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Hydron-Transfer Processes Involving an Organotitanium Oxide and Alcohols

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Thermal treatment of the μ_3-alkylidyne complexes $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CR)]$ [R = H (**1**), Me (**2**)] with alcohols (Ph_3COH, Ph_2CHOH, $PhCH_2OH$, Ph_2CMeOH, *t*BuOH, Me_2CHOH and $MeCH_2OH$) leads to partial hydronation of the alkylidyne moiety supported on the organometallic oxide $[Ti_3(\eta^5\text{-}C_5Me_5)_3O_3]$ and formation of the new oxo derivatives $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu\text{-}CHR)(OR')]$ [R = H, R′ = Ph_3C (**3**), Ph_2CH (**4**), Ph_2CMe (**5**), *t*Bu (**6**); R = Me, R′ = Ph_3C (**7**), Ph_2CH (**8**), Ph_2CMe (**9**), *t*Bu (**10**), Me_2CH (**11**), $MeCH_2$ (**12**)]. The μ-CHR group in these species lies above the Ti_3O_3 ring while the alkoxide ligand is located below it. To gain insight into the mechanism of these reactions, density functional calculations have been performed on the incorporation of alcohols into the model complexes $[\{Ti(\eta^5\text{-}C_5H_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CR)]$ [R = H (**1H**), Me (**2H**)]. Irradiation of solutions containing **1** and the alcohols leads to the compounds $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu\text{-}CH_2)(OR')]$ [R′ = Ph_3C (**13**), Ph_2CH (**14**), Ph_2CMe (**15**), *t*Bu (**16**)] where the methylene (μ-CH_2) and OR′ ligands are located *cis* with respect to the Ti_3O_3 unit. Finally, irradiation of solutions of **1** or **2** and Ph_3COH in a 1:2 ratio gives the compounds $[\{Ti(\mu_3\text{-}O)\}_3(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CHR)(OCPh_3)_2]$ [R = H (**19**), Me (**20**)]. The molecular structures of **3**, **5**, **10**, **11**, **15** and **20** have been established by single-crystal X-ray analysis.

Introduction

The use of molecules other than molecular hydrogen as a hydrogen source in the presence of both heterogeneous and homogeneous catalysts has attracted considerable attention recently as some of the processes involving these molecules, such as asymmetric hydrogen transfer, reduction of organic compounds, catalytic cracking of hydrocarbons, etc. are synthetically important both in the laboratory and industrially.[1]

If catalytic surface reactions are the focal point, hydrogen-transfer processes are among the different elementary reaction steps that hydrocarbyl fragments undergo.[2] This process entails hydrogen abstraction from the reagent by means of the catalyst, followed by hydrogen addition to the unsaturated functional group of the substrate.[3] Most of the employed hydrogen donors are organic molecules such as unsaturated hydrocarbons, amines, alcohols, etc.,[2b] and the use of these reagents provides advantages with respect to dihydrogen in terms of milder reaction conditions and regioselectivity for a particular product.

We have been investigating the potential of the μ_3-alkylidyne complexes $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CR)]$ {R = H (**1**), Me (**2**)}[4] to act as real hydrogen acceptor substrates in their reactions with different reagents. The overall results obtained in the treatment of these species with a large variety of amines[5] and silanols[6] can be considered as sequential hydron-transfer processes of alkylidyne groups on an organometallic oxide under mild conditions. Additionally, the different steps of this process (alkylidene, alkyl and alkane) have been identified.

In light of our ongoing studies of hydron-transfer processes, herein we report full details of the reactions of the μ_3-alkylidyne species **1** and **2** with alcohols. Theoretical studies allow us to propose a plausible reaction mechanism for the reaction course.

Results and Discussion

Treatment of the μ_3-alkylidyne species $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CR)]$ [R = H (**1**), Me (**2**)] with alcohols (Ph_3COH, Ph_2CHOH, $PhCH_2OH$, Ph_2CMeOH, *t*BuOH, Me_2CHOH and $MeCH_2OH$)[7] in hexane at room temperature or under slight heating gives the new oxo derivatives $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu\text{-}CHR)(OR')]$ [R = H, R′ = Ph_3C (**3**), Ph_2CH (**4**), Ph_2CMe (**5**), *t*Bu (**6**); R = Me, R′ = Ph_3C (**7**), Ph_2CH (**8**), Ph_2CMe (**9**), *t*Bu (**10**), Me_2CH (**11**), $MeCH_2$ (**12**)] as reddish orange (**3**–**6**) or violet microcrystalline products (**7**–**12**) in good yields (Scheme 1). The analytical,

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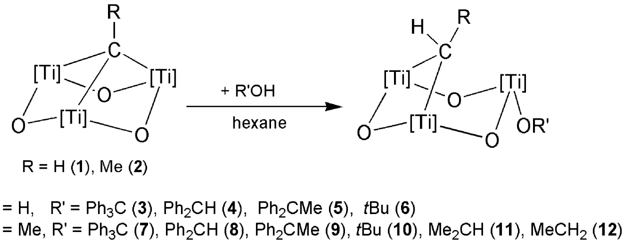
mass and NMR spectroscopic data of these compounds are consistent with partial hydronation of the alkylidyne moiety supported on the organometallic oxide moiety [$Ti_3Cp^*{}_3O_3$].



Scheme 1. Thermal treatment of [{Ti(η^5-C_5Me_5)(μ-O)}$_3$(μ_3-CR)] [R = H (**1**), Me (**2**)] with different alcohols. [Ti] = Ti(η^5-C_5Me_5).

The NMR spectra of these complexes display two types of η^5-C_5Me_5 ligands in a 2:1 ratio, which is consistent with a C_s symmetry and in contrast with the C_{3v} symmetry of the starting materials **1** and **2**, in addition to signals for the alkoxide substituents. Moreover, compounds **3**–**6** exhibit an AB spin system in their ^{1}H NMR spectra assigned to a μ-methylene moiety between two titanium atoms, while complexes **7**–**12** show a doublet and a quartet corresponding to a μ-ethylidene group bridging two metal centers (see Experimental Section). One of the key features of the ^{13}C NMR spectra is the very strong shielding [$\Delta\delta$ = 192–195 (**3**–**6**) and 203–210 ppm (**7**–**12**)] observed for the resonances of the μ-alkylidene carbon atoms (μ-*C*HR) with respect to the starting μ_3-alkylidyne group [δ = 383.5 (**1**), 401.7 (**2**)]. This fact is in agreement with the trend followed by other μ-methylene[4b,5,8,9] and μ-ethylidene[5,6] titanium systems reported in the literature. The parent ion was observed in the EI mass spectra for **10** and **11** and related fragments such as [M – CR_3]$^+$ and [M – CR_3 – CH_2]$^+$ or [M – CR_3 – C_2H_4]$^+$ were the most abundant ions for many of the synthesized complexes.

The structural situation of complexes **3**–**12** shown in Scheme 1, where the alkylidene group lies above the Ti_3O_3 unit and the alkoxide ligand below, was confirmed by the X-ray diffraction studies of **3**, **5**, **10** and **11**. The molecular structures and atom-labeling schemes of **3**, **5** and **11** are shown in Figures 1, 2, and 3, respectively, and the most relevant geometrical parameters are summarized in Table 1. The X-ray diffraction study of **10** was reported in a previous communication.[10]

The crystalline structures of **3**, **5** and **11** reveal trinuclear species with an alkylidene group (μ-CHR) bridging two titanium atoms and an alkoxide (OCR′) ligand on the third metal center, which is located on the opposite side of the Ti_3O_3 unit with respect to the alkylidene ligand in a similar way to the situation found in **10** and other trinuclear titanium oxo derivatives.[10,11] The methyl group of the bridging ethylidene in **11** is oriented towards the less crowded region between the three pentamethylcyclopentadienyl rings.

The environment of each titanium atom can be considered as pseudotetrahedral. The Ti–O distances (range: 1.80–1.82 Å) are very similar to those found in **2**[4a] and other trinuclear oxo complexes.[11–13] The Ti(1)···Ti(2) length is approximately 0.5 Å shorter than the Ti(1)···Ti(3) and Ti(2)···Ti(3) distances in the same molecule, which can be attributed to the bridging alkylidene group in a similar way to the approximate 0.2 Å shortening found in [{Ti(η^5-C_5Me_5)(μ-O)}$_3$(μ-SO_4)Cl][11] and [{Ti(η^5-C_5Me_5)(μ-O)}$_3$-{μ_3-η^2-CC(Me)NAr}] (Ar = 2,6-$Me_2C_6H_3$).[14] This shortening means that the Ti(1)–O(12)–Ti(2) angle (range: 98.2–99.4°) is smaller than the other two Ti–O–Ti angles (range: 122.9–126.6°), although the latter are still narrower than those reported for other trinuclear titanium species where the metal centers are not bridged by chelating ligands (approx. 135°).[12,13]

The bridging alkylidene group has its C(1) atom almost equidistant between the two titanium centers in a tetrahedral environment. The Ti–C(1) bond length (range: 2.087–2.130 Å) is in the expected range for titanium(IV)–C_{sp^3} bonds in trinuclear,[12,13c] mononuclear {[Ti(η^5-C_5Me_5)Me_3] (2.11 Å)},[15] dinuclear {[{Ti(η^5-C_5Me_5)Me(η^2-MeNN-CPh_2)}(μ-O){Ti(η^5-C_5Me_5)Me_2}] (2.11 Å)}[16] and tetranuclear {[Ti_4(η^5-C_5Me_5)$_4$(μ-O)$_5$$Me_2$] (2.11 Å)}[17] systems. The C(1)–C(2) distance in complexes **10** and **11** (range: 1.524–1.533 Å) is close to that of a single C–C (1.54 Å) bond.[18]

The Ti(3)–O(1) distances (range: 1.797–1.819 Å) compare well with other titanium-alkoxide bond lengths found in mononuclear {[CpTi($OC_6H_3i$$Pr_2$-2,6)$Me_2$][19] (1.802 Å) and [Ti($OC_6H_3t$$Bu_2$-2,6)$_3$I][20] (1.808 Å)}, dinuclear {[(2,6-$Ph_2C_6H_3O$)$_2$Ti(μ-Cl)$_2$Ti($OC_6H_3Ph_2$-2,6)$_2$][21] (1.817 Å)} and trinuclear {[Ti_3(μ_3-O)(μ_3-OCH_3)(μ_2-O*i*Pr)$_3$(O*i*Pr)$_6$] (1.798 Å)}[22] systems. The Ti(3)–O(1)–C(5) angle varies between 142.7° and 175.9°, with the narrower values corresponding to those complexes with less sterically demanding ligands such as *tert*-butoxide or isopropoxide. The angle [171.4(8)°] found for one of the independent molecules of **10** can be better explained as a consequence of packing requirements rather than the solid angle of the *t*BuO moiety. The C(5)–O(1) bond lengths (range: 1.357–1.434 Å) are similar to those reported for C_{sp^3}–O bonds (1.36 Å)[18] and are shorter than those corresponding to **10** and **11**, which have a lower degree of steric hindrance.

To investigate the incorporation of the alcohols into the organometallic oxides **1** and **2**, density functional theory (DFT) calculations[23] were carried out on the simplest alcohol substrate CH_3OH and the model complexes [{Ti(η^5-C_5H_5)(μ-O)}$_3$(μ_3-CR)] [R = H (**1H**), Me (**2H**)]. We examined an analogous mechanism to that previously reported for the hydron-transfer processes between silanols and the μ_3-ethylidyne complex **2H**.[6] This mechanism involves the following steps (see Figure 4): 1) hydron transfer from the substrate to one of the oxygen atoms of the Ti_3O_3 ring; 2) intramolecular hydron migration to the alkylidyne moiety; and, in the case of ethylidyne complex **2H**, 3) μ-alkylidene ligand rotation to give the observed product. Interestingly, Corma and Ujaque have recently reported that alcohol solvent molecules play an active role in heterolytic H_2 cleavage by Au^{III} complexes involving hydron migration.[24] However, the participation of alcohol molecules in the intramolecular hydron migration step is unlikely un-

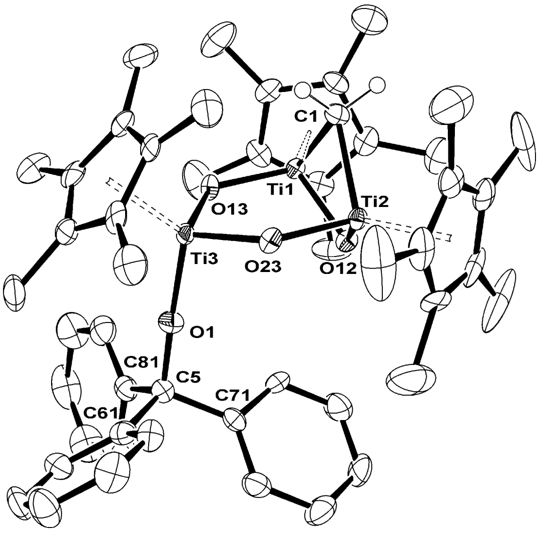


Figure 1. Simplified view of the molecular structure of **3** with thermal ellipsoids at the 50% probability level.

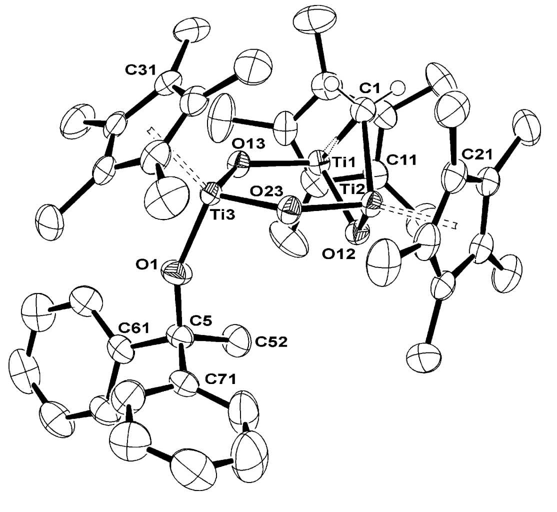


Figure 2. Simplified view of the molecular structure of **5** with thermal ellipsoids at the 50% probability level.

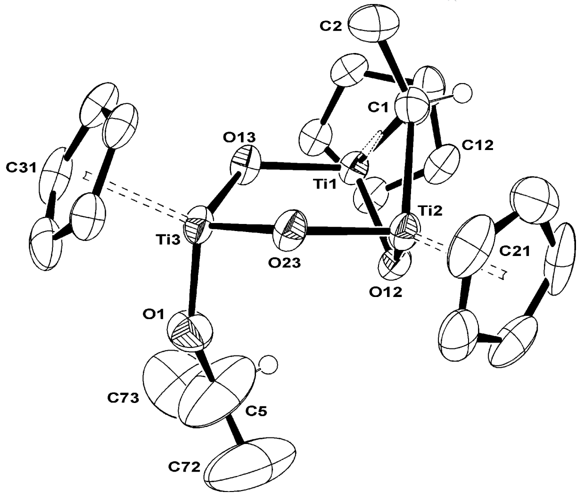


Figure 3. Simplified view of the molecular structure of **11**. Methyl groups of the pentamethylcyclopentadienyl rings have been omitted for clarity. Thermal ellipsoids at the 50% probability level.

der our experimental conditions, where **1** and **2** are treated with alcohols in a 1:1 ratio in an aprotic solvent such as hexane.

Figure 4 shows the reaction mechanisms for the incorporation of alcohols into the organometallic oxides **1H** and **2H**. The results are qualitatively similar to those previously found in the analogous process involving silanols and **2H**.[6] However, the differences between alcohols and silanols, and between the methylidyne complex **1H** and the ethylidyne complex **2H**, merit a more detailed discussion. Table 2 collects the calculated reaction and activation energies for these different processes. First, the computed energy barrier for the hydron transfer from the alcohol to **2H** is still low (56 kJ mol^{-1}), but somewhat higher than that for the hydron transfer from silanol (42 kJ mol^{-1}). Interaction of the MeO fragment with the titanium centre in **1TS$_{BC}$** or **2TS$_{BC}$** elongates the C$_{apical}$–Ti$_1$ bond length in **1H** (2.09 Å) to 2.24 Å in **1TS$_{BC}$** and that in **2H** (2.09 Å) to 2.37 Å in **2TS$_{BC}$**.[25] The C$_{apical}$–Ti$_1$ bond in intermediate **C** is already broken

Table 1. Selected average bond lengths [Å] and angles [°] in complexes **3**, **5**, **10**, **11** and **15**.

	3	**5**	**10**[a]	**11**[a]	**15**
Ti–C(1)	2.127(3)	2.122(10)	2.113(12), 2.113(1)	2.130(2), 2.087(2)	2.114(7)
Ti(3)–O(1)	1.818(3)	1.816(2)	1.790(9), 1.804(9)	1.815(3), 1.819(3)	1.829(2)
Ti–O$_{bridge}$	1.845(12)	1.849(8)	1.840(12), 1.845(8)	1.851(11), 1.852(14)	1.855(12)
Ti(1)···Ti(2)	2.812(1)	2.812(1)	2.805(3), 2.820(3)	2.826(1), 2.822(1)	2.816(1)
Ti(3)···Ti	3.284(2)	3.304(3)	3.240(2), 3.272(7)	3.250(4), 3.264(3)	3.319(1)
C(5)–O(1)	1.434(6)	1.423(4)	1.412(13), 1.405(15)	1.357(6), 1.390(7)	1.429(4)
C(1)–C(2)			1.543(14), 1.523(14)	1.524(6), 1.525(7)	
Ti(1)–C(1)–Ti(2)	82.7(2)	83.0(2)	83.1(4), 83.7(4)	83.1(2), 85.1(2)	83.5(1)
O(12)–Ti–C(1)	85.0(1)	85.1(2)	83.3(1), 83.6(1)	83.9(1), 83.9(1)	85.2(2)
Ti–O(13/23)–Ti	125.9(1)	126.6(3)	123.5(3), 125.2(1)	122.9(4), 124.4(1)	127.1(1)
Ti(1)–O(12)–Ti(2)	99.1(2)	99.1(1)	99.3(3), 99.4(3)	99.4(1), 98.2(2)	98.5(1)
O$_{bridge}$–Ti–O$_{bridge}$	104.0(3)	103.9(5)	104(1), 104(2)	104.2(10), 103.9(8)	103.9(10)
O(1)–Ti(3)–O$_{bridge}$	103.6(3)	105.3(7)	104.4(1), 105.4(6)	104.9(1), 104.4(6)	104.1(3)
Ti–C(1)–C(2)			123(3), 123(1)	122(2), 122.4(2)	
Ti(3)–O(1)–C(5)	175.9(3)	153.8(2)	171.4(8), 157.0(9)	152.0(5), 142.7(4)	157.5(2)
Alkoxide solid angle[b]	213	193	157	163	198

[a] These values correspond to the two independent molecules found in the asymmetric unit. [b] These values were calculated following Tolman's method, taking the donor oxygen atom as reference vertex.

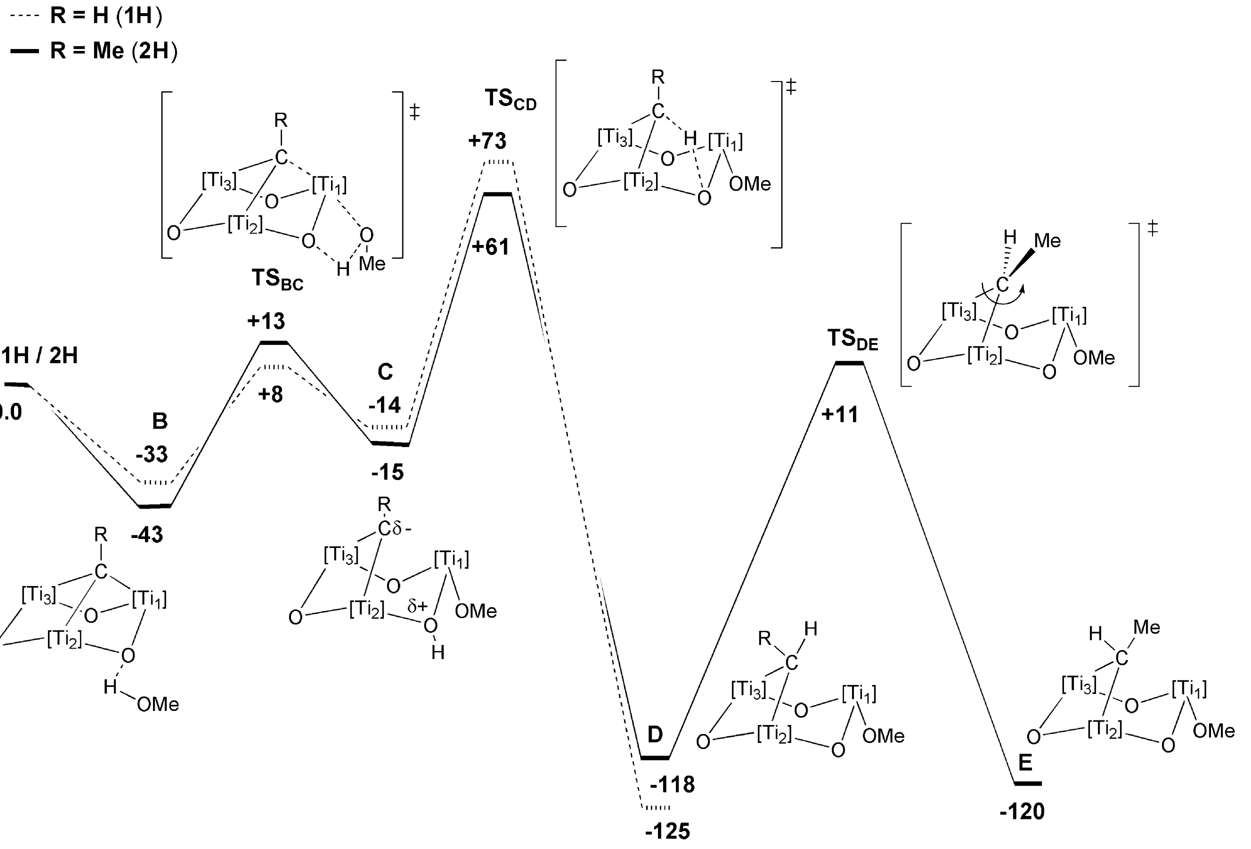


Figure 4. Potential energy profile (kJ mol^{-1}) for the incorporation of alcohols into **1H** and **2H**. [Ti] = Ti(η^5-C$_5$H$_5$).

(**1C**: 2.48 Å; **2C**: 2.84 Å), and the tetrahedral sp^3 environment of the carbon atom becomes closer to planar sp^2. The computed C$_{apical}$–Ti$_1$ distances in the formation of the analogous siloxide complex exhibit a similar pattern, with intermediate values (2.34 and 2.79 Å in the corresponding **TS$_{BC}$** and **C** species, respectively). Note also that formation of the alkoxide complexes (**C**, **D**, **E**) is energetically disfavored with respect to formation of the corresponding siloxide ones (see Table 2).

Table 2. Activation and reaction energies for the different steps during incorporation of MeOH and H$_3$SiOH[a] into **2H**. The values for the incorporation of MeOH into **1H** are given in parentheses. Energies are quoted in kJ mol^{-1}.

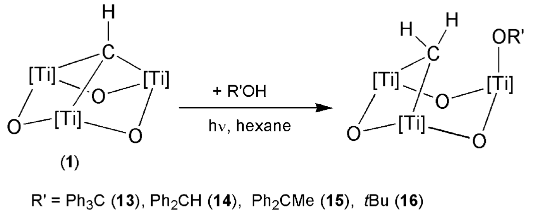
		MeOH	H$_3$SiOH[a]
Substrate proton	ΔE[b] (**C**)	–15 (–14)	–25
Transfer	$\Delta E^{\neq}$ (**B**→**TS$_{BC}$**)	+56 (+41)	+42
Intramolecular	ΔE[b] (**D**)	–118 (–125)	–129
Hydron migration	$\Delta E^{\neq}$ (**C**→**TS$_{CD}$**)	+76 (+87)	+74
μ-Ethylidene	ΔE[b] (**E**)	–120	–132
Rotation	$\Delta E^{\neq}$ (**D**→**TS$_{DE}$**)	+129	+129

[a] Values taken from ref. 6. [b] Energies are calculated relative to the corresponding reactants.

Second, the intramolecular hydron migration from the oxo site to the carbanionic moiety (**1TS$_{CD}$**) requires a larger amount of energy (87 kJ mol^{-1}) than migration to the ethylidyne moiety (**2TS$_{CD}$**, 76 kJ mol^{-1}), in agreement with the shorter C$_{apical}$–Ti$_1$ distance in **1C** (2.48 Å) with respect to that found in complex **2C** (2.84 Å). The HOMO in intermediate **C** is mainly formed by a bonding combination of p orbitals of the bridging carbon atom and d orbitals of the Ti atoms, with the computed energy of the HOMO being lower in complex **1C** (–5.8 eV) than in complex **2C** (–5.4 eV). These results suggest a reduced basicity of the methylene carbon with respect to the ethylidene one, and consequently a reduced reactivity.

Finally, a rotation of the μ-CHMe ligand in the ethylidyne complex **2H** leads to the spatial disposition found experimentally (see for example Figure 3). The computed rotational barrier for the simplified molecular model using η^5-C$_5$H$_5$ ligands is 129 kJ mol^{-1}, which is identical to that calculated for the analogous titanasiloxane complex.[6] We also observed that upon introduction of steric effects through ONIOM calculations with the more realistic [{Ti(η^5-C$_5$Me$_5$)(μ-O)}$_3$(μ$_3$-CMe)] system, the alkylidene rotational barrier is significantly lowered due to the relative destabilization of the intermediate with respect to the final product.[6] Thus, it seems obvious that, for the alkoxide complex, introduction of the steric effects of the pentamethylcyclopentadienyl groups will also reduce the rotational barrier to values closer to those observed experimentally. Hence, the steric effects induced by the η^5-C$_5$Me$_5$ ligands act as a driving force for the μ-alkylidene rotation.

In order to gain further information regarding hydron-transfer processes, we have also studied the photochemical reactions of **1** and **2** with alcohols. Thus, irradiation of hexane solutions of **2** allowed us to identify the formation of complexes **7**–**12**. In the case of **1** formation of complex **13**[26] was detected and tentatively assigned by ^{1}H NMR spectroscopy, while compounds **14**–**16** were characterized and isolated in good yields (78–84%; see Scheme 2). All these species contain the μ-methylene and alkoxide ligands on the same side of the Ti_3O_3 ring, as confirmed by the X-ray diffraction study of **15**.



Scheme 2. Photochemical treatment of **1** with alcohols. [Ti] = Ti(η^5-C_5Me_5).

Compounds **14**–**16** were characterized by NMR and IR spectroscopy, mass spectrometry and microanalysis, and the structure of **15** was elucidated by X-ray crystallography. The NMR spectra of these complexes in solution show two types of C_5Me_5 ligand in a 2:1 ratio, consistent with a C_s symmetry, resonance signals for the μ-methylene group and the corresponding signals for the alkoxide ligands. The molecular structure of **15** is shown in Figure 5, while Table 1 contains a selection of bond lengths and angles. This compound is trinuclear, with a methylene group bridging two titanium atoms and an alkoxide ($OCMePh_2$) ligand linked to the third titanium on the same side of the Ti_3O_3 unit.

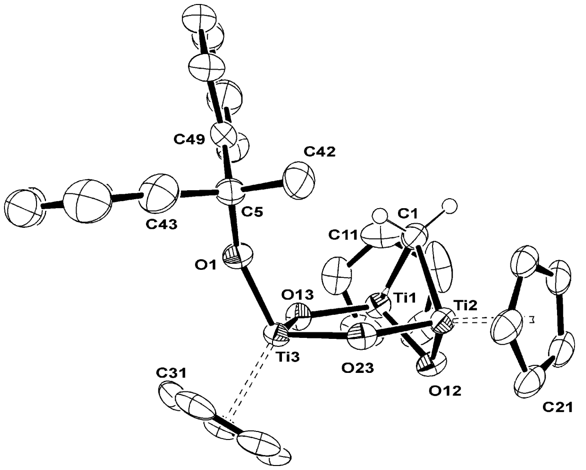
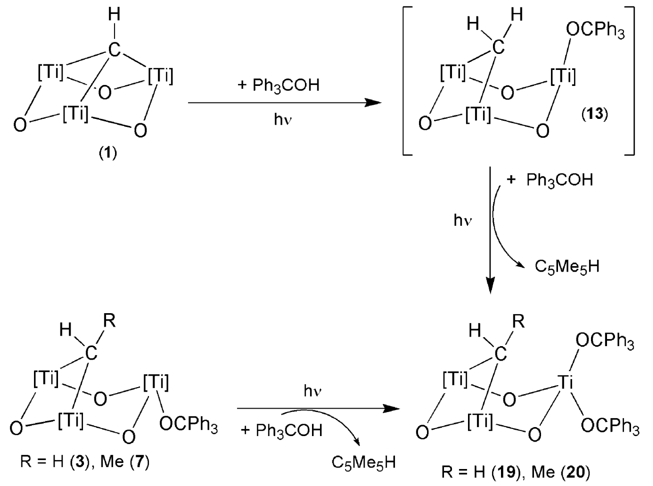


Figure 5. Simplified view of the molecular structure of **15**. Methyl groups of the pentamethylcyclopentadienyl rings have been omitted for clarity. Thermal ellipsoids at the 50% probability level.

As can be seen in Table 1, the geometrical parameters in **15** are very similar to those found for complexes **3**, **5**, **10** and **11**, the only noticeable difference with respect to **5** is the value of the Ti(3)–O(1)–C(5) angle, where the steric hindrance of the μ-methylene moiety forces this angle to be around 3.5° wider.

During the course of these reactions, we discovered that the thermal or photochemical treatment of **1** with 2-propanol or **2** with benzol afforded the complexes [{Ti(η^5-C_5Me_5)(μ-O)}$_3$(μ-CHR)(OR′)] [R = H, R′ = Me_2CH (**17**); R = Me, R′ = $PhCH_2$ (**18**)], although these complexes were always obtained as a clean mixture of two isomers, with the alkoxide ligand in the same or the opposite side with respect to the μ-alkylidene moiety. Attempts to completely separate the mixture of **18** in order to prepare analytically pure complexes were unsuccessful. However, the isomer of **17** containing the alkoxide ligand and the μ-alkylidene moiety on the same side of the Ti_3O_3 ring could be isolated in a pure form after several recrystallization steps (see Experimental Section).

When solutions of μ_3-methylidyne complex **1** and Ph_3COH in an approximate 1:1 ratio were irradiated, we surprisingly observed by NMR spectroscopy that the reaction did not stop in the formation of compound **13** but progressed to give the new complex [{Ti(μ_3-O)}$_3$(η^5-C_5Me_5)$_2$(μ-CH_2)($OCPh_3$)$_2$] (**19**). We therefore added one further equivalent of alcohol, and after several days irradiating with an ultraviolet lamp observed the formation of the oxo derivative **19** and the elimination of C_5Me_5H (Scheme 3). Complex **19** is better obtained on a preparative scale by treating **3** with one equivalent of the alcohol.



Scheme 3. Formation of complexes **19** and **20**. [Ti] = Ti(η^5-C_5Me_5).

In an attempt to extend this study, we tried the same reaction with **1** and the rest of the alcohols and observed how C_5Me_5H elimination was limited to the most sterically crowded alcohols (Ph_2CHOH, Ph_2CMeOH, *t*BuOH). Elimination of C_5Me_5H was observed by ^{1}H NMR spectroscopy in these cases, although attempts to isolate the corresponding pure products [{Ti(μ_3-O)}$_3$(η^5-C_5Me_5)$_2$(μ-CH_2)(OCR_3)$_2$] (R = Ph_2CH, Ph_2CMe, *t*Bu), were unsuccessful.

Solutions of **2** and the alcohols Ph_3COH, Ph_2CHOH, Ph_2CMeOH and *t*BuOH in a 1:2 ratio, or solutions of **7**–**10** and the alcohol (1:1), were also irradiated. The displacement of C_5Me_5H was also identified by ^{1}H NMR spectroscopy, but the corresponding pure compound [{Ti(μ_3-O)}$_3$(η^5-C_5Me_5)$_2$(μ-CHMe)($OCPh_3$)$_2$] (**20**) could only be isolated from the reaction with Ph_3COH (Scheme 3).

The formation of **19** and **20** likely implies a change of hapticity of the pentamethylcyclopentadienyl ligand from η^5 to η^1 on the alkoxide-supporting titanium center when a molecule of the alcohol coordinates to the same titanium atom, as proposed by Bursten et al. for compounds of type [(η^5-C_5H_5)$_3$MX] (M = Zr, Hf), where X is an alkoxide or amido ligand.[27] Subsequent cleavage of the O–H and Ti(η^1-C_5Me_5) bonds would lead to replacement of the pentamethylcyclopentadienyl group by the corresponding alkoxide ligand.

Complexes **19** and **20** were isolated as orange-reddish or dark violet microcrystalline solids, respectively, in good yields, and were characterized by standard analytical and spectroscopic techniques (see Experimental Section). The NMR spectra are in agreement with the structures suggested in Scheme 3 and show the presence of one type of η^5-C_5Me_5 ligand, consistent with a C_s symmetry in solution. The ^{1}H NMR spectrum of **19** reveals an AB spin system assigned to a μ-methylene moiety between two titanium atoms, and that of the complex **20** shows a doublet and a quartet, which correspond to a μ-ethylidene bridge between two metal centers. Signals for the $OCPh_3$ groups are also observed. The most significant features of the ^{13}C NMR spectra include the non-equivalence of the quaternary carbon atoms of the alkoxide ligand (-O*C*Ph_3) [δ = 94.1, 94.5 (**19**), 94.2, 94.6 ppm (**20**)] and a very strong shielding for the resonance of the bridging carbon atom ($\Delta\delta \approx 200$ ppm) with respect to the starting μ_3-alkylidyne group, but quite similar to the starting μ-alkylidene complexes **3**, **7**, and **13**. A single-crystal X-ray diffraction study of **20** was undertaken to confirm the NMR assignments.

Dark violet crystals of [{Ti(μ_3-O)}$_3$(η^5-C_5Me_5)$_2$(μ-CHMe)($OCPh_3$)$_2$] (**20**) were grown from a pentane solution at –20 °C. Figure 6 shows the molecular structure of **20**, which contains an ethylidene group bridging two titanium atoms and two η^5-C_5Me_5 ligands linked to the same titanium atoms, while there are two alkoxide ligands joined to the third titanium atom that are located on opposite sides with respect to the Ti_3O_3 moiety.

The ethylidene C(1) atom is almost equidistant to the two titanium centers in a tetrahedral environment. The Ti–C(1) [av. 2.141(10) Å] bond length compares quite well with those found for **3**, **5**, **10**, **11** and **15** and lies in the range observed for titanium(IV)-C_{sp^3} bond lengths in complexes with different nuclearity.[15–17]

The environment of each titanium atom can be considered as pseudotetrahedral. Analogously to **3**, **5**, **10**, **11** and **15**, the Ti(1)···Ti(2) length is approximately 0.5 Å shorter than the Ti(1)···Ti(3) and Ti(2)···Ti(3) distances in the same molecule, which can be attributed to the bridging alkylidene. This fact produces a Ti(1)–O(12)–Ti(2) [99.7(1)°] angle smaller than the other two Ti–O–Ti angles [av. 124.9(4)°], which are comparable to those reported for other trinuclear titanium species where the metal centers are not bridged by chelating ligands.[12,28]

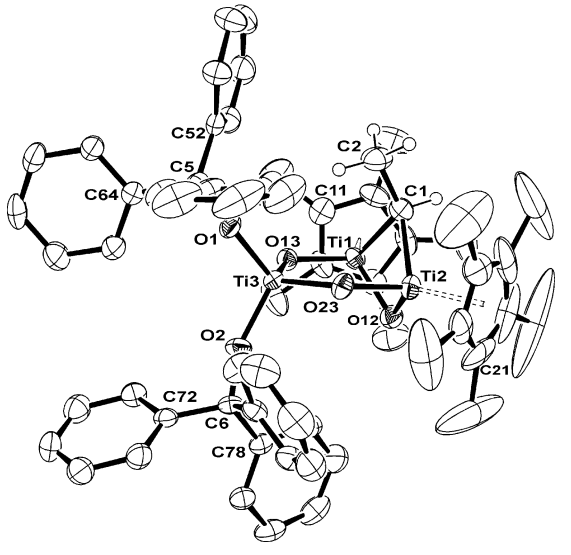


Figure 6. Simplified view of the molecular structure of **20**. Selected bond lengths [Å] and angles [°]: Ti–C(1) 2.141(10), Ti(3)–O(1) 1.794(2), Ti(3)–O(2) 1.807(2), Ti–O_{bridge} 1.849(17), Ti(1)···Ti(2) 2.837(1), Ti(3)···Ti 3.273(2), C(5)–O(1) 1.431(4), C(6)–O(2) 1.441(4), C(1)–C(2) 1.539(6); Ti(1)–C(1)–Ti(2) 83.0(1), O(12)–Ti–C(1) 84.5(3), Ti–O(13/23)–Ti 124.9(4), Ti(1)–O(12)–Ti(2) 99.7(1), O_{bridge}–Ti–O_{bridge} 104.9(10), O(1)–Ti(3)–O_{bridge} 110.1(14), O(2)–Ti(3)–O_{bridge} 109.7(4), Ti–C(1)–C(2) 121(2), Ti(3)–O(1)–C(5) 175.2(2), Ti(3)–O(2)–C(6) 151.7(2), O(1)–Ti(3)–O(2) 110.8(1). Thermal ellipsoids at the 50% probability level.

It can be seen that the O(1)–Ti(3)–O(2) angle [110.8(1)°] lies in the range found for simple four-coordinate mononuclear {[(Ar′′O)$_2$Ti($OCPh_2C_4Et_4$)] [112.48(5)°]} and dinuclear {[(Ar′′O)$_2$Ti(μ-PhCN)$_2$Ti(OAr′′)$_2$] [117.3(2)°]} complexes.[29] The Ti–$O_{alkoxide}$ distances [1.794(2), 1.807(2) Å] compare well with the range typically found for aryloxide ligands bound to Ti^{IV} metal centers.[30] The steric hindrance of the μ-alkylidene ligand forces the Ti–O–$C_{alkoxide}$ angle located on the same side with respect to the Ti_3O_3 unit to be 175.2(2)°, in other words almost linear. As the Ph_3C fragment shows a relatively high solid angle (213°), the repulsion between the two alkoxide ligands makes the second Ti–O–$C_{alkoxide}$ angle around 24° narrower.

Conclusions

In summary, complexes **1** and **2** react with a variety of alcohols (primary, secondary and tertiary), through a hydron transfer to the μ_3-alkylidyne moiety supported on the organometallic oxide [Ti_3(η^5-C_5Me_5)$_3O_3$], to give the alkylidene derivatives [{Ti(η^5-C_5Me_5)(μ-O)}$_3$(μ-CHR)(OR′)] containing the alkoxide ligand and the alkylidene fragment in a *cis* or *trans* disposition with respect to the Ti_3O_3 ring. Crowded alcohols such as Ph_3COH, Ph_2CHOH, Ph_2CMeOH and *t*BuOH are able to replace a pentamethylcyclopentadienyl ligand from the starting compounds. DFT calculations have allowed us to describe the incorporation of the alcohols at a mechanistic level. The proposal initially suggests a hydron transfer from the alcohols to one oxygen atom of the Ti_3O_3 ring, followed by an intramolecular hydron migration to give a μ-alkylidene moiety, and a μ-ethylidene ligand rotation, which leads to the experimentally observed product.

Experimental Section

General: All manipulations of the described compounds were carried out in the absence of air and moisture using Schlenk line or glovebox techniques. Solvents were carefully dried with the appropriate drying agents and distilled prior to use.

$[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CR)]$ [R = H (**1**), Me (**2**)] were synthesized according to the published procedures.[4] Ph_3COH, Ph_2CHOH, $PhCH_2OH$, Ph_2CMeOH, *t*BuOH, Me_2CHOH and $MeCH_2OH$ were purchased from Aldrich and sublimed or dried/distilled before use.

Elemental analysis (C, H, N) was performed with a Heraeus CHN-O-RAPID and/or Perkin–Elmer 2400-Serie II C, H, N, S/O. IR spectra were obtained for KBr pellets with a FT-IR Perkin–Elmer SPECTRUM 2000 spectrophotometer. NMR spectra were recorded with Varian NMR System spectrometers: Unity-300 or Mercury-VX. Trace amounts of protonated solvents or carbon of the solvent were used as references; chemical shifts are reported relative to TMS. Mass spectra were measured with a Hewlett–Packard 5988A spectrometer.

Preparation of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu_3\text{-}O)\}_3(\mu\text{-}CH_2)(OCPh_3)]$ (3): A solution of **1** (0.20 g, 0.33 mmol) and Ph_3COH (85 mg, 0.33 mmol) in hexane (50 mL) was placed in an amber-stained 100-mL Carius tube fitted with a Young's valve and stirred overnight at 120 °C. The reddish solution was concentrated and cooled to obtain red crystals of **3** (yield 0.26 mg, 93%). IR (KBr): $\tilde{\nu}$ = 2908 (s), 1489 (m), 1443 (s), 1374 (s), 1208 (w), 1151 (m), 1086 (s), 1055 (vs), 1027 (s), 940 (w), 918 (m), 899 (m), 819 (s), 749 (vs), 698 (vs), 667 (vs), 624 (s), 487 (s), 420 (s) cm^{-1}. ^1H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 1.90 (s, 15 H, C_5Me_5), 1.96 (s, 30 H, C_5Me_5), 5.55, 6.31 (AB spin system, $^2J_{H,H}$ = 9.0 Hz, 2 H, μ-CH_2), 7.00–7.70 (15 H, $OCPh_3$) ppm. ^{13}C NMR (75 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 11.6, 11.9 (q, $J_{C,H}$ = 125.7 Hz, C_5Me_5), 93.5 (s, $OCPh_3$), 120.3, 123.4 (m, C_5Me_5), 126.5, 127.7, 128.9, 149.1 ($OCPh_3$), 188.5 (t, $J_{C,H}$ = 123.9 Hz, μ-CH_2) ppm. EI MS: *m/z* (%) 736 (1) $[M - C_5Me_5]^+$, 627 (3) $[M - CPh_3]^+$, 610 (1) $[M - HOCPh_3]^+$. $C_{50}H_{62}O_4Ti_3$ (870.64): calcd. C 68.97, H 7.18; found C 68.37, H 6.90.

Preparation of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu_3\text{-}O)\}_3(\mu\text{-}CH_2)(OCHPh_2)]$ (4): Ph_2CHOH (60 mg, 0.33 mmol) was added to a solution of **1** (0.2 g, 0.33 mmol) in hexane (50 mL) in an amber-stained Carius tube and the mixture stirred and heated at 50 °C for a day. The resulting reddish solution was filtered, concentrated and cooled to –20 °C to afford 0.21 g (82%) of dark-red microcrystalline solid identified as **4** slightly contaminated with compound **14** (approx. 10% by ^1H NMR). ^1H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 1.95 (s, 30 H, C_5Me_5), 2.05 (s, 15 H, C_5Me_5), 5.66, 6.29 (AB spin system, $^2J_{H,H}$ = 9.0 Hz, 2 H, μ-CH_2), 6.78 (s, 1 H, $OCHPh_2$), 7.00–7.60 (10 H, $OCHPh_2$) ppm. ^{13}C NMR (75 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 11.7 (q, $J_{C,H}$ = 125.5 Hz, C_5Me_5 overlapping), 86.4 (d, $J_{C,H}$ = 141.7 Hz, $OCHPh_2$), 120.5, 123.1 (m, C_5Me_5), 126.8, 127.0, 128.2, 147.1 ($OCHPh_2$), 189.6 (t, $J_{C,H}$ = 123.9 Hz, μ-CH_2) ppm. $C_{44}H_{58}O_4Ti_3$ (794.54): calcd. C 66.50, H 7.36; found C 66.35, H 7.00.

Preparation of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu_3\text{-}O)\}_3(\mu\text{-}CH_2)(OCMePh_2)]$ (5): Compound **5** was prepared similarly to **3** from **1** (0.20 g, 0.33 mmol) and Ph_2CMeOH (65 mg, 0.33 mmol) in hexane (50 mL) at 120 °C for one day. The amber-stained Carius tube was opened in a glovebox and the solution was filtered, concentrated and cooled to –20 °C to yield 0.23 g (87%) of **5** as a dark red microcrystalline solid. IR (KBr): $\tilde{\nu}$ = 2908 (s), 1493 (m), 1450 (s), 1375 (m), 1358 (m), 1203 (s), 1092 (bs), 1025 (s), 905 (w), 765 (vs), 654 (s), 559 (s), 499 (m), 461 (m), 391 (s) cm^{-1}. ^1H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 1.97 (s, 15 H, C_5Me_5), 1.99 (s, 30 H, C_5Me_5), 2.05 (s, 3 H, $OCMePh_2$), 5.64, 6.30 (AB spin system, $^2J_{H,H}$ = 9.2 Hz, 2 H, μ-CH_2), 7.00–7.70 (10 H, $OCMePh_2$) ppm. ^{13}C NMR (75 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 11.8, 11.9 (q, $J_{C,H}$ = 125.4 Hz, C_5Me_5), 33.1 (q, $J_{C,H}$ = 126.4 Hz, $OCMePh_2$), 88.0 (m, $OCMePh_2$), 120.3, 123.0 (m, C_5Me_5), 126.5, 126.9, 127.9, 150.5 ($OCHPh_2$), 189.2 (t, $J_{C,H}$ = 125.2 Hz, μ-CH_2) ppm. EI MS: *m/z* (%) 673 (2) $[M - C_5Me_5]^+$, 627 (6) $[M - CMePh_2]^+$, 493 (100) $[M - C_5Me_5 - CMePh_2]^+$, 477 (32) $[M - C_5Me_5 - OCMePh_2]^+$. $C_{45}H_{60}O_4Ti_3$ (808.57): calcd. C 66.84, H 7.48; found C 66.84, H 7.79.

Preparation of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu_3\text{-}O)\}_3(\mu\text{-}CH_2)(OCMe_3)]$ (6): Complex **1** (0.195 g, 0.32 mmol), *tert*-butanol (27 mg, 0.32 mmol) and hexane (50 mL) were placed in an amber-stained 100-mL Carius tube and the mixture heated at 100 °C for one day. The isolated compound **6** was obtained in a total yield of 82% (0.18 g). IR (KBr): $\tilde{\nu}$ = 2910 (s), 2856 (m), 1493 (w), 1435 (m), 1374 (m), 1261 (w), 1185 (w), 1065 (w), 1010 (m), 784 (vs), 757 (vs), 673 (m), 629 (w) cm^{-1}. ^1H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 1.34 (s, 9 H, $OCMe_3$), 2.01 (s, 15 H, C_5Me_5), 2.10 (s, 30 H, C_5Me_5), 5.67, 6.25 (AB spin system, $^2J_{H,H}$ = 9.2 Hz, 2 H, μ-CH_2) ppm. ^{13}C NMR (75 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 11.8, 11.9 (q, $J_{C,H}$ = 125.4 Hz, C_5Me_5), 32.4 (qm, $J_{C,H}$ = 124.5 Hz, $OCMe_3$), 81.2 (m, $OCMe_3$); 120.0, 122.3 (m, C_5Me_5), 189.2 (t, $J_{C,H}$ = 126.0 Hz, μ-CH_2) ppm. EI MS: *m/z* (%) 684 (1) $[M]^+$, 627 (10) $[M - CMe_3]^+$, 611 (2) $[M - OCMe_3]^+$, 549 (35), $[M - C_5Me_5]^+$. $C_{35}H_{56}O_4Ti_3$ (684.44): calcd. C 61.41, H 8.25; found C 61.59, H 7.96.

Preparation of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu_3\text{-}O)\}_3(\mu\text{-}CHMe)(OCPh_3)]$ (7): A mixture of **2** (0.10 g, 0.16 mmol) and Ph_3COH (42 mg, 0.16 mmol) in hexane (50 mL) was placed in a 100-mL Carius tube fitted with a Young's valve and stirred overnight at room temperature. The final solution was concentrated and cooled to obtain violet crystals of **7** (yield 88 mg, 62%). IR (KBr): $\tilde{\nu}$ = 2904 (s), 1489 (m), 1445 (s), 1374 (m), 1227 (m), 1156 (m), 1088 (m), 1058 (vs), 1028 (s) 812 (vs), 743 (vs), 656 (vs) cm^{-1}. ^1H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 1.91 (s, 15 H, C_5Me_5), 1.92 (s, 30 H, C_5Me_5), 1.97 (d, $^3J_{H,H}$ = 7.8 Hz, 3 H, μ-$CHMe$), 5.96 (q, $^3J_{H,H}$ = 7.8 Hz, 1 H, μ-$CHMe$), 6.90–7.70 (15 H, $OCPh_3$) ppm. ^{13}C NMR (75 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 11.4, 12.4 (q, $J_{C,H}$ = 125.8 Hz, C_5Me_5), 28.9 (qm, $J_{C,H}$ ≈ 123 Hz, μ-$CHMe$), 93.6 (s, $OCPh_3$), 119.9, 123.1 (m, C_5Me_5), 126.6, 127,3, 129.2, 147.7 ($OCPh_3$), 203.7 (dq, $J_{C,H}$ = 108.5 Hz, μ-$CHMe$) ppm. EI MS: *m/z* (%) 721 (1) $[M - C_5Me_5 - C_2H_4]^+$, 641 (1) $[M - CPh_3]^+$, 613 (8) $[M - CPh_3 - C_2H_4]^+$. $C_{51}H_{64}O_4Ti_3$ (884.66): calcd. C 69.24, H 7.29; found C 69.76, H 7.01.

Preparation of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu_3\text{-}O)\}_3(\mu\text{-}CHMe)(OCHPh_2)]$ (8): This complex was prepared in a similar manner to **7** from Ph_2CHOH (0.15 g, 0.80 mmol), **2** (0.50 g, 0.80 mmol) and hexane (50 mL) except that the reaction mixture was stirred for four hours at room temperature. The final solution was concentrated and cooled to obtain **8** as a violet microcrystalline solid (yield 0.64 g, 98%). IR (KBr): $\tilde{\nu}$ = 2908 (m), 1492 (w), 1447 (m), 1376 (m), 1169 (w), 1093 (m), 1064 (m), 1026 (m) 770 (s), 746 (vs), 707 (s), 654 (s), 622 (m), 487 (w), 423 (m), 388 (m) cm^{-1}. ^1H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 1.88 (s, 30 H, C_5Me_5), 1.94 (d, $^3J_{H,H}$ =

7.8 Hz, 3 H, μ-CH*Me*), 2.12 (s, 15 H, C$_5$*Me*$_5$), 6.13 (q, $^3J_{H,H}$ = 7.8 Hz, 1 H, μ-C*H*Me), 6.76 (s, 1 H, OC*H*Ph$_2$), 7.00–7.50 (m, 10 H, OCH*Ph*$_2$) ppm. ^{13}C NMR (75 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 11.3, 12.0 (q, $J_{C,H}$ = 126.2 Hz, C$_5$*Me*$_5$), 30.5 (qm, $J_{C,H}$ = 125.5 Hz, μ-CH*Me*), 87.0 (d, $J_{C,H}$ = 143.6 Hz, O*C*HPh$_2$), 120.0, 122.8 (m, *C*$_5$Me$_5$), 126.8, 127.3, 128.1, 146.8 (OCH*Ph*$_2$), 209.0 (dm, $J_{C,H}$ = 111.8 Hz, μ-*C*HMe) ppm. EI MS: *m*/*z* (%) 641 (9) [M – Ph$_2$CH]$^+$, 625 (2) [M – Ph$_2$CHO]$^+$, 613 (83) [M – Ph$_2$CH – C$_2$H$_4$]$^+$. C$_{45}$H$_{60}$O$_4$Ti$_3$ (808.57): calcd. C 66.84, H 7.48; found C 66.99, H 7.71.

Preparation of [{Ti(η^5-C$_5$Me$_5$)(μ$_3$-O)}$_3$(μ-CHMe)(OCMePh$_2$)] (9): Ph$_2$CMeOH (0.13 g, 0.64 mmol) was added to a solution of **2** (0.40 g, 0.64 mmol) in hexane (50 mL) in a Carius tube fitted with a Young's valve and stirred at 50 °C for one day. The resulting violet solution was filtered, concentrated and cooled to 4 °C to afford 0.52 g (98%) of violet crystals identified as **9**. IR (KBr): ṽ = 2908 (s), 2854 (s), 1492 (m), 1444 (s), 1374 (m), 1233 (w), 1194 (w), 1116 (m), 1101 (s), 1062 (s), 986 (s), 742 (vs), 726 (vs), 698 (s), 651 (s), 623 (s), 576 (m), 421 (m), 386 (m) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 1.93 (s, 3 H, OC*Me*Ph$_2$), 1.94 (s, 30 H, C$_5$*Me*$_5$), 1.96 (d, $^3J_{H,H}$ = 7.5 Hz, 3 H, μ-CH*Me*), 2.01 (s, 15 H, C$_5$*Me*$_5$), 6.06 (q, $^3J_{H,H}$ = 7.8 Hz, 1 H, μ-C*H*Me), 6.90–7.60 (10 H, OCMe*Ph*$_2$) ppm. ^{13}C NMR (75 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 11.4, 12.1 (q, $J_{C,H}$ = 125.3 Hz, C$_5$*Me*$_5$), 29.4 (qm, $J_{C,H}$ = 124.6 Hz, μ-CH*Me*), 34.6 (q, $J_{C,H}$ = 127.6 Hz, OC*Me*Ph$_2$), 88.4 (m, O*C*MePh$_2$), 119.7, 122.6 (m, *C*$_5$Me$_5$), 126.7, 127.2, 127.9, 149.7 (OCMe*Ph*$_2$), 207.0 (dm, $J_{C,H}$ = 116.1 Hz, μ-*C*HMe) ppm. EI MS: *m*/*z* (%) 641 (4) [M – Ph$_2$CMe]$^+$, 613 (25) [M – Ph$_2$CMe – C$_2$H$_4$]$^+$, 478 (27) [M – Ph$_2$CMe – C$_2$H$_4$ – C$_5$Me$_5$]$^+$, 343 (24) [M – Ph$_2$CMe – C$_2$H$_4$ – 2C$_5$Me$_5$]$^+$. C$_{46}$H$_{62}$O$_4$Ti$_3$ (822.60): calcd. C 67.16, H 7.60; found C 67.55, H 7.83.

Preparation of [{Ti(η^5-C$_5$Me$_5$)(μ$_3$-O)}$_3$(μ-CHMe)(OCMe$_3$)] (10): *tert*-Butanol (12 mg, 0.16 mmol) was added to a solution of **2** (0.10 g, 0.16 mmol) in hexane (50 mL) in a Carius tube fitted with a Young's valve and stirred overnight at room temperature. The solution was filtered, concentrated and cooled to obtain violet crystals of **10** (yield 0.11 g, 99%). IR (KBr): ṽ = 2965 (s), 2908 (vs), 2856 (s), 1491 (w), 1438 (m), 1377 (m), 1262 (w), 1227 (m), 1183 (s), 1021 (vs), 740 (vs), 654 (vs), 621 (s), 566 (s) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 1.28 (s, 9 H, OC*Me*$_3$), 1.94 (d, $^3J_{H,H}$ = 7.8 Hz, 3 H, μ-CH*Me*), 1.99 (s, 30 H, C$_5$*Me*$_5$), 2.13 (s, 15 H, C$_5$*Me*$_5$), 6.08 (q, $^3J_{H,H}$ = 7.8 Hz, 1 H, μ-C*H*Me) ppm. ^{13}C NMR (75 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 11.4, 12.2 (q, $J_{C,H}$ = 126.1 Hz, C$_5$*Me*$_5$), 29.5 (qm, $J_{C,H}$ = 124.6 Hz, μ-CH*Me*), 32.8 (qm, $J_{C,H}$ = 124.6 Hz, OC*Me*$_3$), 81.7 (m, O*C*Me$_3$), 119.5, 121.8 (m, *C*$_5$Me$_5$), 207.0 (dq, $J_{C,H}$ = 116.5 Hz, μ-*C*HMe) ppm. EI MS: *m*/*z* (%) 698 (1) [M]$^+$, 641 (6) [M – CMe$_3$]$^+$, 613 (30) [M – CMe$_3$ – C$_2$H$_4$]$^+$. C$_{36}$H$_{58}$O$_4$Ti$_3$ (698.46): calcd. C 61.90, H 8.37; found C 61.40, H 7.79.

Preparation of [{Ti(η^5-C$_5$Me$_5$)(μ$_3$-O)}$_3$(μ-CHMe)(OCHMe$_2$)] (11): 2-Propanol (37 μL, 0.48 mmol) was added to a solution of **2** (0.30 g, 0.48 mmol) in hexane (50 mL) in a 100-mL Carius tube fitted with a Young's valve and stirred for two hours at room temperature. The final solution was concentrated and cooled to obtain violet crystals of **11** (yield 0.30 g, 90%). IR (KBr): ṽ = 2963 (s), 2909 (vs), 2856 (s), 1493 (w), 1438 (m), 1374 (s), 1332 (w), 1262 (w), 1146 (s), 1123 (s), 1021 (m), 994 (s), 849 (w), 743 (vs), 656 (vs), 623 (s), 600 (s), 569 (m), 451 (w), 391 (s) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 1.16 (d, $^3J_{H,H}$ = 6.0 Hz, 6 H, OCH*Me*$_2$), 1.95 (d, $^3J_{H,H}$ = 7.8 Hz, 3 H, μ-CH*Me*), 1.97 (s, 30 H, C$_5$*Me*$_5$), 2.14 (s, 15 H, C$_5$*Me*$_5$), 4.68 (sept, $^3J_{H,H}$ = 6.0 Hz, 1 H, OC*H*Me$_2$), 6.16 (q, $^3J_{H,H}$ = 7.8 Hz, 1 H, μ-C*H*Me) ppm. ^{13}C NMR (75 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 11.3, 11.9 (q, $J_{C,H}$ = 125.4 Hz, C$_5$*Me*$_5$), 26.5 (qm, $J_{C,H}$ = 124.2 Hz, μ-CH*Me*), 30.3 (qd, $J_{C,H}$ = 124.5 Hz, OCH*Me*$_2$), 76.4 (dm, $J_{C,H}$ = 141.8 Hz, O*C*HMe$_2$), 119.6, 122.0 (m, *C*$_5$Me$_5$), 208.8 (dm, $J_{C,H}$ = 117.1 Hz, μ-*C*HMe) ppm. EI MS: *m*/*z* (%) 684 (2) [M],$^+$ 656 (2) [M – CHMe]$^+$, 641 (10) [M – CHMe$_2$]$^+$, 625 (10) [M – OCHMe$_2$]$^+$, 613 (89) [M – CHMe$_2$ – C$_2$H$_4$]$^+$, 597 (12) [M – OCHMe$_2$ – C$_2$H$_4$]$^+$. C$_{35}$H$_{56}$O$_4$Ti$_3$ (684.44): calcd. C 61.41, H 8.25; found C 60.88, H 8.42.

Preparation of [{Ti(η^5-C$_5$Me$_5$)(μ$_3$-O)}$_3$(μ-CHMe)(OCH$_2$Me)] (12): This complex was prepared in a similar manner to **11** from **2** (0.30 g, 0.48 mmol), ethanol (28 μL, 0.48 mmol) and hexane (50 mL). Yield 0.25 g (76%). IR (KBr): ṽ = 2908 (m), 2852 (m), 1495 (w), 1436 (m), 1374 (m), 1129 (s), 1068 (m), 1028 (w), 919 (w), 772 (vs), 676 (vs), 625 (s), 584 (s), 416 (s) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 1.16 (t, $^3J_{H,H}$ = 6.6 Hz, 3 H, OCH$_2$*Me*), 1.95 (d, $^3J_{H,H}$ = 7.8 Hz, 3 H, μ-CH*Me*), 1.97 (s, 30 H, C$_5$*Me*$_5$), 2.15 (s, 15 H, C$_5$*Me*$_5$), 4.30 (q, $^3J_{H,H}$ = 6.9 Hz, 2 H, OC*H*$_2$Me), 6.19 (q, $^3J_{H,H}$ = 7.8 Hz, 1 H, μ-C*H*Me) ppm. ^{13}C NMR (75 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 11.3, 11.7 (q, $J_{C,H}$ = 125.4 Hz, C$_5$*Me*$_5$), 20.0 (qm, $J_{C,H}$ = 124.6 Hz, μ-CH*Me*), 30.5 (qm, $J_{C,H}$ = 124.5 Hz, OCH$_2$*Me*), 71.2 (tm, $J_{C,H}$ = 139.9 Hz, O*C*H$_2$Me), 119.7, 122.1 (m, *C*$_5$Me$_5$), 209.3 (dm, $J_{C,H}$ = 117.1 Hz, μ-*C*HMe) ppm. EI MS: *m*/*z* (%) 613 (7) [M – CH$_2$Me – C$_2$H$_4$]$^+$, 597 (2) [M – OCH$_2$Me – C$_2$H$_4$]$^+$. C$_{34}$H$_{54}$O$_4$Ti$_3$ (670.41): calcd. C 60.91, H 8.12; found C 60.61, H 8.59.

Preparation of [{Ti(η^5-C$_5$Me$_5$)(μ$_3$-O)}$_3$(μ-CH$_2$)(OCHPh$_2$)] (14): This compound was prepared from **1** (0.20 g, 0.33 mmol) and Ph$_2$CHOH (61 mg, 0.33 mmol) in hexane (60 mL) upon irradiation with a sun lamp for 10 h to give a dark-red microcrystalline solid. Yield 0.20 g (78%). IR (KBr): ṽ = 2911 (s), 2854 (m), 1492 (w), 1449 (m), 1374 (m), 1186 (m), 1123 (s), 1070 (m), 1027 (m), 909 (w), 756 (vs), 672 (vs), 627 (vs) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$] benzene, 20 °C, TMS): δ = 1.98 (s, 30 H, C$_5$*Me*$_5$), 2.04 (s, 15 H, C$_5$*Me*$_5$), 5.91, 6.40 (AB spin system, $^2J_{H,H}$ = 9.3 Hz, 2 H, μ-C*H*$_2$), 6.70 (s, 1 H, OC*H*Ph$_2$), 7.00–7.50 (10 H, OCH*Ph*$_2$) ppm. ^{13}C NMR (75 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 11.77, 11.80 (q, $J_{C,H}$ = 125.8 Hz, C$_5$*Me*$_5$), 86.5 (d, $J_{C,H}$ = 140.5 Hz, O*C*HPh$_2$), 120.1, 122.9 (m, *C*$_5$Me$_5$), 126.9, 127.1, 128.2, 146.8 (OCH*Ph*$_2$), 191.9 (t, $J_{C,H}$ = 126.4 Hz, μ-*C*H$_2$) ppm. EI MS: *m*/*z* (%) 627 (2) [M – HCPh$_2$]$^+$, 613 (9) [M – HCPh$_2$–CH$_2$]$^+$, 492 (5) [M – C$_5$Me$_5$ – HCPh$_2$]$^+$, 479 (12) [M – C$_5$Me$_5$ – HCPh$_2$ – CH$_2$]$^+$. C$_{44}$H$_{58}$O$_4$Ti$_3$ (794.54): calcd. C 66.50, H 7.36; found C 66.52, H 7.52.

Preparation of [{Ti(η^5-C$_5$Me$_5$)(μ$_3$-O)}$_3$(μ-CH$_2$)(OCMePh$_2$)] (15): Complex **2** (0.20 g, 0.33 mmol) and Ph$_2$CMeOH (66 mg, 0.33 mmol) were dissolved in toluene (60 mL) in a 100-mL Carius tube fitted with a Young's valve and the reaction mixture irradiated with a sun lamp for 8 h. The solution was then filtered, concentrated and cooled to –20 °C to give **15** as dark-red crystals suitable for a X-ray diffraction study (yield 0.22 g, 84%). IR (KBr): ṽ = 2908 (s), 1490 (w), 1441 (m), 1373 (m), 1211 (w), 1104 (m), 1067 (m), 1026 (w), 977 (s), 755 (vs), 670 (s), 671 (s), 624 (m), 574 (m), 468 (w), 418 (w), 390 (m) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 1.96 (s, 15 H, C$_5$*Me*$_5$), 1.99 (s, 3 H, OC*Me*Ph$_2$), 2.01 (s, 30 H, C$_5$*Me*$_5$), 5.75, 6.34 (AB spin system, $^2J_{H,H}$ = 9.3 Hz, 2 H, μ-C*H*$_2$), 7.00–7.60 (10 H, OCMe*Ph*$_2$) ppm. ^{13}C NMR (75 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 11.9, 12.1 (q, $J_{C,H}$ = 125.8 Hz, C$_5$*Me*$_5$), 31.7 (q, $J_{C,H}$ = 127.0 Hz, OC*Me*Ph$_2$), 86.9 (m, O*C*MePh$_2$), 120.0, 123.0 (m, *C*$_5$Me$_5$), 126.5, 127.1, 127.9, 150.9 (OCH*Ph*$_2$), 194.5 (t, $J_{C,H}$ = 126.4 Hz, μ-*C*H$_2$) ppm. EI MS: *m*/*z* (%) 673 (3) [M – C$_5$Me$_5$]$^+$, 627 (17) [M – CMePh$_2$]$^+$, 492 (35) [M – C$_5$Me$_5$ – CMePh$_2$]$^+$, 476 (21) [M – C$_5$Me$_5$ – OCMePh$_2$]$^+$. C$_{45}$H$_{60}$O$_4$Ti$_3$ (808.57): calcd. C 66.84, H 7.48; found C 66.76, H 7.79.

Preparation of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu_3\text{-}O)\}_3(\mu\text{-}CH_2)(OCMe_3)]$ (16): Complex **1** (0.20 g, 0.33 mmol) and CMe_3OH (25 mg, 0.33 mmol) were dissolved in hexane (50 mL) in a 100-mL Carius tube fitted with a Young's valve and the mixture irradiated with a sun lamp for 6 h (at approx. 10 °C). The solution was then filtered, concentrated and cooled to –20 °C to give 183 mg (83%) of dark-red microcrystalline solid identified as **16** and slightly contaminated with compound **6** (approx. 10% by ^1H NMR). ^1H NMR (300 MHz, $[D_6]$benzene, 20 °C, TMS): δ = 1.32 (s, 9 H, $OCMe_3$), 2.01 (s, 30 H, C_5Me_5), 2.12 (s, 15 H, C_5Me_5), 5.99, 6.38 (AB spin system, $^2J_{H,H}$ = 9.0 Hz, 2 H, $\mu\text{-}CH_2$) ppm. ^{13}C NMR (75 MHz, $[D_6]$benzene, 20 °C, TMS): δ = 11.8, 12.2 (q, $J_{C,H}$ = 125.8 Hz, C_5Me_5), 32.5 (qm, $J_{C,H}$ = 124.5 Hz, $OCMe_3$), 81.2 (m, $OCMe_3$); 119.8, 122.2 (m, C_5Me_5), 189.9 (t, $J_{C,H}$ = 127.0 Hz, $\mu\text{-}CH_2$) ppm. EI MS: *m*/*z* (%) 684 (1) $[M]^+$, 627 (6) $[M - CMe_3]^+$, 611 (1) $[M - OCMe_3]^+$, 549 (24) $[M - C_5Me_5]^+$, 492 (21) $[M - CMe_3 - C_5Me_5]^+$, 478 (27) $[M - CMe_3 - C_5Me_5 - CH_2]^+$. $C_{35}H_{56}O_4Ti_3$ (684.44): calcd. C 61.41, H 8.25; found C 60.84, H 8.25.

Preparation of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu_3\text{-}O)\}_3(\mu\text{-}CH_2)(OCHMe_2)]$ (17): 2-Propanol (51 µL, 0.64 mmol) was added to a solution of **1** (0.40 g, 0.64 mmol) in 50 mL of hexane in a 100-mL Carius tube fitted with a Young's valve and stirred and irradiated with a sun lamp for 7 h. The solution was then concentrated, filtered and cooled to afford a red solid which consisted of a mixture of two isomers. After several recrystallization steps, 0.211 g of complex **17** with a *cis* disposition could be isolated in a pure form (49%). IR (KBr): $\tilde{\nu}$ = 2964 (s), 2909 (s), 1493 (w), 1435 (m), 1374 (s), 1329 (m), 1124 (s), 1017 (s), 849 (m), 757 (vs), 671 (s), 625 (s) cm^{-1}. ^1H NMR (300 MHz, $[D_6]$-benzene, 20 °C, TMS): δ = 1.18 (d, $^3J_{H,H}$ = 6.0 Hz, $OCHMe_2$), 2.01 (s, 30 H, C_5Me_5), 2.12 (s, 15 H, C_5Me_5), 4.73 (sept., $^3J_{H,H}$ = 6.0 Hz, $OCHMe_2$), 6.01, 6.40 (AB spin system, $^2J_{H,H}$ = 9.1 Hz, $\mu\text{-}CH_2$) ppm. ^{13}C NMR (75 MHz, $[D_6]$benzene, 20 °C, TMS): δ = 11.7, 11.8 ($J_{C,H}$ = 125.7 Hz, C_5Me_5), 26.3 (qm, $J_{C,H}$ = 124.2 Hz, $OCHMe_2$), 75.1 (dm, $J_{C,H}$ = 140.0 Hz, $OCHMe_2$), 119.8, 122.2 (m, C_5Me_5), 189.6 (t, $J_{C,H}$ = 126.4 Hz, $\mu\text{-}CH_2$) ppm. EI MS: *m*/*z* (%) 670 (1) $[M]^+$, 627 (3) $[M - HCMe_2]^+$, 613 (11) $[M - HCMe_2 - CH_2]^+$, 611 (17) $[M - OHCMe_2]^+$, 535 (25) $[M - C_5Me_5]^+$, 492 (37) $[M - C_5Me_5 - HCMe_2]^+$. $C_{34}H_{54}O_4Ti_3$ (670.41): calcd. C 60.91, H 8.12; found C 61.39, H 7.77.

Preparation of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu_3\text{-}O)\}_3(\mu\text{-}CHMe)(OCH_2Ph)]$ (18): An amber-stained 100-mL Carius tube was charged with **2** (0.40 g, 0.64 mmol), $PhCH_2OH$ (67 µL, 0.67 mmol) and hexane (40 mL), and the mixture stirred at room temperature for one hour. The solution was then concentrated and cooled to –20 °C to give a clean mixture, with the alkoxide ligand in the same or the opposite side with respect to the µ-alkylidene moiety, in a 63% yield (0.29 g). ^1H NMR (300 MHz, $[D_6]$benzene, 20 °C, TMS): δ = 1.93, 2.00 (s, 30 H, C_5Me_5), 2.02, 2.15 (s, 15 H, C_5Me_5), 1.94, 2.09 (d, $^3J_{H,H}$ = 7.8 Hz, 3 H, $\mu\text{-}CHMe$), 5.37, 5.41 (s, OCH_2Ph), 6.19, 6.28 (q, $^3J_{H,H}$ = 7.8 Hz, $\mu\text{-}CHMe$), 7.00–7.50 (OCH_2Ph) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $[D_6]$benzene, 20 °C, TMS): δ = 11.3–11.8 (C_5Me_5), 29.7, 30.4 ($\mu\text{-}CHMe$), 75.3, 77.2 (OCH_2Ph), 119.5, 120.0, 122.4, 122.5 (C_5Me_5), 126.4–144.3 ($OCHPh_2$), 209.5, 210.4 ($\mu\text{-}CHMe$) ppm.

Preparation of $[\{Ti(\mu_3\text{-}O)\}_3\{(\eta^5\text{-}C_5Me_5)(OCPh_3)\}_2(\mu\text{-}CH_2)]\cdot C_6H_{14}$ (19): A solution of **3** (0.30 g, 0.34 mmol) and Ph_3COH (90 mg, 0.34 mmol) in hexane (50 mL) was placed in a 100-mL Carius tube fitted with a Young's valve and irradiated with a UV lamp for thirteen days. The final solution was filtered, concentrated and cooled to obtain **19**$\cdot C_6H_{14}$ as a dark orange microcrystalline solid (yield 0.27 g, 73%). IR (KBr): $\tilde{\nu}$ = 3057 (w), 3022 (w), 2911 (m), 1597 (w), 1490 (m), 1445 (s), 1376 (m), 1207 (w), 1161 (m), 1056 (s), 1026 (s), 940 (w), 920 (w), 898 (w), 835 (m), 775 (vs), 669 (vs), 683 (s), 637 (m), 628 (m), 495 (m) cm^{-1}. ^1H NMR (300 MHz, $[D_6]$benzene, 20 °C, TMS): δ = 1.86 (s, 30 H, C_5Me_5), 5.84, 6.36 (AB spin system, $^2J_{H,H}$ = 9.9 Hz, 2 H, $\mu\text{-}CH_2$); 7.0–7.6 (30 H, $OCPh_3$) ppm. ^{13}C NMR (75 MHz, $[D_6]$benzene, 20 °C, TMS): δ = 11.5 (q, $J_{C,H}$ = 126.4 Hz, C_5Me_5), 94.1, 94.5 (s, $OCPh_3$), 122.1 (m, C_5Me_5), 126.5–130.0, 148.9, 149.0 ($OCPh_3$), 194.6 (t, $J_{C,H}$ = 125.8 Hz, $\mu\text{-}CH_2$) ppm. EI MS: *m*/*z* (%) 627 (27) $[M - CH_2Me]^+$, 613 (11) $[M - CH_2Me - CH_2]^+$, 521 (36) $[M - C_5Me_5]^+$, 492 (16) $[M - C_5Me_5 - CH_2Me]^+$, 478 (17) $[M - C_5Me_5 - CH_2Me - CH_2]^+$. $C_{59}H_{62}O_5Ti_3\cdot C_6H_{14}$ (1080.9): calcd. C 72.22, H 7.09; found C 72.37, H 6.40.

Preparation of $[\{Ti(\mu_3\text{-}O)\}_3\{(\eta^5\text{-}C_5Me_5)(OCPh_3)\}_2(\mu\text{-}CHMe)]$ (20): To a toluene solution of **7** (0.30 g, 0.48 mmol), Ph_3COH (0.13 g, 0.48 mmol) was added. The reaction mixture was placed in a 100-mL Carius tube with Young's valve and irradiated with an UV lamp for two days. The final solution was filtered, concentrated and cooled to obtain violet crystals of **20** (Yield 0.46 g (95%)). IR (KBr): $\tilde{\nu}$ = 3055 (w), 3021 (w), 2911 (m), 2858 (m), 2835 (m), 1596 (w), 1489 (m), 1444 (s), 1376 (m), 1318 (w), 1201 (w), 1179 (m), 1161 (m), 1104 (m), 1072 (s), 1046 (vs), 1025 (vs), 1001 (m), 939 (w), 920 (w), 899 (m), 834 (m), 764 (vs), 729 (vs), 699 (vs), 671 (vs), 637 (m), 559 (m), 524 (m), 494 (m), 484 (m) cm^{-1}. ^1H NMR (300 MHz, $[D_6]$benzene, 20 °C, TMS): δ = 1.64 (d, $^3J_{H,H}$ = 7.8 Hz, 3 H, $\mu\text{-}CHMe$), 1.84 (s, 30 H, C_5Me_5), 6.34 (q, $^3J_{H,H}$ = 7.8 Hz, 1 H, $\mu\text{-}CHMe$); 6.9–7.6 (30 H, $OCPh_3$) ppm. ^{13}C NMR (75 MHz, $[D_6]$benzene, 20 °C, TMS): δ = 11.2 (q, $J_{C,H}$ = 126.4 Hz, C_5Me_5), 32.1 (q, $J_{C,H}$ = 122.0 Hz, $\mu\text{-}CHMe$), 94.2, 94.6 (s, $OCPh_3$), 121.5 (m, C_5Me_5), 126.5–130.0, 148.9, 149.0 ($OCPh_3$), 216.3 (dm, $J_{C,H}$ = 118.9 Hz, $\mu\text{-}CHMe$) ppm. $C_{60}H_{64}O_5Ti_3\cdot C_5H_{12}$ (1080.90): calcd. C 72.22, H 7.0; found C 72.61, H 6.31.

X-ray Structure Analysis of 3, 5, 11, 15 and 20: Crystals of complexes **3**, **5**, **11**, **15** and **20** were grown from saturated hexane or pentane solutions at –20 °C, removed from the Schlenks and covered with a layer of a viscous perfluoropolyether (Fomblin® Y). A suitable crystal was selected with the aid of a microscope, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream of the diffractometer. The intensity data sets were collected at 200 K on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit. Crystallographic data for all the complexes are presented in Table 3. The structures were solved, using the WINGX package,[31] by direct methods (SHELXS-97) and refined by least-squares against F^2 (SHELXL-97).[32]

Compound **3** crystallized with half a molecule of hexane. Several attempts were made to model the solvent molecule but all were unsuccessful, therefore the Squeeze[33] procedure was applied to remove its contribution from the structure factors. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were positioned geometrically and refined by using a riding model.

All non-hydrogen atoms of complexes **5** and **15** were refined anisotropically. The hydrogen atoms were positioned geometrically and refined using a riding model, except for those of the methylene fragment, which were located in the Fourier difference map and refined isotropically.

Two independent molecules of complex **11** were found in the asymmetric unit. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were refined using a riding model, except those of the Cα of the ethylidene fragments, which were located in the Fourier difference map and refined isotropically.

Compound **20** crystallized with one molecule of pentane. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were refined using a riding model, except those of the ethyl-

Table 3. Crystal data and structure refinement for **3**, **5**, **11**, **15** and **20**.

Compound	**3**·0.5C_6H_{14}	**5**	**11**	**15**	**20**·C_5H_{12}
Empirical formula	$C_{50}H_{62}O_4Ti_3$·0.5C_6H_{14}	$C_{45}H_{60}O_4Ti_3$	$C_{35}H_{56}O_4Ti_3$	$C_{45}H_{60}O_4Ti_3$	$C_{60}H_{64}O_5Ti_3$·C_5H_{12}
Formula weight	913.78	808.63	684.5	808.63	1080.96
Temperature [K]	200(2)	200(2)	200(2)	200(2)	200(2)
λ (Mo-K_α) [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	orthorhombic	monoclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	*Pbca*	$P2_1/a$	$P\bar{1}$
a [Å]	10.8989(15)	11.5553(8)	17.660(7)	17.314(3)	11.2413(12)
α [°]	80.288(10)	111.878(19)			87.39(2)
b [Å]	11.3763(15)	12.834(4)	21.957(3)	11.447(3)	16.558(4)
β [°]	82.952(12)	93.858(19)		106.141(13)	72.109(10)
c [Å]	22.666(4)	16.053(4)	39.108(9)	22.935(8)	17.476(4)
γ [°]	63.619(10)	101.226(15)			83.224(18)
Volume [Å^3]; Z	2478.0(6); 2	2141.3(9); 2	15165(7); 16	4366(2); 4	3073.7(12); 2
$\rho_{calcd.}$ [g cm^{-3}]	1.225	1.254	1.199	1.230	1.168
μ [mm^{-1}]	0.514	0.585	0.649	0.574	0.425
F(000)	970	856	5824	1712	1144
Crystal size [mm]	0.35 × 0.27 × 0.24	0.28 × 0.27 × 0.20	0.49 × 0.45 × 0.16	0.18 × 0.16 × 0.15	0.30 × 0.30 × 0.20
θ range [°]	3.08 to 27.50	3.07 to 27.50	3.02 to 27.51	3.03 to 27.52	3.29 to 27.50
Index ranges	–14 to 14, –14 to 14, –29 to 28	–15 to 14, –16 to 16, –20 to 20	–22 to 22, –28 to 28, –50 to 50	–22 to 22, –14 to 14, –29 to 29	–14 to 14, –21 to 21, –22 to 22
Collected reflections	47757	77613	128763	97993	57659
Independent reflections	11336	9813	17403	10001	13995
Goodness-of-fit on F^2	1.017	1.007	0.973	0.850	1.019
Final R indices [$F > 4\sigma(F)$]	$R1 = 0.096$ $wR2 = 0.176$	$R1 = 0.058$ $wR2 = 0.120$	$R1 = 0.075$ $wR2 = 0.149$	$R1 = 0.062$ $wR2 = 0.167$	$R1 = 0.066$ $wR2 = 0.140$
R indices (all data)	$R1 = 0.203$ $wR2 = 0.204$	$R1 = 0.137$ $wR2 = 0.141$	$R1 = 0.182$ $wR2 = 0.177$	$R1 = 0.124$ $wR2 = 0.198$	$R1 = 0.168$ $wR2 = 0.173$
Largest diff. peak/hole [e Å^{-3}]	0.653/–0.444	0.340/–0.378	0.528/–0.448	0.652/–0.410	0.665/–0.354

idene fragment, which were located in the Fourier difference map and refined isotropically.

CCDC-706609 (for **3**), -706610 (for **5**), -706611 (for **11**), -706612 (for **15**), and -706613 (for **20**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details: Quantum mechanical calculations on the simplest substrate MeOH and the model complexes [{Ti(η^5-C_5H_5)(μ-O)}$_3$(μ_3-CR)] [R = H (**1H**), Me (**2H**)] were performed with the GAUSSIAN03 series of programs[34] within the framework of Density Functional Theory (DFT)[23] using the B3LYP functional.[35] A quasi-relativistic effective core potential operator was used to represent the 10 innermost electrons of the Ti atom.[36] The basis set for the Ti atom was that associated with the pseudopotential,[36] with a standard double-ξ LANL2DZ contraction.[34] The 6-31G(d) basis set was used for C and O atoms[37] and the 6-31G(p) basis set was used for the migrating hydrogen,[37] whereas the 6-31G basis set was used for the other hydrogens.[37] Geometry optimizations were carried out without any symmetry restrictions and all stationary points were optimized with analytical first derivatives. Transition states were characterized by a single imaginary frequency whose normal mode corresponded to the expected motion.

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