Synthesis and Properties of the Titanaoxacyclobutane Derived from $(Me_5C_5)_2Ti(O)(L)$ and Allene

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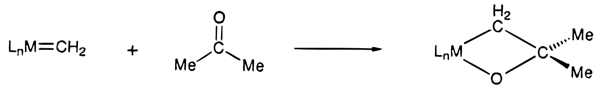
The oxo compound $(C_5Me_5)_2TiO(pyr)$ (**1**) undergoes a 2 + 2 cycloaddition reaction with allene to give $(Me_5C_5)_2\overline{Ti[OC(CH_2)C}H_2]$ (**2**), which contains a puckered $TiOC_2$ ring in the solid state. The metallacyclobutane **2** does not exchange with either free allene or pyridine on the NMR time scale and slowly converts to the ring-metalated product $(C_5Me_5)(C_5Me_4CH_2)Ti[OC(CH_2)Me]$ (**3**) in solution and to the enolate complex $(C_5Me_5)_2Ti[H][OC(CH_2)Me]$ (**4**) in the presence of 1 atm of H_2.

Oxametallacyclobutanes, or metallaoxetanes as they are alternatively known, are an important class of molecules due to their role in the metal-catalyzed conversion of olefins to epoxides.[1] Oxametallacyclobutanes have been prepared by two principal synthetic routes: (a) reaction of a metal carbene or vinylidene complex with a carbonyl functional group (eq 1)[2] or (b) oxygen atom insertion into a coordinated olefin (eq 2).[3] Related oxygen atom insertions into coordinated alkynes and metal−carbon bonds, to give the corresponding oxametallacyclobutenes, have also been reported.[4] Some miscellaneous and less general synthetic routes have also been published.[5] The synthesis of an oxametallacyclobutane complex from reaction of an isolated metal−oxo compound with an olefin (eq 3) has never been described.



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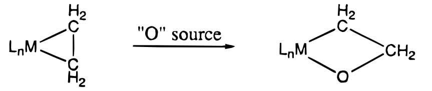

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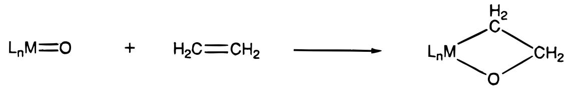

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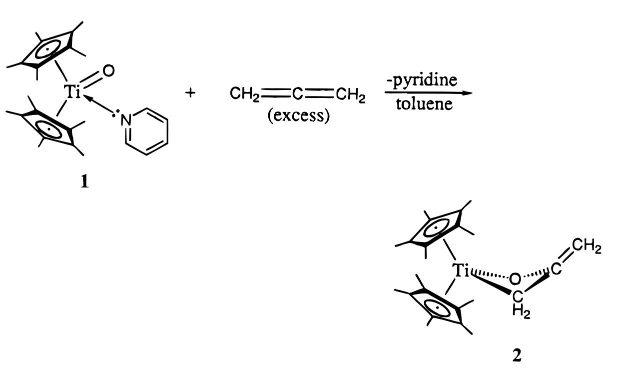

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We have recently prepared the monomeric oxo compound $(Me_5C_5)_2Ti(O)(L)$ (**1**),[6] where L is pyridine or a substituted pyridine, and have shown that pyridine can be displaced by acetylenes to give the corresponding titanaoxacyclobutenes.[7] In this manuscript, we show that the titanyl compound **1** reacts with allene to give the titanaoxacyclobutane $(Me_5C_5)_2\overline{Ti[OC(CH_2)C}H_2]$ (**2**) (eq 4), in which the four-membered $TiOC_2$ ring is puckered in the solid state.

Results and Discussion

Addition of an excess of allene to a deep yellow toluene solution of **1** gives a color change to deep green, over the course of several minutes. Dark green-brown crystals of **2** can be isolated from this solution by removing the solvent under reduced pressure, redissolving the solid in pentane, and slowly cooling this solution to −80 °C. While **2** is stable indefinitely as a

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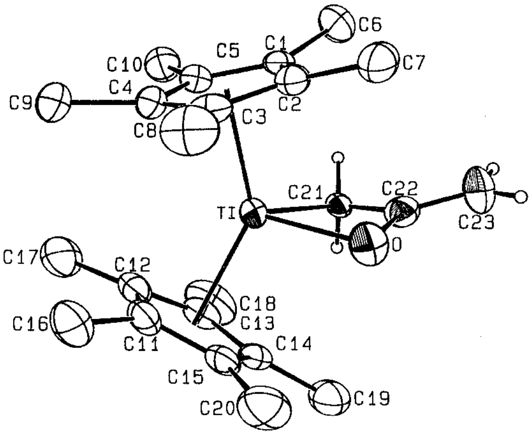


Figure 1. ORTEP diagram of **2**, 50% probability thermal ellipsoids.

Table 1. Crystallographic Data for $(C_5Me_5)_2\overline{Ti[OC(CH_2)C}H_2]$ (2)

chem formula	$C_{23}H_{34}OTi$
mol wt	374.42
cryst size, mm	0.32 × 0.35 × 0.15
T, °C	−96
space group	$P\bar{1}$
a, Å	8.595(2)
b, Å	9.090(2)
c, Å	13.454(4)
α, deg	86.80(2)
β, deg	85.65(2)
γ, deg	74.07(2)
V, Å^3	1007.2(4)
Z	2
d(calc), g cm^{-3}	1.234
μ(calc), cm^{-1}	4.26
rflns measd	$+h,\pm k,\pm l$
2θ range	3−45°
no. rflns collcd	2846
abs corr	$I_{min}/I_{max} = 0.74$
no. atoms in least squares	25
no. unique rflns	2632
no. rflns with $(F_o)^2 > 3\sigma(F_o)^2$	1937
p factor	0.05
no. params	227
R^a	0.0525
R_w	0.0665
R_{all}	0.0792
GOF	1.73
diff Fourier, e Å^{-3}	+0.34, −0.34

[a] The definitions for R and R_w are as follows: $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

Table 2. Atomic Coordinates and B Values (Å^2) for the Non-Hydrogen Atoms of 2[a,b]

atom	x	y	z	B
Ti	0.2207(1)	0.2912(1)	0.25451(6)	1.84(2)
O	0.4138(4)	0.3734(4)	0.2422(3)	3.73(9)
C1	0.2489(5)	0.2051(5)	0.4294(3)	2.0(1)
C2	0.3928(5)	0.1300(5)	0.3762(4)	2.3(1)
C3	0.3555(6)	0.0341(6)	0.3071(4)	2.5(1)
C4	0.1885(6)	0.0449(5)	0.3223(4)	2.6(1)
C5	0.1194(5)	0.1571(5)	0.3942(3)	2.2(1)
C6	0.2344(6)	0.3001(6)	0.5184(4)	3.4(1)
C7	0.5590(6)	0.1372(6)	0.3965(4)	3.5(1)
C8	0.4783(7)	−0.0768(7)	0.2425(5)	4.2(2)
C9	0.1048(7)	−0.0669(6)	0.2862(4)	3.9(1)
C10	−0.0525(6)	0.2036(6)	0.4358(4)	3.2(1)
C11	0.1557(6)	0.2141(6)	0.0959(4)	2.7(1)
C12	0.0066(6)	0.2856(6)	0.1474(4)	3.0(1)
C13	0.0029(6)	0.4396(6)	0.1564(4)	2.8(1)
C14	0.1471(6)	0.4638(6)	0.1113(3)	2.5(1)
C15	0.2430(6)	0.3230(6)	0.0752(3)	2.5(1)
C16	0.1993(7)	0.0597(7)	0.0483(4)	4.4(1)
C17	−0.1396(7)	0.2254(8)	0.1686(5)	4.8(2)
C18	−0.1391(7)	0.5626(8)	0.1990(5)	5.2(2)
C19	0.1875(7)	0.6135(6)	0.0968(4)	4.0(1)
C20	0.4056(7)	0.2965(8)	0.0199(4)	4.4(2)
C21	0.1752(5)	0.4960(5)	0.3266(3)	1.8(1)
C22	0.3452(6)	0.4813(6)	0.3155(4)	2.6(1)
C23	0.4289(7)	0.5496(6)	0.3663(4)	4.4(1)

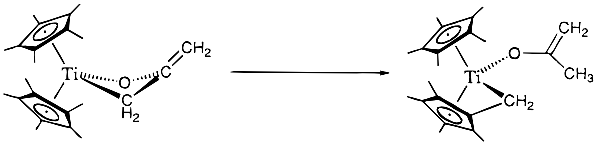
[a] Numbers in parentheses give estimated standard deviations. [b] Equivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table 3. Selected Intramolecular Distances (Å) and Angles (deg) in 2[a]

Bond Distances			
Ti−C21	2.074(4)	Ti−O	1.992(4)
Ti−C22	2.472(6)	Ti−C23	3.754(7)
Ti−Cp1	2.11	Ti−Cp2	2.11
C21−C22	1.428(7)	C22−C23	1.318(9)
C22−O	1.408(6)		
Bond Angles			
C21−Ti−O	68.7(2)	Ti−O−C22	91.7(3)
Ti−C21−C22	87.8(3)	C21−C22−C23	127.5(4)
C21−C22−O	108.1(4)	O−C22−C23	124.3(4)
Cp1−Ti−Cp2	139	Cp1−Ti−O	108
Cp2−Ti−O	106	Cp1−Ti−C21	107
Cp2−Ti−C21	106		

[a] All distances and angles involving the C_5Me_5 rings were calculated using the ring centroid positions; these positions are abbreviated as Cp1 and Cp2.

solid, it is unstable in the solution state, converting cleanly to the ring-metalated product $(C_5Me_5)(C_5Me_4\text{-}CH_2)Ti[OC(CH_2)Me]$ (**3**) (eq 5). The solution behavior of **2** will be discussed in more detail below.



(5)

2 **3**

Solid-State Structure of 2. The complex **2** crystallizes in the triclinic crystal system in space group $P\bar{1}$; an ORTEP diagram is shown in Figure 1. The four hydrogen atoms of the oxametallacyclobutane ring were located in a difference Fourier map near the end of the refinement, ruling out the possibility of a Ti−CH_2/Ti−O disorder. The crystallographic data (Table 1), positional parameters (Table 2), and selected intramolecular distances and angles (Table 3) are listed. As is apparent from inspection of Figure 1, complex **2** results from the 2 + 2 addition of the titanyl group and an olefinic double bond of allene (eq 4), giving a compound that contains a puckered oxametallacyclobutane ring with an exocyclic double bond. The $(Me_5C_5)_2Ti$ portion of the molecule is normal for $(C_5Me_5)_2TiXY$ molecules.[8] The averaged Ti−C(Me_5C_5) distance is 2.43(1) Å, the Ti−(ring centroid) distance is 2.11 Å, and the (ring centroid)−Ti−(ring centroid) angle is 139°.

The structural features of principal interest are the bond parameters associated with the nonplanar $TiOC_2$ ring. The Ti−C21 distance of 2.074(4) Å is shorter than typically found for Ti−C(sp^3) bonds, which range 2.14−2.21 Å.[8] A specific example is the two independent Ti−C distances in $(C_5H_5)_2TiMe_2$, 2.170(2) and 2.181(2)

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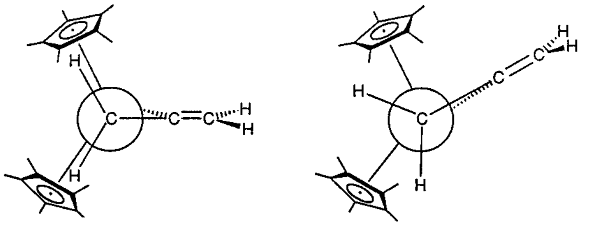
[8] Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1. The average Ti−C(C_5Me_5) distance for 61 $(C_5Me_5)_2TiXY$ compounds is 2.40 Å, and the average Ti−ring centroid distance is 2.09 Å.

Å.[9] Conversely, the Ti−O distance of 1.992(4) Å is longer than expected, relative to Ti−O distances in titanium alkoxide complexes in which the average Ti−O distance is 1.85 Å.[8] A specific example is the Ti−O distance of 1.855(2) Å found in $(C_5H_5)_2Ti(OEt)(Cl)$.[10] However, in $(C_5H_5)_2Ti[OC(N{-}cyclohexyl)C(CH_2)]$,[2e] the Ti−O distance in the four-membered ring is 1.983(2) Å, and in a related compound in which the oxygen atom is part of a six-membered ring, the Ti−O distance is 1.910(1) Å.[2f] Further, in the four-membered planar ring oxametallacyclobutene complexes $(C_5Me_5)_2\overline{Ti[OC(Ph)C}H]$ and $(C_5Me_5)_2\overline{Ti[OC(Ph)C}Ph]$, the Ti−O distances are 1.978(5) and 1.952(7) Å, respectively.[7] Apparently, when the oxygen atom is part of a metallacycle ring, the Ti−O distance is lengthened relative to the typical Ti−O distances observed in titanium alkoxide complexes; this is possibly a result of diminished Ti−O π-bonding.[11] The C21−C22 distance of 1.428(7) Å is lengthened relative to the C−C distance in allene, 1.310(5) Å, but is slightly shorter than unconjugated C(sp^3)−C(sp^2) distances, which average 1.48 Å.[12] The exocyclic double bond distance, C22−C23, of 1.318(9) Å is very similar to that found in free allene.[12] The C22−O distance of 1.408(6) Å is slightly longer than typically found for C(sp^2)−O distances in ring systems, 1.37 Å.[13] The nonplanar nature of the $TiOC_2$ ring, with a C21−Ti−O/C21−C22−O dihedral angle of 22.5°, is unusual. As a result, C22 and C23 approach the Ti center, to within 2.472(6) and 3.754(7) Å, respectively.

The origin of the puckering of the $TiOC_2$ metallacycle ring is not obvious. A recent theoretical study concluded that a planar ground-state structure is more stable than a puckered one in molecules of the type $X_2\overline{TiOC(CH_2)C}H_2$;[11] puckering was found to weaken the Ti−O bond. It is noteworthy that, in the planar conformation, the calculations yield a Ti−C distance of 2.05 Å, very similar to the value found for **2**, 2.074(4) Å. In contrast, the calculated Ti−O distance of *ca.* 1.8 Å is substantially shorter than that found in **2**, 1.992(4) Å. The calculated distance is close to that found in titanium alkoxide compounds but almost 0.2 Å shorter than that found in both planar and puckered $TiOC_2$ rings.[2e,f,7] If it is assumed that the calculations on the model compounds give the correct electronic ground-state conformations, then the origin of the puckering may be due to steric rather than electronic effects.

The conformations of four-membered rings in carbon chemistry have been extensively studied,[14] and the reasons for puckered or planar rings may by applicable to $TiOC_2$ rings. Cyclobutane is puckered with a dihedral angle of 34°, while oxetane is planar. This has been explained as resulting from destabilizing interactions between adjacent CH_2 groups, which are eclipsed in planar C_4H_8 but staggered in the puckered ring. These destabilizing interactions are absent in the oxetane ring, resulting in a planar conformation. This reasoning may be extended to **2**; inspection of Newman projections (Figure 2) show that the hydrogens of the $TiCH_2$ group are eclipsed with the C_5Me_5 rings in the planar conformation (Figure 2a), a result of the pseudotetrahedral geometry about the Ti center. In contrast, these groups are staggered in a puckered ring conformation (Figure 2b). Consistent with this, when the α-carbon atom is sp^2-hybridized, as found in the titanaoxametallacyclobutenes, the planar conformation is observed.[7] It is also possible that the puckering of the metallacycle ring in **2** is a result of solid-state crystal packing effects.



(a) (b)

Figure 2. Newman projections of **2** viewed down the Ti−C21 bond: (a) planar ring conformation; (b) puckered ring conformation, with degree of puckering exaggerated for purposes of illustration.

Solution-State Properties. The ^1H NMR spectrum of **2** in C_6D_6 shows that the C_5Me_5 rings are equivalent (δ 1.74 ppm). The α-CH_2 protons (equivalent on the NMR time scale; see below) give rise to a doublet of doublets at δ 1.80 ppm (J_{HH} = 1.25 Hz to both (inequivalent) exocyclic hydrogens), and each of the exocyclic methylene protons give rise to a doublet of triplets (δ 4.39 and 4.02 ppm, J_{HH} = 1.56, 1.25 Hz). The $^{13}C\{^1H\}$ spectrum shows the Me_5C_5 methyl and ring carbon resonances at δ 11.3 and 122.3 ppm, respectively. The $\overline{Ti(OC_a(C_bH_2)C}_cH_2)$ resonances occur at δ 152.8 (C_a), 80.2 (C_b), and 47.0 (C_c) ppm (assigned on the basis of a $^{13}C\{^1H\}$ DEPT135 spectrum). Both the ^1H and $^{13}C\{^1H\}$ values of **2** are in the range reported for the unsubstituted titanocene derivative, $(C_5H_5)_2\overline{Ti[OC(CH_2)C}H_2]$.[2a] The equivalency of the C_5Me_5 rings and of the α-CH_2 protons of **2** indicates either that the $TiOC_2$ ring in **2** is planar in solution or that a fast (on the NMR time scale) "flipping" of the ring pucker results in the observed identical averaged environments. Given the puckering of the $TiOC_2$ ring in the solid-state structure of **2**, the latter possibility is considered the more likely one.

Grubbs and co-workers have found that cooling a solution of $(C_5H_5)_2\overline{Ti[OC(CH_2)C}H_2]$ results in decoalescence of the averaged C_5H_5 and $TiCH_2$ resonances into two C_5H_5 and two $TiCH_2$ resonances.[2a] They postulated that the $TiOC_2$ ring in this compound is puckered and that interconversion of the two puckered ring conformations, fast at room temperature, is slowed upon cooling. The barrier to this process was found to be 13.0(2) kcal mol^{-1}. The barrier for the analogous process for the phenyl-substituted derivative, $(C_5H_5)_2\overline{Ti[OC(CPh_2)C}H_2]$, was found to be higher, 19.0(2) kcal mol^{-1}. We have found that the C_5Me_5 rings and the $TiCH_2$ protons of **2** are equivalent on the NMR time scale down to −90 °C. Evidently, the barrier to the intramolecular (see below) ring-flip process in **2** is much lower than in the C_5H_5 derivatives. As the origin of the barrier is presumably

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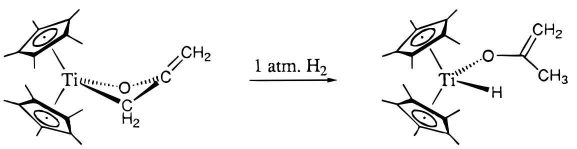
the energy difference between the puckered and planar ring conformations, this energy gap is apparently smaller for the C_5Me_5 derivative, **2**, relative to the C_5H_5 derivatives.[15]

As mentioned above, solutions of **2** convert to the ring-metalated product **3** over time (eq 5). The extent of this decomposition varies from sample to sample, over a given period of time. Only *ca.* 10% conversion is observed over the course of 48 h (25 °C, C_6D_6) for certain samples, whereas for other seemingly identical samples complete conversion occurs over this same time period. This appears to be the result of varying amounts of adventitious water present in the NMR samples. When a C_6D_6 solution of **2** is prepared with 1 equiv of $(C_5H_5)_2ZrMe_2$, the extent of conversion is significantly less than that of an identical sample (*same* solution of **2**) without added $(C_5H_5)_2ZrMe_2$. The $(C_5H_5)_2ZrMe_2$ is presumably acting as a water scavenger.[16] Neither silylation of the NMR tube nor addition of $(C_5Me_5)_2Ti(OH)_2$ (1 equiv) has a significant effect on the rate or extent of conversion.

The **2** → **3** conversion is not significantly affected by the presence of either excess pyridine or allene.[17] In addition, a small amount of free allene (2−4%) is observed in a C_6D_6 sample of **2** that has been allowed to stand at 25 °C for several days. Excess pyridine does not increase the extent of this alternative pathway: a sample of **2** in C_6D_6 with 60 equiv of pyridine also shows only 2−4% allene after standing at 25 °C for several days (resonances arising from **1** are also present, also of *ca* 2−4% intensity, indicating that conversion of **2** to **1** has occurred). Sharp resonances for **2** and free allene are present in the ^1H spectrum of a sample of **2** containing excess allene, indicating that exchange of "free" and "bound" allene is slow on the NMR time scale. Complex **3** is stable indefinitely in C_6D_6 solution under 1 atm of N_2 and is unreactive toward H_2 (1 atm, 48 h). There is no deuterium incorporation into **3** when a C_6D_6 sample of **3** is allowed to stand under 1 atm of D_2 for several days (^1H integration, ^2H NMR).[18,19]

In contrast, placing 1 atm of H_2 over a C_6D_6 sample of **2** results in conversion to a new complex, $(C_5Me_5)_2Ti[H][OC(CH_2)Me]$ (**4**), over the course of 24 h (eq 6). Presumably, the mechanism of this reaction is simply addition of H_2 across the Ti−C bond of **2**. Consistent with this, $(C_5Me_5)_2Ti[D][OC(CH_2)(CH_2D)]$ is formed as the sole isotopomer product, when deuterium gas is used (^1H NMR). No deuterium incorporation into the C_5Me_5 rings or into the olefinic positions of **4** can be detected by ^2H NMR.



(6)

2 **4**

In conclusion, we have shown that the titanium oxo compound **1** undergoes a 2 + 2 cycloaddition reaction with allene to give the titanaoxacyclobutane complex **2**. The $TiOC_2$ ring of **2** is puckered in the solid state, with a low barrier to ring flipping in solution (fast on the NMR time scale, down to −90 °C). One possible rationalization of the puckering of the ring, involving steric interactions, has been discussed. While **2** is stable in the solid state, it slowly converts to $(C_5Me_5)(C_5Me_4CH_2)Ti[OC(CH_2)Me]$ (**3**) in solution under N_2 and to $(C_5Me_5)_2Ti[H][OC(CH_2)Me]$ (**4**) when placed under 1 atm of H_2.

Experimental Details

General Comments. All reactions and product manipulations were carried out under dry nitrogen using standard Schlenk and drybox techniques. Solvents and reagents were dried and purified as described previously.[20] Complex **1** was prepared as previously described.[6] Allene was bought from PCR Inc. and was used as received; pyridine was freshly distilled from sodium prior to use. Infrared spectra, melting points, elemental analyses, and the NMR spectra were obtained as previously described.[20] ^1H and ^{13}C NMR shifts were recorded at 300 and 75 MHz, respectively, at 25 °C, and are relative to tetramethylsilane; the residual solvent peak was used as an internal reference.

Compounds **3** and **4** are obtained as dark brown oils when prepared on a 400 mg scale, and they have not been isolated in pure form. The NMR-scale **2** → **3** and **2** → **4** conversions are, however, clean by ^1H and $^{13}C\{^1H\}$ NMR; the ^1H and $^{13}C\{^1H\}$ data for **3** and **4** are given below.

$(C_5Me_5)_2\overline{Ti[OC(CH_2)CH_2]}$ (2). Two liters of allene (STP) were condensed and frozen in a Schlenk tube at −196 °C, and the frozen material was exposed to a dynamic vacuum for 10 min. The head space above a toluene solution (50 mL) of **1** (0.86 g, 2.1 mmol) in a 250 mL Schlenk tube was evacuated, and the Schlenk tube was than exposed to the allene sample (giving a closed evacuated system containing the two Schlenk tubes). Slow warming of the allene solid resulted in uptake of the allene by the toluene solution of **1** and a gradual color change to dark green (over the course of several minutes). The resulting solution was stirred at 25 °C for 4 h, and the solvent was then removed under reduced pressure. The dark brown solid residue was dissolved in pentane (50 mL), filtered, and concentrated. Slow cooling of this solution to −80 °C yielded **2** as dark green-brown crystals (0.45 g, 58%[21]), mp 135−150 °C (decomposition to a dark brown oil). ^1H NMR (C_6D_6) (also see text): δ 4.39 (dt, J = 1.56, 1.25 Hz, 1H, $C{=}CH_2$), 4.02 (dt, J = 1.56, 1.25 Hz, 1H, $C{=}CH_2$), 1.80 (dd, J = 1.25 Hz, 1H, $TiCH_2$), 1.74 (s, 30H, C_5Me_5) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ

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(15) (a) This may result from greater destabilization of the puckered conformation for **2**, due to steric interactions between the exocyclic methylene group and the methyl groups of the C_5Me_5 rings (Figure 2b), relative to the analogous conformation for the C_5H_5 derivatives. This low barrier is also consistent with the possibility that the puckering of the metallacycle ring of **2** in the solid state results from crystal packing effects. (b) One of the reviewers raised the possibility that the Grubbs' compounds are dimers in solution (with a structure containing two planar $TiOC_2$ rings fused along the TiO edges to give a planar Ti_2O_2 ring). The C_5H_5 rings for such a dimer would be inequivalent in the absence of intra- or intermolecular exchange processes. This possibility has also been mentioned for $(C_5H_5)_2Zr[OC(CPh_2)CH_2]$: Seyferth, D.; Wang, T.; Davis, W. M. *Organometallics* **1994**, *13*, 4134. We thank Professor Seyferth for a copy of this paper.

(16) Proulx, G.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 6382.

(17) This is a qualitative statement only, as the extent of **2** → **3** conversion varies from sample to sample.

(18) (a) Bercaw, J. E.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1991**, *93*, 2045. (b) Miller, F. D.; Sanner, R. D. *Organometallics* **1988**, *7*, 818.

(19) We have found that two different isomers of **3** can be resolved in the ^1H NMR spectra of a sample in d_8-toluene, below *ca.* −30 °C. The ratio of the two isomers is *ca.* 2:1. Most likely, the two isomers result from slowing of rotation about the Ti−O bond, at the lower temperatures.

(20) Schwartz, D. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1995**, *117*, 4014.

(21) The relatively low yield results from a yellow powder that is left behind during the pentane extraction step. This solid is unreacted **1** (^1H NMR). Stirring the reaction solution for longer periods of time results in more difficulty in isolating pure samples of **2**; this is likely a result of slight conversion of **2** to **3** during this longer reaction time.

152.8 (TiO*C*), 122.3 (*C*$_5$Me$_5$), 80.2 (C=*C*H$_2$), 47.0 (Ti*C*H$_2$), 11.3 (C$_5$*Me*$_5$) ppm. IR: 2722 m, 1519 s, 1498 s, 1457 s, 1439 s, 1412 s, 1378 s, 1365 m, 1340 m, 1289 m, 1262 w, 1188 s, 1164 m, 1097 w, 1065 m, 1052 w, 1022 m, 938 s, 855 s, 805 m, 757 s, 722 w, 696 m, 660 s, 648 m, 624 w cm^{-1}. Anal. Calcd for $C_{23}H_{34}OTi$: C, 73.8; H, 9.15. Found: C, 73.7; H, 9.28.

NMR data for **3** are as follows. ^{1}H NMR (C_6D_6): δ 3.77 (m, 1H, C=C*H*$_2$), 3.51 (d, J = 1.2 Hz, 1H, C=C*H*$_2$), 2.86 (d, J = 2.7 Hz, 1H, TiC*H*$_2$), 2.08 (broad, 1H, TiC*H*$_2$), 1.85 (s, 15H, C$_5$Me$_5$), 1.80 (s, 3H, C$_5$*Me*$_4$CH$_2$), 1.67 (s, 6H, C$_5$*Me*$_4$CH$_2$), 1.65 (s, 3H, OCC*H*$_3$), 1.30 (s, 3H, C$_5$*Me*$_4$CH$_2$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 164.4 (TiO*C*), 137.1, 123.9, 122.7, 121.0, 118.7 (*C*$_5$Me$_5$), 113.0, 84.3 (*C*CH$_2$), 72.6 (Ti*C*H$_2$), 24.6 (OC*C*H$_3$), 11.9 (C$_5$*Me*$_5$), 11.5, 11.4, 11.3, 10.7 ppm. (The ^{1}H and ^{13}C{^{1}H} assignments were made based on a ^{1}H/^{13}C{^{1}H} correlation spectrum.)

NMR data for **4** are as follows. ^{1}H NMR (C_6D_6): δ 4.12 (broad s, 1H, Ti−*H*), 3.84 (broad, 1H, C=C*H*$_2$), 3.79 (broad, 1H, C=C*H*$_2$), 1.93 (s, 30H, C$_5$*Me*$_5$), 1.79 (s, 3H, OCC*H*$_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 164.8 (TiO*C*), 119.1 (*C*$_5$Me$_5$), 84.0 (*C*CH$_2$), 25.0 (OC*C*H$_3$), 11.6 (C$_5$*Me*$_5$) ppm.

X-ray Structure Determination of 2. X-ray-quality crystals of **2** were grown from pentane at −80 °C. The crystals were placed in Paratone N oil, mounted on the end of a cut quartz capillary tube, and placed under a flow of cold nitrogen on an Enraf-Nonius CAD4 diffractometer. Crystal data and numerical details of the structure determination are given in Tables 1−3. Intensities were collected with graphite-monochromatized Mo Kα (λ = 0.710 73 Å) radiation using the $\theta-2\theta$ scan technique. Lattice parameters were determined using automatic peak search and indexing procedures; **2** was found to crystallize in a triclinic lattice, with two molecules/unit cell. Intensity standards were measured every 1 h of data collection.

The raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. Correction for crystal decomposition was not necessary (1% decay). An empirical absorption correction based on averaged azimuthal ψ scans for three reflections with $\chi > 80°$ was applied to the raw data. The Freidel pairs that were collected were averaged (316 total reflections averaged).

The coordinates of the independent Ti atom were determined by Patterson techniques; the non-hydrogen atoms were located using standard least-squares and Fourier techniques.[22,23] All non-hydrogen atoms were refined anisotropically. A Fourier difference map revealed peaks at the expected positions of the methylene and olefinic hydrogen atoms associated with the metallaoxacyclobutane ring. These atoms, as well as the hydrogen atoms belonging to the C$_5$Me$_5$ rings, were placed in calculated positions and included in the structure factor calculation but not refined. All hydrogen atoms were given isotropic thermal parameters 1.3 times the B_{iso} value of the atom to which they were bonded.

The least-squares program minimized the expression $\sum w(|F_o| - |F_c|)^2$, where w is the weight of a given observation. A value of 0.05 for the p-factor was used to reduce the weight of intense reflections in the refinements. Prior to the final refinement, one reflection was rejected from the data set, on the basis of an anomalously high $w(\Delta)^2$ value. The analytical forms of the scattering factor tables for the neutral atoms were used, and all non-hydrogen scattering factors were corrected for both real and imaginary components of anomalous dispersion.

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Supporting Information Available: Tables of complete bond lengths and angles, anisotropic thermal parameters, and root-mean-square amplitudes of thermal vibration and a packing diagram for **2**, ^{1}H spectra of samples of **2** converting to **3**, with and without $(C_5H_5)_2ZrMe_2$, and of the **2** + H$_2$ → **4** and **2** + D$_2$ → **4**-d_2 reaction mixtures and the ^{1}H/^{13}C correlation spectrum of **3** (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[22] All calculations were performed on a DEC Microvax II or a DEC Microvax 4000 using locally modified Nonius-SDP software operating under Micro-VMS operating system.

[23] (a) Frenz, B. A. In *Structure Determination Package Users Guide*; Texas A & M University and Enraf-Nonius: College Station, TX, and Delft, The Netherlands, 1985. (b) Fair, C. K. In *MolEN Molecular Structure Solution Procedures*; Enraf-Nonius, Delft Instruments, X-ray Diffraction BV: Delft, The Netherlands, 1990.