Preparation, Structure, and Reactivity of a (Pentamethylcyclopentadienyl)titanium Dimer Bridged by Oxygen and Tetramethylmethylenecyclopentadienyl

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The reaction between "Cp^*_2Ti" ($Cp^* = \eta^5\text{-}C_5(CH_3)_5$) and N_2O in toluene affords $[(Cp^*Ti)_2\text{-}\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5(CH_3)_4CH_2)(\mu\text{-}O)_2]$ (I). The structure of the product was determined by X-ray diffraction; it crystallizes in the orthorhombic space group *Pnma* with a = 10.650 (5) Å, b = 15.283 (3) Å, c = 17.064 (8) Å, and Z = 4. The structure was refined to R = 0.048 and R_w = 0.052 for 256 parameters and 1226 observed reflections. The molecule consists of two $(\eta^5\text{-}C_5(CH_3)_5)Ti$ units bridged unsymmetrically by two oxygen atoms (Ti(1)–O = 1.961 (3) Å and Ti(2)–O = 1.787 (3) Å) and an $\eta^1{:}\eta^5\text{-}C_5(CH_3)_4CH_2$ ligand (η^1 to Ti(2) and η^5 to Ti(1)). The bond distances are in agreement with the description of the $C_5(CH_3)_4CH_2$ bridge as a truly methylenic $\eta^1{:}\eta^5$ ligand and not as an $\eta^2{:}\eta^4$ olefinic ligand. The Ti(2)–CH_2 distance is 2.178 (6) Å; all other C–C and Ti–C distances are normal for Cp*Ti units. The methylenic description of $C_5(CH_3)_4CH_2$ is supported by NMR ($\delta(CH_2)$ 50.4 in the ^{13}C spectrum) and IR (ν(C–H) 2960, 2900, and 2850 cm^{-1}) spectroscopies and also explains the remarkable stability of I (no reaction with H_2, CO, or C_2H_4) since both titanium atoms are Ti(IV). With HCl, I gives $Cp^*_2TiCl_2$ and Cp^*TiCl_3.

Introduction

One of the driving forces behind research on transition-metal clusters is the idea that such clusters may serve as models for heterogeneous metal catalysts.[1] Both the pure metal catalyst and the metal atoms in the model cluster are in the zero oxidation state. In fact metal oxides are of almost equal importance to pure metals in heterogenous catalysis, and this is particularly true of early transition-metal oxides such as TiO_2 and Cr_2O_3. It is therefore desirable to prepare organometallic clusters containing oxygen as models for such metal oxides. These necessarily have metals in higher oxidation states. Most organometallic oxides are intractable polymers of variable composition,[2] though some discrete dimers,[3-7] trimers,[8] and tetramers[9,10] of titanium are known. We have used N_2O an as oxidant for Cp_2M ($Cp = \eta^5\text{-}C_5H_5$; M = V, Cr) and obtained the clusters $Cp_5V_5O_6$ and $Cp_4Cr_4O_4$.[11] The cluster $Cp_6Ti_6O_8$ was obtained by Caulton from the reaction between $Cp_2Ti(CO)_2$ and H_2;[12] this cluster is actually the product of the attack of H_2O on $Cp_2Ti(CO)_2$,[13] as was surmised by Caulton.[12] Reaction of N_2O with "Cp_2Ti" (prepared by the method of Brintzinger et al.[14]) gave paramagnetic "$(Cp_2Ti)_2O$",[15] but this compound has not been crystallized and hence the possibility that it contains C_5H_n (n < 5) rings other than $\eta^5\text{-}C_5H_5$ cannot be discounted. In order to obtain a crystalline material we turned to Cp^*_2Ti[14] ($Cp^* = \eta^5\text{-}C_5(CH_3)_5$), and from the reaction between this and N_2O obtained $[(Cp^*Ti)_2\text{-}\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5(CH_3)_4CH_2)(\mu\text{-}O)_2]$ (I) on which we have briefly reported.[16] This compound contains a bridging $C_5(CH_3)_4CH_2$ ligand; such deprotonated species have been postulated as intermediates in a wide variety of reactions of complexes of the early transition metals containing Cp* ligands,[17] and in the case of $[Cp^*(C_5(CH_3)_4CH_2)TiCH_3]$ (II) the complex was isolated,[14,18] though no crystal structure could be determined.[18] We present here full details of the preparation, structure, and chemical and physical properties of I and compare it to II.

Table I. Bond Distances (A) (Esd's in Parentheses)

Ti2–Ti1	2.724 (1)	O1–Ti2	1.787 (3)
O1–Ti1	1.961 (3)	C10–Ti2	2.178 (6)
	Ring C		
C2–C1	1.408 (6)	C5–C2	1.514 (10)
C4–C1	1.511 (14)	C6–C3	1.511 (12)
C3–C2	1.397 (7)	C3–C3′	1.393 (11)
	Ring A		
C9–C8	1.402 (6)	C9–C9′	1.416 (9)
C11–C8	1.509 (7)	C8–C7	1.419 (6)
C12–C9	1.503 (8)	C10–C7	1.479 (9)
	Ring B		
C14–C13	1.413 (6)	C17–C14	1.509 (8)
C16–C13	1.484 (11)	C18–C15	1.496 (7)
C15–C14	1.430 (6)	C15–C15′	1.394 (9)

Results and Discussion

Bright green I was obtained by the reaction between N_2O and a toluene solution of Cp^*_2Ti[14] at 0 °C. The yield, 54% based on Cp^*_2Ti, is remarkably high considering the transformation involved. As a check that the reaction

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Table II. Bond Angles (deg) (Esd's in Parentheses)

Ti2-Ti1-O1	40.9 (1)	C10-C7-C8	126.1 (3)
O1-Ti1-O1	79.9 (2)	C9-C8-C7	109.0 (4)
C10-Ti2-Ti1	81.0 (2)	C11-C8-C7	124.6 (5)
C10-Ti2-O1	91.8 (1)	C11-C8-C9	126.3 (5)
Ti1-Ti2-O1	46.0 (2)	C9'-C9-C8	107.8 (4)
O1-Ti2-O1'	89.6 (2)	C12-C9-C8	124.1 (4)
Ti2-O1-Ti1	93.1 (1)	C12-C9-C9'	126.8 (5)
C2-C1-C2'	107.1 (4)	C7-C10-Ti2	101.7 (4)
C4-C1-C2	126.2 (3)	C14-C13-C14'	107.1 (3)
C3-C2-C1	108.2 (4)	C16-C13-C14	125.4 (3)
C5-C2-C1	125.8 (7)	C15-C14-C13	108.4 (4)
C5-C2-C3	126.0 (7)	C17-C14-C13	126.8 (5)
C3'-C3-C2	108.2 (6)	C17-C14-C15	124.3 (4)
C6-C3-C3'	125.9 (5)	C15'-C15-C14	107.9 (4)
C6-C3-C2	125.8 (6)	C18-C15-C15'	127.7 (5)
C8-C7-C8'	106.4 (5)	C18-C15-C14	124.3 (4)

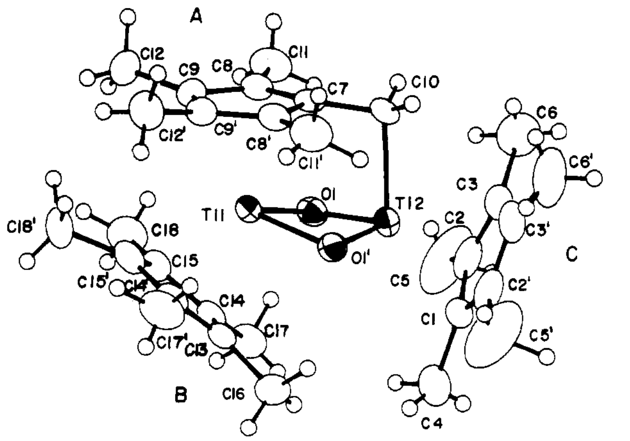

Figure 1. Molecular structure of $[(Cp^*Ti)_2\text{-}\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5(CH_3)_4CH_2)(\mu\text{-}O)_2]$.

actually involves Cp^*_2Ti, the known dinitrogen complex $[(Cp^*_2Ti)_2N_2]$[19,20] was prepared and reacted with N_2O; the product I was the same and the yield similar to that in the direct reaction. A second brown product that contained titanium could be obtained by removal of solvent from the filtrate after collecting I. However, we were unable to obtain a pure complex from this residue, which was extremely soluble in hexane. The apparently simple stoichiometry

$$2Cp^*_2Ti + 2N_2O \rightarrow [(Cp^*Ti)_2(C_5(CH_3)_4CH_2)(O)_2] + 2N_2 + Cp^*H$$

is not provable because of the other unknown product(s), and therefore we do not speculate about the mechanism of the reaction.

Crystals of I were obtained by recrystallization from toluene. The distances and angles determined by the X-ray diffraction experiment are given in Tables I and II, respectively, and the relevant atom numbers are shown in Figure 1. There is a crystallographic mirror plane containing Ti(1), Ti(2), C(1), C(4), C(7), C(10), C(13), and C(16) which bisects the three rings. The bridging oxygen atoms lie on either side of this plane. Other relevant planes are given in Table III.

The average Ti–C distances to the three rings are 2.416 (5) (ring A), 2.443 (5) (ring B), and 2.397 (6) Å (ring C), and the equivalent Ti–ring centroid distances are 2.100, 2.212, and 2.088 Å, respectively. The marginally shorter Ti–ring C distances, compared to A and B, are probably due to the low formal electron count (12) of Ti(2) compared

Table III. Mean Planes

Ring C

$$-0.5966X + 0.0000Y + 0.8025Z = 2.2598$$

C1	0.011	C4[a]	−0.121
C2	−0.009	C5[a]	−0.034
C3	0.004	C6[a]	−0.059
C2'	−0.009		
C3'	0.004		

Ring A

$$0.5135X + 0.0000Y + 0.8581Z = 10.6345$$

C7	0.010	C10[a]	−0.224
C8	−0.008	C11[a]	0.054
C9	0.003	C12[a]	0.279
C8'	−0.008		
C9'	0.003		

Ring B

$$0.9415X - 0.0000Y + 0.3371Z = 1.9295$$

C13	−0.023	C16[a]	−0.421
C14	0.019	C17[a]	−0.067
C15	−0.007	C18[a]	−0.077
C14'	0.019		
C15'	−0.007		

[a] Atom not included in the calculation of the plane.

to the 16 of Ti(1). However, the Ti–ring distances are all comparable to those in $Cp^*_2TiCl_2$ (average Ti–C = 2.442 (4) Å and average Ti–ring centroid = 2.127 (4) Å).[21] The average C–C(aromatic) distance in the rings, 1.408 (7) Å, and the average C–CH_3 distance 1.502 (10) Å, are also the same as those in $Cp^*_2TiCl_2$, 1.409 (5) and 1.496 (6) Å, respectively. The ring A–Ti(1)–ring B angle of 140.6° is similar to that in $Cp^*_2TiCl_2$ (137.4°).[21] Note the close correspondence with the Ti(IV) complex $Cp^*_2TiCl_2$ which is different from the Ti(II) complex $[(Cp^*_2Ti)_2N_2]$, as discussed by Bercaw and co-workers.[20] The methyl groups are bent out of the plane of the aromatic rings (the average distance from the plane is 0.15 Å; the range is from 0.034 (C(5)) to 0.021 Å (C(16)), Table III). Such bending is common in Cp*M complexes.[19,20]

Two features of the structure are remarkable and require a more detailed discussion. These are the Ti(μ-O)$_2$Ti unit and the $C_5(CH_3)_4CH_2$ bridging ligand. The Ti(μ-O)$_2$Ti unit is not planar, the angle between the planes Ti(1)–O(1)–O(1′) and Ti(2)–O(1)–O(1′) being 158.8°, and the Ti–O distances are unsymmetrical, Ti(1)–O(1) being 1.961 (3) Å and Ti(2)–O(1) being 1.787 (3) Å. The latter distance is identical with the Ti–μ-O distances in other $[(CpTiX_2)_2(\mu\text{-}O)]$ complexes which contain Ti(IV) with formally 12 electrons around the Ti atom; these distances average 1.78 Å.[4,8-10] The Ti(1)–O(1) distance of 1.961 (3) Å is much longer than in other $[(CpTiX_2)(\mu\text{-}O)]$ complexes which have 16 electrons around Ti(IV); the average in such complexes is 1.85 Å.[3,5-9,22,23] We presume that the high effective electronegativity of the 12-electron Ti(2) produces a normal, short, Ti(2)–O bond and thereby reduces the ability of the oxygen to donate a further pair of electrons to Ti(1). The shortest contact between rings B and C is between hydrogen atoms on C(4) and C(18) and measures 2.33 Å. Therefore, the Ti–Ti distance may be sterically at a minimum, but it is still not clear why the Ti(1)–O(1) distance is so long while the Ti(2)–O(1) distance is normal.

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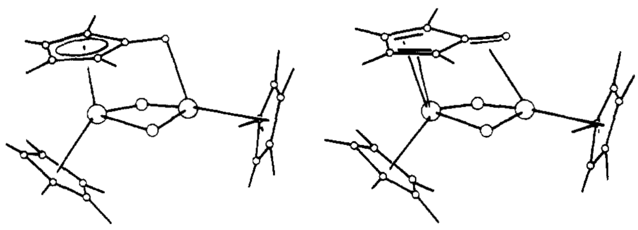


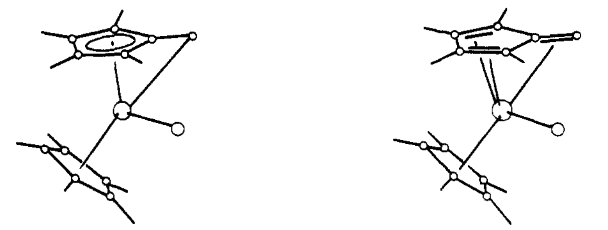
A B

Figure 2. Modes of bonding in $[(Cp^*Ti)_2\text{-}\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5(CH_3)_4CH_2)(\mu\text{-}O)_2]$.

An unsymmetrical Ti–O bridge was also observed in $Cs_4\{[TiO(NTA)]_4\}\cdot 6H_2O$ (Ti–O average 1.90 or 1.75₅ Å).[24]

The Ti–Ti distance, 2.724 (1) Å, is the shortest yet observed. For comparison, the Ti–Ti distance in metallic titanium is 3.212 Å,[25] in TiO_2 it is 3.569 Å,[25] in $Cp_6Ti_6O_8$, it is 2.891 (1) Å,[12] in $[(CH_3O)_2Ti(\mu\text{-}CH_3O)_2(\mu\text{-}(CH_2)_2P(CH_3)_2)_2Ti(OCH_3)_2]$ it is 3.25 Å,[26] and in $[CpTi\text{-}\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5H_4)TiCp]$ (for which a Ti–Ti bond is proposed) it is 3.336 (4) Å.[27] As discussed in detail below, the structural parameters, spectroscopic evidence, and reactivity of I all clearly point to a methylene-bridged structure in which both titanium atoms are formally Ti(IV) and there are no electrons available for a Ti–Ti bond. The very short Ti–Ti distance is produced by the bridging oxygen and $C_5(CH_3)_4CH_2$ ligands.

The two structures A and B shown in Figure 2 may be drawn for I. The structural parameters clearly show that we are dealing with the methylene-bridged structure A and not the olefin-bridged structure B. The important evidence is as follows (using the numbering scheme in Figure 1). (1) The C–C ($C_5(CH_3)_4CH_2$) distances in ring A are 1.419 (6) (C(7)–C(8)), 1.402 (6) (C(8)–C(9)), and 1.416 (9) Å (C(9)–C(9′)) and the average C–C (C_5–$(CH_3)_5$) distance in rings B and C is 1.406 (7) Å, with a range from 1.393 (11) to 1.430 (6) Å. The range of distances in ring A is actually less than in ring B. This indicates that ring A is a normal $C_5R_5^-$ ring. (2) The C(7)–C(10) distance of 1.479 (9) Å is not significantly (i.e., less than three standard deviations) different from the average C–CH_3 distance in the three rings (1.505 (9) Å). (3) The Ti(1)–C $C_5(CH_3)_4CH_2$) distances to ring A (Ti(1)–C(7) = 2.401 (6), Ti(1)–C(8) = 2.399 (4), and Ti(1)–C(9) = 2.449 (4) Å) are all in the normal range for a Cp*Ti(IV) compound (see above). The Ti(1)–C(7) distance is not the longest in this ring, as it would be if structure B in Figure 2 were correct. (4) Ring A is planar (see Table III); there is no significant deviation of C(7) from the plane. The CH_3 atoms in ring A are bent out of the plane (average distance 0.167 Å) and C(10) (the CH_2 group) is similarly 0.224 Å out of the plane. (5) The Ti(2)–C(10) (CH_2) distance, 2.178 (6) Å, falls exactly in the region expected for a Ti–C(sp³) σ bond.[22,23,28] (6) The Ti(2)–C(7) distance of 2.870 (6) Å is much too long for any interaction between these atoms; for comparison we note that the Ti–C distances in the only known molecule containing a two-carbon η^2-bonded ligand which has been investigated by X-ray diffraction, namely, $Cp_2Ti(CO)(\eta^2\text{-}PhC_2Ph)$, are 2.230 (7) and 2.107 (7) Å.[29] (7) The C(7)–C(10)–Ti(2) angle is 101.7 (4)°, close to the tetrahedral angle expected at a methylene bridge. In $Cp_2Ti(CO)(\eta^2\text{-}PhC_2Ph)$ the C–C–Ti angles are 78.1 (5) and 67.6 (4)°.[29]



A B

Figure 3. Modes of bonding in $Cp^*(C_5(CH_3)_4CH_2)TiCH_3$.

From this evidence alone, we conclude that structure A in Figure 2 accurately represents the form of I. This methylene bridged formulation is in contrast to $Cp^*(C_5(CH_3)_4CH_2)TiCH_3$ (II), for which the olefinic structure B in Figure 3 is preferred. No X-ray structure of II is available because of a disorder problem. However, the carbon atom of the CH_2 resonates in the olefinic region (73.9 ppm) in the ¹³C NMR spectrum, and an olefinic C–H stretching vibration is observed at 3040 cm⁻¹ in the infrared spectrum of II.[18] In I the carbon atom of the CH_2 group resonates at 50.4 ppm, in the same region as the $TiCH_3$ resonance of II (41.4 ppm[18]). In the IR spectrum of I the ν(C–H) vibrations are observed at 2960, 2900, and 2850 cm⁻¹; there is no absorption band above 3000 cm⁻¹. Hence, the spectral data for I are in agreement with the structural data and with the methylene-bridged structure A in Figure 2. The differences between the spectra of I and II indicate that the two complexes have different structures, the former the methylenic structure A and the latter the olefinic B. In II the question of which structure, A or B, is preferred is in essence only a question of the location of a pair of electrons; when the pair is in a molecular orbital with a large contribution from the atomic orbitals of the carbon atom of the CH_2 group, then the methylenic description A (Figure 3) is the most appropriate; when the pair is in an orbital with a large contribution from the Ti atomic orbitals, then the olefinic structure B is appropriate. On the other hand, in I the pair of electrons must be distributed between the *two* Ti atoms if the olefinic structure B of Figure 2 is correct. This can be accomplished either via a Ti–Ti band as shown in Figure 2 or by localizing the electron pair on one of the two Ti atoms. Whichever solution is adopted, there is a lack of electrons for π-back-bonding to the olefin on one or both Ti atoms. Hence, for I the methylenic structure A is preferred; however, we see no reason why II should so clearly prefer the olefinic structure B.

The methylene-bridged structure of I is probably responsible for its remarkable inertness compared to II. It is stable toward O_2 but is slowly hydrolyzed by even traces of H_2O to give an insoluble polymer. It does not react with CO, ethylene, or, most surprisingly, H_2 at room temperature and atmospheric pressure. With HCl there is formation of $Cp^*_2TiCl_2$ and Cp^*TiCl_3. In contrast, II reacts instantaneously with H_2 at 0 °C to give Cp^*_2Ti and CH_4.[14] The olefinic structure B of II gives the titanium a formal oxidation state of II and thus allows oxidative addition of H_2 at the metal to produce, as an intermediate, $[Cp^*(C_5(CH_3)_4CH_2)Ti(H)_2CH_3]$. Transfer of H to the CH_3 and

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Table IV. Fractional Atomic Coordinates for Non-Hydrogen Atoms (Esd's in Parentheses)

atom	*x/a*	*y/b*	*z/c*
Ti1	0.0889 (1)	0.25	0.5497 (1)
Ti2	0.2926 (1)	0.25	0.4532 (1)
O1	0.1853 (3)	0.3324 (2)	0.4853 (1)
C1	0.3240 (6)	0.25	0.3162 (4)
C2	0.3881 (5)	0.3241 (3)	0.3444 (3)
C3	0.4874 (5)	0.2956 (3)	0.3914 (3)
C4	0.2180 (11)	0.25	0.2573 (7)
C5	0.3546 (14)	0.4184 (6)	0.3271 (7)
C6	0.5830 (9)	0.3536 (9)	0.4312 (5)
C7	0.2830 (6)	0.25	0.6213 (3)
C8	0.2137 (4)	0.3244 (3)	0.6459 (2)
C9	0.1066 (4)	0.2963 (3)	0.6867 (2)
C10	0.3894 (6)	0.25	0.5656 (4)
C11	0.2552 (8)	0.4179 (4)	0.6346 (4)
C12	0.0255 (6)	0.3552 (4)	0.7358 (3)
C13	0.8614 (6)	0.25	0.5731 (4)
C14	0.8916 (4)	0.3244 (3)	0.5276 (3)
C15	0.9324 (4)	0.2956 (3)	0.4521 (2)
C16	0.7810 (9)	0.25	0.6441 (5)
C17	0.8705 (7)	0.4189 (4)	0.5496 (4)
C18	0.9637 (6)	0.3554 (4)	0.3855 (3)

$C_5(CH_3)_4CH_2$ ligands can then take place readily. The methylenic structure A of I gives a formal oxidation state of IV to the titanium, and no oxidative addition can occur. Direct attack of H_2 at a d^0 transition metal, via the σ electrons, has been proposed previously[17,30,31] but is obviously a high energy pathway in the present case. The energy barrier for conversion of the methylenic structure A into the olefinic B must be large also so that the structures are not resonance forms. Reaction with HCl can readily occur by initial coordination of the Cl atom of HCl to Ti(2) (which has three vacant orbitals of low energy); proton transfer to the $C_5(CH_3)_4CH_2$ can then readily occur, and no oxidative addition is involved in the reaction. We have not been able to isolate the presumed initial product of the reaction, $Cp^*_2Ti(\mu\text{-}O)_2Ti(Cp^*)Cl$, only the two halves $Cp^*_2TiCl_2$ and Cp^*TiCl_3.

The reacton between I and NO gives a brown intractable solid and N_2O gas. Since Ti(2) formally has only 12 electrons, coupling of two NO atoms on this atom is possible. However, the titanium-containing product is obviously a polymer and therefore oxidation of the Cp* and/or $C_5(CH_3)_4CH_2$ must also occur.

Experimental Section

$Cp^*_2TiCl_2$ was converted into Cp^*_2Ti or $[(Cp^*_2Ti)_2(N_2)]$ by the methods of Brintzinger and co-workers.[14] Other chemicals were reagent grade. All reagents and solvents were dried and deoxygenated before use, and all operations were conducted under argon or in vacuum.

Preparation of Bis(μ-oxo)(η^1:η^5-1,2,3,4-tetramethyl-5-methylene-1,3-cyclopentadiene)bis[(η-pentamethylcyclopentadienyl)titanium]. A solution of Cp^*_2Ti (0.224 g, 0.704 mmol) in toluene (50 cm^3) was cooled in ice under vacuum. While the solution was stirred vigorously, N_2O (1 atm static pressure) was admitted. After a short incubation period, the red-brown solution began to froth and turned green-brown. After frothing had ceased (approximately 5 min), the excess N_2O was pumped away and then the solution stirred for a further 30 min. The solvent was removed under vacuum and hexane (30 cm^3) added, giving a lime green precipitate and a brown solution. The mixture was filtered and the solid washed with hexane, then a mixture of hexane/ether (1:1), and finally with hexane/toluene (3:1). Recrystallization from toluene/hexane gave 0.10 g of $[(\eta^5\text{-}C_5(CH_3)_5Ti)_2\text{-}\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5(CH_3)_4CH_2)(\mu\text{-}O)_2]$ (54% based on Cp^*_2Ti): ^1H NMR 2.12 ppm ($C_5(CH_3)_5$); ^{13}C NMR 122.29 ($C_5(CH_3)_5$); 50.41 ppm ($C_5(CH_3)_4CH_2$); IR ν(C-H) 2960, 2900, 2850 cm^{-1}. Anal. Calcd for $C_{30}H_{44}O_2Ti_2$: C, 67.7; H, 8.3; Ti, 18.0. Found: C, 66.8; H, 7.9; Ti (as TiO_2), 18.9.

Reaction of $[(Cp^*Ti)_2\text{-}\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5(CH_3)_4CH_2)(\mu\text{-}O)_2]$ with HCl. Formation of $Cp^*_2TiCl_2$ and Cp^*TiCl_3. To a solution of $[(Cp^*Ti)_2\text{-}\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5(CH_3)_4CH_2)(\mu\text{-}O)_2]$ (0.42 g, 0.07 mmol) in toluene (20 cm^3) was added HCl gas (one atmosphere static pressure). The green solution immediately turned red-brown. After the solution was stirred for 1 h, the excess HCl gas was pumped away, the toluene removed under vacuum, and hexane (30 cm^3) added. After being stirred for a few minutes, the mixture was filtered, giving a purple-brown precipitate of $Cp^*_2TiCl_2$ (0.041 g, 13.5%): ^1H NMR 2.00 ppm ($C_5(CH_3)_5$) (lit.[14] 2.00 ppm); ^{13}C NMR 12.96 ($C_5(CH_3)_5$), 128.54 pm ($C_5(CH_3)_5$. Anal. Calcd for $C_{20}H_{30}Cl_2Ti$: C, 61.7; H, 7.8. Found: C, 58.20 H, 6.79.

The filtrate after removal of $Cp^*_2TiCl_2$ was evaporated under vacuum until red Cp^*TiCl_3 crystallized (yield 0.05 g, 22.8%): ^1H NMR 2.27 ppm ($C_5(CH_3)_5$) (lit.[14] 2.35 ppm); ^{13}C NMR 13.37 ($C_5(CH_3)_5$), 134.05 ppm ($C_5(CH_3)_5$). Anal. Calcd for $C_{10}H_{15}Cl_3Ti$: C, 41.5; H, 5.2. Found: C, 41.1; H, 4.4.

Determination of the Crystal and Molecular Structure of $[(Cp^*Ti)_2\text{-}\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5(CH_3)_4CH_2)(\mu\text{-}O)_2]$. Collection and Reduction of Intensity Data. A crystal approximately 0.20 × 0.35 × 0.40 mm was grown from a toluene/hexane solution. It was coated with "Apiezon" grease and mounted in a sealed tube under argon. Space group and symmetry information were obtained by using Weissenberg and precession photographs and intensity data were collected on a Picker FACS-1 four-circle diffractometer. Cell dimensions, at 20 °C, were determined from the coordinates of 12 Friedel pairs of reflections with $2\theta > 35°$, accurately centered on the diffractometer. Crystal data: $C_{30}H_{44}O_2Ti_2$; M_r = 532.5; orthorhombic; *Pnma*; a = 10.650 (5) Å, b = 15.283 (3) Å, c = 17.063$_5$ (8$_5$) Å; Z = 4; Mo $K\bar{\alpha}$ radiation, λ = 0.710 69 Å; μ = 5.66 cm^{-1}; D_{calcd} = 1.27 g cm^{-3}; 1904 independent reflections measured to $2\theta = 45°$; 1226 observed reflections ($|F_1| > 3\sigma(|F|)$); 256 variables; $R = (\sum|\Delta|F|/\sum|F_o|) = 0.048$; $R_w = (\sum w(|\Delta F|)^2/\sum w|F_o|^2)^2 = 0.052$; maximum residual intensity = 0.38 e Å^{-3}, minimum residual intensity = −0.37 e Å^{-3}. No absorption or extinction corrections were applied since μ is very low and no reflections appeared anomalous during the refinement.

Structure Solution and Refinement. Preliminary positions for the titanium atoms were obtained by using the MULTAN direct methods procedure.[32] The positions of these atoms were used in the phasing of Fourier syntheses, and the position of all non-hydrogen atoms were subsequently determined by Fourier, difference Fourier, and partial refinement techniques. Refinement was by standard least-squares techniques,[33] minimizing the function $\sum w(\Delta F)^2$ with a weighting scheme of the form $w = 1/(\sigma(F)^2 + kF^2)$ based on counting statistics. Scattering factors were taken from ref 34 and were corrected for both the real and the imaginary parts of the anomalous dispersion. Anisotropic parameters were used for all atoms except H, the latter being refined isotropically. The positional parameters for the non-hydrogen atoms from the final refinement are given in Table IV. Tables of hydrogen atom positions, thermal parameters, and $|F_o|$ and $|F_c|$ are available as supplementary material.

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Supplementary Material Available: Tables of hydrogen atom positions, thermal parameters, and structure factors (9 pages). Ordering information is given on any current masthead page.

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