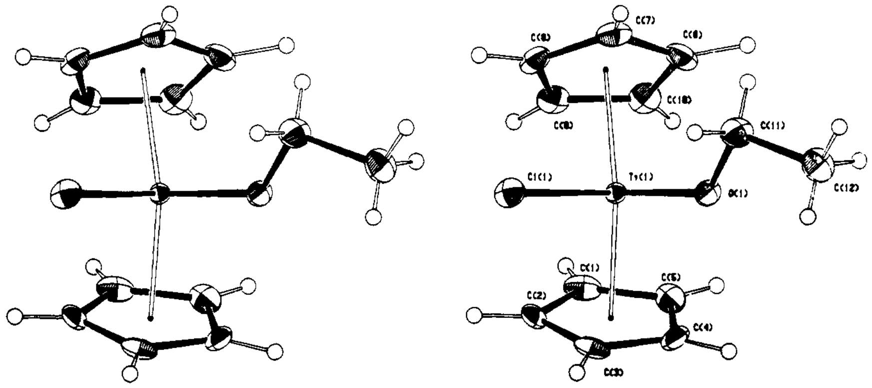


Figure 1. Stereoscopic view of the molecular structure of $(C_5H_5)_2Ti(OC_2H_5)Cl$. Hydrogen atom thermal parameters have been arbitrarily reduced for clarity.

Table IV. Bond Angles in $Cp_2Ti(OC_2H_5)Cl$

			angle, deg
Cl(1)	Ti(1)	O(1)	93.1(1)
O(1)	Ti(1)	M(1)	105.9
O(1)	Ti(1)	M(2)	109.8
Cl	Ti(1)	M(1)	105.6
Cl	Ti(1)	M(2)	105.5
M(1)	Ti(1)	M(2)	130.5
Ti(1)	O(1)	C(11)	133.2(2)
O(1)	C(11)	C(12)	111.0(3)
C(2)	C(1)	C(5)	108.2(3)
C(1)	C(2)	C(3)	107.9(3)
C(2)	C(3)	C(4)	107.6(3)
C(3)	C(4)	C(5)	108.4(3)
C(1)	C(5)	C(4)	107.8(3)
C(7)	C(6)	C(10)	107.7(3)
C(6)	C(7)	C(8)	108.6(3)
C(7)	C(8)	C(9)	108.3(3)
C(8)	C(9)	C(10)	107.6(3)
C(6)	C(10)	C(9)	107.9(3)

Table V. Distances from Least-Squares Planes and Dihedral Angles in $(C_5H_5)_2Ti(OC_2H_5)Cl$

element no.	atoms defining element	atom	distance of atom from plane, Å
1	C(1) C(2) C(3) C(4) C(5)	Ti	2.09
2	C(6) C(7) C(8) C(9) C(10)	Ti	2.08
3	TiClO		
4	line Ti-M(1)		
5	line Ti-M(2)		

elements	dihedral angle, deg
1,2	128.5
4,5	130.5
1,4	88.6
2,5	89.2
1,3	24.6
2,3	27.0
3,4	66.8
3,5	63.6

uration is an inequality in Ti-C distances within a given ring. These distances vary by 19σ to the C(1)-C(5) ring and 10σ to the C(6)-C(10) ring. The minor canting of the rings is also evident in the angles between the ring planes and the line from the ring midpoint (Table V). The inequalities follow no pattern traceable to intramolecular effects. However, atom C(4), which shows the longest Ti-C distance, shows the shortest intramolecular contact (2.71 Å to O(1)).

Comparison of this structure to that of Cp_2TiCl_2[6] shows equivalence in C-C and Ti-C distances to within 2σ. The Ti-Cl distance, however, is 0.041 Å (13σ) longer in the chloroethoxide complex. This result permits two conclusions. First, since $Cp_2TiCl(OEt)$ is a complex in which Cl and OEt compete for bonding to an *apparently* unsaturated metal center, the observed Ti-Cl lengthening is a structural verification of π donation by ethoxide; indeed, we conclude that OEt is a more effective π donor than Cl. Note that there is no evidence for any steric contribution to this lengthening. By implication, we may also conclude that π donation by chloride indeed exists in Cp_2TiCl_2. Consequently, chlorine is not simply a one-electron donor ligand in Cp_2TiCl_2, and so it is not appropriate to think of Cp_2TiCl_2 as an unsaturated (16-electron) complex. This provides an explanation for the observation that Cp_2TiCl_2 does not add Lewis bases.

There exists a series of structural studies on CpCp′Ti-Cl(OAr) complexes in which Cp′ represents a ring-substituted cyclopentadienyl unit.[7] In all cases, the phenoxy rings carry ortho substituents. Consequently, the TiOC angles range from 140 to 151°, compared to the 133° observed for $Cp_2Ti(OEt)Cl$. This steric inhibition of alkoxide π donation[8] uniformly produces a Ti-Cl bond length (2.374 (2) Å) shorter than that in $Cp_2Ti(OEt)Cl$ but longer than in Cp_2TiCl_2 (2.364 (2) Å); in addition, this steric inhibition causes the Ti-OAr bond to be longer (1.87-1.88 Å) than the Ti-O bond in the ethoxide (1.855 Å).

In summary, then, comparison of the structural parameters of the above Cp_2TiXY complexes strongly supports the concept of π donation and multielectron donation by alkoxide ligands and, to a lesser extent, by chloride. To complete the argument, it is only necessary to show that bond shortening disappears when Cl or OR becomes bound to a 17-electron fragment. Consider $Cp_2MoCl(C_2H_5)$.[9] Here, d(Mo-Cl) − d(Mo-CH_2CH_3) is equal to 0.22 Å, which is precisely the difference between the covalent radii of Cl and C(sp^3). π donation is confirmed to be nonexistent in this complex.

Description of the Structure of $[CpTiCl_2]_2O_2C_2Me_4$. In the solid state $[CpCl_2Ti]_2O_2C_2Me_4$ has a centrosymmetric structure in which two $CpTi^{IV}Cl_2{}^+$ units are bridged by a pinacolate dianion. This confirms the conclusion of Coutts, Wailes, and Martin.[3] The crystallographic center of symmetry displayed by the dimer imposes a trans (staggered) conformation about the central C-C bond of the pinacolate ligand (Figure 3). The disparate steric requirements of the $CpCl_2TiO$ and methyl substituents result in some distortion of torsional angles about the C(6)-C(6′) bond, as shown in Figure 3. All methyl groups adopt a staggered conformation.

The cyclopentadienyl ring is planar (deviations ≤ 2.5σ); the ring hydrogens are systematically displaced toward the metal, but such displacements are only 1σ-3σ. A line from the metal

Table VI. Fractional Coordinates and Thermal Parameters for $[(C_5H_5)TiCl_2]_2O_2C_2(CH_3)_4$

	10^4x	10^4y	10^4z	$10B_{iso}$[a]
Ti(1)	2763(0)	921(1)	3670(0)	12
Cl(1)	1448(1)	3192(1)	2904(0)	19
Cl(2)	4383(1)	2868(1)	4411(0)	21
O(1)	1501(2)	227(3)	4361(1)	18
C(1)	3374(3)	−2375(4)	3519(2)	18
C(2)	4704(3)	−1316(4)	3560(2)	19
C(3)	4691(3)	−104(4)	2879(2)	20
C(4)	3348(3)	−388(4)	2415(2)	21.
C(5)	2519(3)	−1785(4)	2825(2)	21
C(6)	539(3)	−802(4)	4856(2)	18
C(7)	−280(3)	−2388(5)	4354(2)	27
C(8)	1476(3)	−1709(5)	5564(2)	28
H(1)	3180(39)	−3133(60)	3890(22)	33(8)
H(2)	5474(41)	−1329(62)	3970(20)	33(8)
H(3)	5403(35)	864(51)	2760(18)	27(7)
H(4)	3020(36)	235(55)	1963(21)	28(7)
H(5)	1721(39)	−2186(52)	2722(19)	24(7)
H(6)	9025(35)	6966(49)	4654(17)	22(6)
H(7)	−642(46)	−2013(62)	3839(24)	42(9)
H(8)	452(48)	−3422(71)	4266(24)	51(10)
H(9)	2227(46)	−2676(62)	5362(23)	47(9)
H(10)	2054(49)	−672(73)	5880(24)	60(12)
H(11)	838(38)	−2396(52)	5918(19)	23(7)

[a] The isotropic thermal parameter listed for those atoms refined anisotropically is the isotropic equivalent. These appear without an esd.

Table VII. Bond Distances (Å) in $[CpCl_2Ti]_2O_2C_2Me_4$

Ti(1)	Cl(1)	
Ti(1)	Cl(2)	2.276(1)
Ti(1)	O(1)	1.750(2)
Ti(1)	M(1)	2.019
Ti(1)	C(1)	2.328(3)
Ti(1)	C(2)	2.344(3)
Ti(1)	C(3)	2.374(3)
Ti(1)	C(4)	2.366(3)
Ti(1)	C(5)	2.315(3)
O(1)	C(6)	1.430(3)
C(1)	C(2)	1.401(4)
C(1)	C(5)	1.395(4)
C(2)	C(3)	1.398(4)
C(3)	C(4)	1.401(4)
C(4)	C(5)	1.418(4)
C(6)	C(6′)	1.565(5)
C(6)	C(7)	1.520(4)
C(6)	C(8)	1.524(4)

atom to the ring midpoint makes an angle of 88.3° with the plane C(1)–C(5). This deviation from orthogonality is real and is caused by the inequivalent Ti–C distances (Δ/σ as large as 20). This ring tilt may be a consequence of an alkoxide trans effect (C(3) and C(4) are trans to O(1) and most distant from Ti) or a packing effect. Regarding the latter, the molecules pack so that H(3) of a symmetry-related molecule ($1 - x$, $-y$, $1 - z$) contacts every ring carbon at less than 2.94 Å. Atoms C(5) and C(1), which are closest to the metal, experience the shortest intermolecular contacts with H(3) (2.71 and 2.75 Å, respectively).

Distances (C–O and $C-CH_3$) within the pinacolate ligand duplicate those in the free diol[10] to within 1σ. There is thus no evidence for the curious shortening of metal alkoxide O–R bonds observed in an earlier X-ray study.[11] A lengthening of the bond between the tertiary carbons (e.g., C(6) and C(6′)) is found in both the free pinacol and $[CpTiCl_2]_2O_2C_2Me_4$; in the titanium complex, however, this bond is 0.021 Å (4σ) longer than in free pinacol.

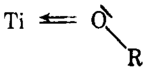
Table VIII. Bond Angles (deg) in $[CpCl_2Ti]_2O_2C_2Me_4$

Cl(1)	Ti(1)	Cl(2)	101.3(0)
Cl(1)	Ti(1)	O(1)	102.1(1)
Cl(2)	Ti(1)	O(1)	103.3(1)
M(1)	Ti(1)	O(1)	118.8
M(1)	Ti(1)	Cl(1)	115.0
M(1)	Ti(1)	Cl(2)	114.2
Ti(1)	O(1)	C(6)	166.2(2)
C(6′)	C(6)	C(7)	111.9(3)
C(6′)	C(6)	C(8)	111.7(3)
C(7)	C(6)	C(8)	110.7(3)
O(1)	C(6)	C(7)	109.0(2)
O(1)	C(6)	C(8)	108.3(2)
C(2)	C(1)	C(5)	108.1(3)
C(1)	C(2)	C(3)	108.2(2)
C(2)	C(3)	C(4)	108.3(2)
C(3)	C(4)	C(5)	107.4(2)
C(1)	C(5)	C(4)	107.9(2)

The Ti–O interaction constitutes the most remarkable portion of the structure. The Ti–O bond length is 0.105 Å (35σ) shorter than in $Cp_2Ti(OEt)Cl$. It is also 0.022 Å (11σ) shorter than in $[CpTiCl_2]_2O$,[12] a compound with a linear oxo bridge which is typically cited as having a double bond to each metal atom. It is evident from the comparison in Table IX that the formal replacement of C_5H_5 by Cl ($Cp_2Ti(OEt)Cl \rightarrow [CpTiCl_2]_2O_2C_2Me_4$) affects more than simply the Ti–O bond.[13] Although the Ti–O distance is notable because of the low absolute value achieved in $[CpTiCl_2]_2O_2C_2Me_4$, the magnitude of the Ti–Cl contraction is actually larger. With the structural verification of the π-donor potential of Cl and OR (see above), the contraction of the bonds to these ligands becomes predictable: in $Cp_2Ti(OEt)Cl$, the ligands OEt and Cl bond to the 14-electron fragment Cp_2Ti; in $[CpTiCl_2]_2O_2C_2Me_4$, the ligands OR and 2Cl bond to the 9-electron fragment CpTi. The degree of coordinative unsaturation, hence the Lewis acidity, of the metal is higher in the dimeric compound.

The question remains, however, as to why the Ti–Cl bond undergoes a larger contraction than the Ti–O bond if, as claimed above, alkoxide is truly the better π donor. This becomes comprehensible if we note that, in $Cp_2Ti(OEt)Cl$, the Ti–Cl bond is almost purely σ in character while the Ti–O bond has substantial π character already. The transformation from $Cp_2Ti(OEt)Cl$ to $[CpCl_2Ti]_2O_2C_2Me_4$ thus demands π donation from either a σ-bonded chlorine or an already multiply bonded alkoxide. Since compression of a titanium–oxygen multiple bond is more energetically costly than that of a Ti–Cl single bond (alternatively, the alkoxide oxygen in $Cp_2Ti(OEt)Cl$ is formally $\delta+$), it is the chlorine which responds most. The additional π donation by oxygen is substantial, however; the result is the shortest Ti–OR bond observed to date. The shortest Ti–O bond of any type yet recorded is that in the TiO^{2+} unit bound to a porphyrin:[14] 1.619 Å.

A corollary consequence of the strong multiple Ti–O bonding in $[CpTiCl_2]_2O_2C_2Me_4$ is the 166.2° Ti–O–C angle, the most obtuse yet observed to a hydrocarbon-substituted alkoxide ligand.[15] We suggest, on the basis of this evidence, that the pinacolate ligand in $[CpTiCl_2]_2O_2C_2Me_4$ donates at least three electrons to the metal (I).



I

There is also a shrinkage of metal–ring bonds in replacing one Cp ligand by one Cl; each of the five bonds contracts by an average of 0.059 Å (15σ). Since a C_5H_5 ligand has ex-

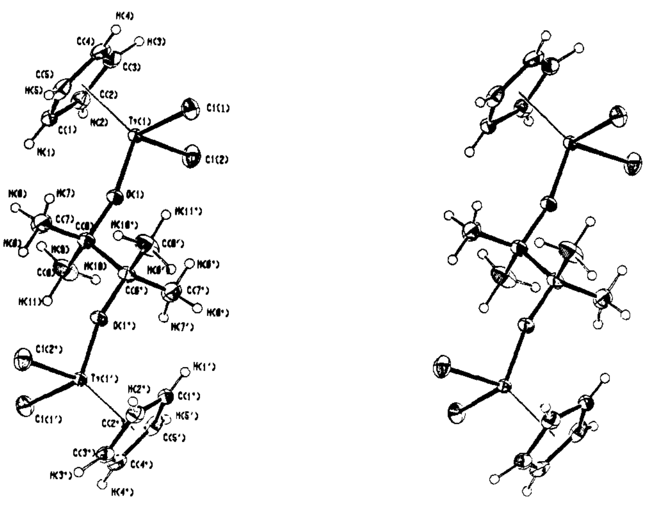


Figure 2. Stereoscopic view of the molecular structure of $[(C_5H_5)TiCl_2]_2O_2C_2(CH_3)_4$. Hydrogen atom thermal parameters have been arbitrarily reduced.

hausted its donor capacity when it bonds in a pentahapto mode, this shrinkage cannot be attributed to a bonding effect. We therefore suggest that the "shortening" is only apparent, being due in fact to a sterically imposed lengthening of Ti-C bonds in the biscyclopentadienyl compouund (i.e., ring-ring repulsions). Crowding within the coordination sphere in $Cp_2Ti(OEt)Cl$ is evident by the reduced Cl-Ti-O angle in that compound relative to the pinacolate dimer.

Discussion

The oxophilic nature of the early transition elements is well supported by observations of chemical reactivity. Reports of structural manifestations are less common; although early X-ray work recorded short Ti-OR distances (with large associated angles), these were flawed by problems with disorder, hydrolysis and the generally lower quality of data collection and refinement procedures employed.[11,16]

We feel that there is substantial utility in trying to extend the 18-electron rule to ligands (e.g., alkoxide) which are not commonly found in organometallic compounds, as well as to higher metal oxidation states. This may be done by recognizing the possibility that terminal chlorine (considered formally as uncharged) and especially alkoxy groups may formally donate three (or more) electrons to the pool of valence electrons; for each ligand this becomes an alternative to dimerization (by ligand bridging) as a route to coordinative saturation.[17] Alkoxide thus joins NO, allyl, and N_2R as ligands which have variable donor numbers; catalytic activity may be associated with such compounds. Another obvious application of this concept is to $TiCl_4$[18] (Ti-Cl = 2.170 Å, a shortening whose magnitude is clearly too large to attribute solely to steric effects[19]). The high Lewis acidity of tetravalent titanium makes this an ideal metal ion on which to observe ligand π donation.

The bond-length contraction resulting from multiple bonding may be assessed more quantitatively. Comparing the Ti-CH_3 distance in $(indenyl)_2TiMe_2$[20] (2.21 Å) with that in $Cp_2Mo(C_2H_5)Cl$ (2.28 Å), we deduce that Ti is 0.07 Å smaller than molybdenum, each in the Cp_2MXY environment. This allows a prediction of a Ti-Cl single bond length in $Cp_2Ti(Cl)Y$ of 2.50 − 0.07 = 2.43 Å, which is 0.07 and 0.02 Å longer than in Cp_2TiCl_2 and $Cp_2Ti(OEt)Cl$, respectively. Employing a correction (0.77 − 0.66 = 0.11 Å) for the different sp^3 radii of carbon and oxygen, we predict a Ti-O single bond length of 2.21 − 0.11 = 2.10 Å; we report here Ti-O distances which are shorter than this by 0.25–0.35 Å.

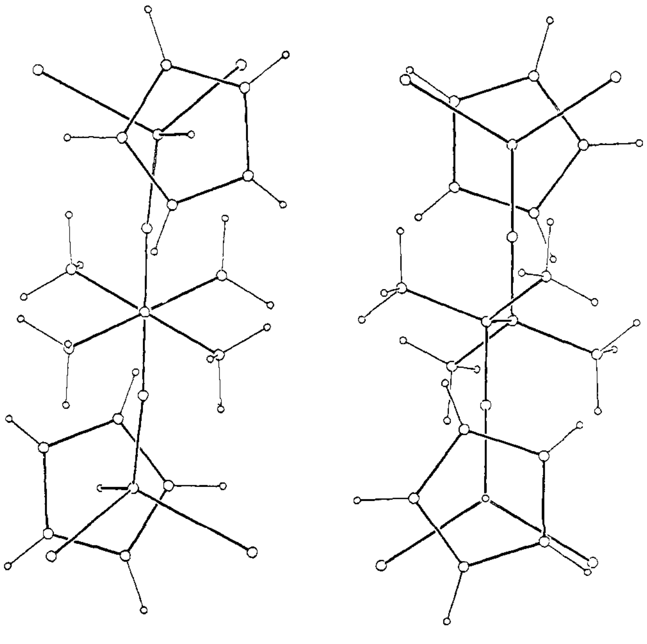


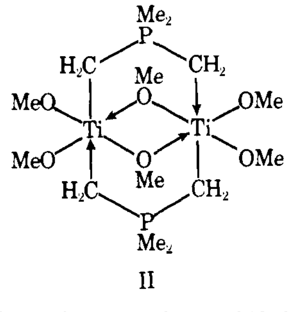
Figure 3. $[(C_5H_5)TiCl_2]_2O_2C_2(CH_3)_4$ viewed down the central C-C bond (left) and viewed perpendicular to the C_5H_5 plane (right).

Table IX. Comparison of Selected Structural Parameters

	Cp_2Ti-(OEt)Cl	$[CpTiCl_2]_2O_2C_2Me_4$	Δ[a]	Δ/σ
$\overline{\text{Ti-C}}$	2.404(3)	2.345(3)	0.059(4)	15
Ti-Cl	2.405(1)	2.271(1)	0.134(1)	100
Ti-O	1.855(2)	1.750(2)	0.105(3)	35
$\overline{\text{O-C}}$	1.415(4)	1.430(3)	−0.015(3)	3
$\overline{\text{C-C}}$ (Cp ring)	1.404(5)	1.403(4)	−0.001(6)	0
∠Cl-Ti-O	93.1(1)	102.7(1)		
∠Ti-O-C	133.2(3)	166.2(2)		

[a] Δ = distance in monomer minus distance in dimer.

Other recent structural data may be interpreted with the proposed electron counting rules. The complex $[Ti(OCH_3)_3]_2[\mu_2\text{-}(CH_2)_2P(CH_3)_2]_2$[21] (II) will achieve a



II

16-electron configuration at each metal if all terminal methoxides π bond (donate three electrons); these Ti-O bond lengths are 1.78 Å, with Ti-O-C angles of 143 and 157°. The chelated diolato ligand in the highly unsaturated complex $[Me_2TiO_2C_6H_{12}]_2$[22] forms short (1.78 Å) Ti-O bonds; even with the constraint of a chelate ring, the angle at oxygen averages 145.3°. Predictably, the carboxylate ligand is an inferior π donor compared to alkoxide. The somewhat curious structure[23] of Cp_2Ti(*p*-nitrobenzoate$)_2$ contains two monodentate benzoate ligands; one ligand has a Ti-O distance of 2.04 Å and an angle at oxygen of 136°; the other ligand has parameters 1.94 Å and 157°. The formal positive charge on oxygen makes coordinated ether ligands "non π donors"; in $Cp_2Ti(THF)(acetone)^+$ the distances[24] are 2.21 and 2.13 Å, respectively.

The Chisholm–Cotton collaboration has provided a massive amount of data on molybdenum alkoxide structures,[25] mainly with bulky isopropoxy and *tert*-butoxy ligands. All would have electron counts grossly deficient from 18 if each alkoxide donated one electron. These compounds generally exhibit Mo–O bond lengths in the range 1.85–1.89 Å and Mo–O–C angles in the range 130–140°. As has been recognized by those authors,[26] Mo–O multiple bonding is indicated. Based on the ideas proposed here, the high reactivity of these dimers toward donor reagents may be as much related to alkoxide bending (creating an unsaturated metal center) as it is with the multiple metal–metal bond. Similarly, the isopropoxide ligand in $Mo(HBpz_3)(NO)Cl(O\text{-}i\text{-}Pr)$, where three-electron donation by alkoxide is required for an 18-electron configuration, forms a short Mo–O bond (1.863 Å) with a 132.4° angle at oxygen.[17]

In searching for soluble reagents which might effect some of the transformations shown by heterogeneous recipes,[2] the structural data reported here clearly indicates stronger Ti–O bonding, and therefore greater potential synthetic utility, in the monocyclopentadienyl species. As indicated above (eq 5), such compounds may be prepared by coupling (via carbon–carbon bond formation) of ketones using $[CpTiCl_2]_n$.[3] We will report subsequently on the transformation of these diolato dimers to deoxygenated organic products.

Acknowledgment. This work was supported by the M. H. Wrubel Computing Center, National Science Foundation (CHE 77-10059), and by a Grant-in-Aid-for-Research by Indiana University.

Supplementary Material Available: A listing of anisotropic thermal parameters and observed and calculated structure factors for $Cp_2Ti(OC_2H_5)Cl$ and $[CpCl_2Ti]_2O_2C_2(CH_3)_4$ (38 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Huffman, J. C.; Stone, J. G.; Krusell, W. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1977**, *99*, 5829.

(2) Tyrlik, S.; Wołochowicz, I.; Stepowska, H. *J. Organomet. Chem.* **1975**, *93*, 353. Tyrlik, S. *J. Chem. Soc., Chem. Commun.* **1975**, 781, and references cited therein. Sobota, P.; Jezowska-Trzebiatowska, B. *Coord. Chem. Rev.* **1978**, *26*, 71. McMurry, J.; Silvestri, M.; Fleming, M.; Hoz, T.; Grayston, M. *J. Org. Chem.* **1978**, *43*, 3249. McMurry, J.; Fleming, M.; Kees, K.; Krepski, L. *Ibid.* **1978**, *43*, 3255, and references cited therein.

(3) Coutts, R. S. P.; Wailes, P. C.; Martin, R. L. *J. Organomet. Chem.* **1973**, *50*, 145.

(4) Nesmeyanov, A. N.; Nogina, O.; Berlin, A.; Girshovich, A.; Shatalov, G. V. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1961**, 2008.

(5) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

(6) Clearfield, A.; Warner, D.; Saldarriaga-Molena, C.; Ropal, R.; Bernal, I. *Can. J. Chem.* **1975**, *53*, 1622.

(7) Besancon, J.; Top, S.; Tirouflet, J.; Dusausoy, Y.; Lecomte, C.; Protas, J. *J. Organomet. Chem.* **1977**, *127*, 153.

(8) The 133° Ti–O–C angle in $Cp_2Ti(OEt)Cl$ represents an energy minimum for a sterically unencumbered $Cp_2Ti(OR)Cl$ unit. It follows that a forced opening of this angle gives a less stable geometry, and that the Ti–O bonding is, therefore, *weaker* in such a complex.

(9) Prout, K.; Cameron, T. S.; Forder, R.; Critchley, S.; Denton, B.; Rees, G. V. *Acta Crystallogr., Sect. B* **1974**, *30*, 2290.

(10) Jeffrey, G. A.; Robbins, A. *Acta Crystallogr., Sect. B* **1978**, *34*, 3817.

(11) Wright, D. A.; Williams, D. A. *Acta Crystallogr., Sect. B* **1968**, *24*, 1107.

(12) Thewalt, V.; Schomburg, D. *J. Organomet. Chem.* **1977**, *127*, 169.

(13) The $C\text{–}CH_3$ bond lengths in the two compounds agree to within 3σ.

(14) Dwyer, P. N.; Puppe, L.; Buchler, J. W.; Scheidt, W. R. *Inorg. Chem.* **1975**, *14*, 1782.

(15) Trialkylsiloxy ligands commonly approach linearity at oxygen, due to multiple bonding to silicon; this cannot be a steric effect (compared to O-*t*-Bu), since the trimethylsilyl group is actually smaller (smaller cone angle measured from oxygen). See: Chisholm, M. H.; Reichert, W.; Thornton, P. *J. Am. Chem. Soc.* **1978**, *100*, 2744, and references cited therein.

(16) Ibers, J. A. *Nature (London)* **1963**, *197*, 686. Witters, R. D.; Caughlan, C. N. *Ibid.* **1965**, *205*, 1312.

(17) The π-donor capacity of alkoxide has certainly been recognized: Bradley, D. C. *Adv. Inorg. Radiochem.* **1972**, *15*, 259. Adaptation of this idea to the 18-electron formalism is less widely recognized. See, however, McCleverty, J. A.; Seddon, D.; Bailey, N. A.; Walker, N. W. *J. Chem. Soc., Dalton Trans.* **1976**, 898.

(18) Morino, Y.; Uehara, H. *J. Chem. Phys.* **1966**, *45*, 4543.

(19) Compare the 2.50-Å Mo–Cl distance in $Cp_2Mo(Et)Cl$ to the Mo–Cl distances (2.45–2.50 Å) in a variety of Mo(IV) compounds: Lam, C. T.; Lewis, D. L.; Lippard, S. J. *Inorg. Chem.* **1976**, *15*, 989.

(20) Atwood, J.; Hunter, W.; Hrncir, D.; Samuel, E.; Alt, H.; Rausch, M. D. *Inorg. Chem.* **1975**, *14*, 1757.

(21) Scharf, W.; Neugebauer, D.; Schubert, U.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 601. This compound has no direct metal–metal bond.

(22) Yoshino, A.; Shuto, Y.; Iitaka, Y. *Acta Crystallogr., Sect. B* **1970**, *26*, 744.

(23) Kuntsevich, T. S.; Gladkikh, E.; Lebedev, V. A.; Lineva, A.; Belov, N. V. *Sov. Phys.: Crystallogr.* **1976**, *21*, 40.

(24) Allmann, R.; Batzel, V.; Pfeil, R.; Schmid, G. *Z. Naturforsch. B* **1976**, *31*, 1329.

(25) Chisholm, M. H., *Transition Met. Chem.* **1978**, *3*, 321. Chisholm, M. H.; Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 356, and references cited therein.

(26) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *Inorg. Chem.* **1979**, *18*, 116.

Preparation and Structural Characterization of Polypeptide Complexes of Dimolybdenum(II). 1. A Tetrakis(glycylglycine) Complex

Avi Bino and F. Albert Cotton*

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. *Received September 17, 1979*

Abstract: The unique capacity of the Mo_2^{4+} cation to form complexes with polypeptide ligands in which only the carboxyl terminus is coordinated and the rest of the zwitterionic molecule is left conformationally free is described. This principle is then illustrated by the isolation and structural characterization of the $[Mo_2(\text{glycylglycine})_4]^{4+}$ ion in the form of the compound $[Mo_2(GG)_4]Cl_4\cdot 6H_2O$. The structure has been solved and refined in space group $P\bar{1}$ with $Z = 1$ by conventional methods using diffractometer data. The unit cell dimensions are $a = 9.775$ (2) Å, $b = 10.886$ (2) Å, $c = 9.495$ (2) Å, $\alpha = 107.06$ (2)°, $\beta = 113.15$ (2)°, $\gamma = 91.07$ (2)°, $V = 877.8$ (1) Å^3. Each of the two crystallographically independent glycylglycine ligands contains a central peptide linkage that conforms very closely to the generally accepted standard dimensions and planar trans conformation for peptide links.

Introduction

Several years ago it was reported[1] that in aqueous solution the affinity of the carboxyl groups of amino acids for the Mo_2^{4+} ion, introduced conveniently as the chloro complex $[Mo_2Cl_8]^{4-}$, is very high, and one such compound, $Mo_2(O_2CCH_2NH_3)_4(SO_4)_2\cdot 3.5H_2O$, was isolated and structurally characterized. Recently the present authors have

0002-7863/80/1502-3014$01.00/0