DOI: 10.1002/ejic.200600082

Titanium–Alkaline Earth Molecular Oxides as Supports for Carbanions Derived from μ_3-Ethylidyne Groups

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Dedicated to Professor Victor Riera on the occasion of his 70th birthday

Keywords: Alkaline earth metals / Alkylidyne complexes / Carbanions / O ligands / Titanium

Treatment of the μ_3-ethylidyne complex [{TiCp*(μ-O)}$_3$(μ_3-CMe)] (**1**) (Cp* = η^5-C_5Me_5) with the alkaline earth amides [M{N(SiMe$_3$)$_2$}$_2$(thf)$_2$] (M = Mg, Ca, Sr) promotes the deprotonation of the alkylidyne moiety μ_3-CMe and leads to the oxoheterometallocubane derivatives [{(thf)$_x$(Me$_3$Si)$_2$NM}-(μ_3-O)$_3${Ti$_3$Cp*$_3$(μ_3-CCH$_2$)}] [M = Mg, *x* = 0 (**2a**); Ca, *x* = 1 (**3**); Sr, *x* = 1 (**4**)]. In the case of the magnesium amide, complex **2a** is obtained together with the isomer [{(Me$_3$Si)$_2$NMg}-(μ_3-O)$_3${Ti$_3$Cp*$_3$(μ_3-η^2-CHCH)}] (**2b**). The addition of pentamethylcyclopentadiene (C_5Me_5H) or triphenylmethanol (Ph_3COH) to these compounds causes the displacement of the amide fragment to give the heterometallocubanes [RM(μ_3-O)$_3${Ti$_3$Cp*$_3$(μ_3-C_2H_2)}] [R = C_5Me_5, M = Ca (**5**), Sr (**6**); R = Ph_3CO, M = Mg (**7a**,**b**), Ca (**8**), Sr (**9**)]. This substitution can also be performed on **3** and **4** by treatment with the starting complex **1**, which gives the corner-shared double cubanes [M{(μ_3-O)$_3$(Ti$_3$Cp*$_3$)(μ_3-CCH$_2$)}$_2$] [M = Ca (**11**), Sr (**12**)]. Complexes **2a**,**b** do not react with **1**, and heating of this mixture affords the edge-linked double cubane [Mg(μ_4-O)-(μ_3-O)$_2${Ti$_3$Cp*$_3$(μ_3-CCH)}]$_2$ (**10**). The combination of the barium reagents [Ba(CH$_2$Ph)$_2$] or [Ba{N(SiMe$_3$)$_2$}$_2$] with **1** leads to the corner-shared double cubane [Ba{(μ_3-O)$_3$(Ti$_3$Cp*$_3$)(μ_3-CCH$_2$)}$_2$] (**13**). The molecular structures of **3** and **10** have been established by single-crystal X-ray analysis.

Introduction

The alkylidyne groups of the complexes [{TiCp*(μ-O)}$_3$-(μ_3-CR)] (Cp* = η^5-C_5Me_5; R = H, Me)[1] have revealed a surprising and unprecedented reactivity[2] that allows us to form an understanding between molecular and surface chemistry.[3] Both discrete systems may provide relevant information about the mechanisms and the presence of intermediate species on catalytic surfaces even though the reaction conditions are different.

Ethylidyne, in particular, is a well-known hydrocarbon fragment in the dehydrogenation of ethylene on metallic surfaces and its transformation has been actively investigated.[4] However, at present, detailed studies concerning the titanium surface reactivity are scarce and evidence for the formation of ethylidyne has only recently appeared during the decomposition of ethylene on carbon–modified titanium surfaces.[5] Nevertheless, complete dissociation to produce carbon and hydrogen takes place when a clean titanium surface interacts with ethylene.[5] However, the pathways for ethylidyne dehydrogenation to C_2H_2, C_2H or carbonaceous species and possible hydrogen exchange have not been well established.

In our molecular approach to the interaction of hydrocarbons with a surface, we have shown that μ_3-ethylidyne groups supported on a Ti_3O_3 core can be sequentially hydrogenated (ethylidene, ethyl, and ethane) upon reaction with amines (see Scheme 1).[2d] The dehydrogenation of the μ_3-ethylidyne ligand has also been observed during the incorporation of ketones into the complex [{TiCp*(μ-O)}$_3$-(μ_3-CMe)] (**1**) by an insertion of the carbonyl groups into a Ti–H bond of the hydridovinylidene intermediate [{TiCp*(μ-O)}$_3$(μ-CCH$_2$)(H)] formed in situ.[2b] Recently, we have also shown how the incorporation of alkali metal cations into the organometallic titanium oxide **1** takes place with proton abstraction from the alkylidyne and formation of the species [M(μ_3-O)$_3${Ti$_3$Cp*$_3$(μ_3-CCH$_2$)}] (M = Li, Na, K, Rb, Cs).[6]

Herein we discuss the evolution of the ethylidyne fragment when the molecular model [{TiCp*(μ-O)}$_3$(μ_3-CMe)] (**1**) tries to incorporate alkaline-earth derivatives.

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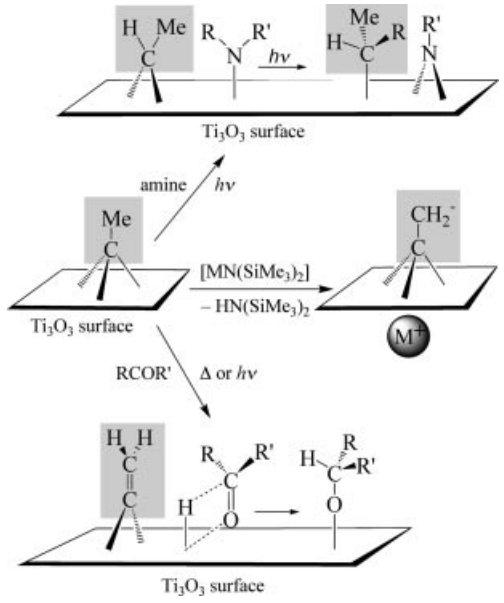
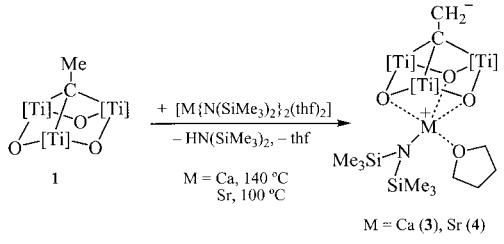


Scheme 1. Chemical reactivity of the μ_3-ethylidyne group on the Ti_3O_3 core with amines, alkali metal amides, and ketones.

Results and Discussion

We began our study with the reaction between the beryllium amide $Be[N(SiMe_3)_2]_2$ and $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}CMe)]$ (**1**), but we did not observe any reaction, even when heating the mixture to over 200 °C. However, the thermal treatment of **1** with $[M\{N(SiMe_3)_2\}_2(thf)_2]$ (M = Ca, Sr) in a 1:1 ratio, in hexane or toluene, leads to the oxoheterometallocubanes $[\{(thf)(Me_3Si)_2NM\}(\mu_3\text{-}O)_3\{Ti_3Cp^*_3(\mu_3\text{-}CCH_2)\}]$ [M = Ca (**3**), Sr (**4**)] in high yields (Scheme 2). The isolated compounds **3** and **4** proved to be stable under argon at room temperature and sufficiently soluble in most common solvents (toluene, hexane, dichloromethane...).



Scheme 2. Reactivity of **1** with calcium and strontium bis(trimethylsilyl)amides. [Ti] = $Ti(\eta^5\text{-}C_5Me_5)$.

The NMR spectra of these species in $[D_6]$benzene show the equivalence of the $\eta^5\text{-}C_5Me_5$ groups, with only one signal in the ^1H NMR [δ = 1.99 (**3**) and 2.00 ppm (**4**)] and two in the $^{13}C\{^1H\}$ NMR spectra [δ = 11.7 (**3**) and 11.6 ppm (**4**) for $C_5\mathit{Me}_5$ and δ = 117.9 (**3**) and 117.5 ppm (**4**) for C_5Me_5]. The NMR spectra also display resonances due to the $\mu_3\text{-}CCH_2^-$ group, as a singlet at δ = 2.82 (**3**) and 2.72 ppm (**4**) in the ^1H NMR spectra and a triplet at δ = 82.3 (**3**) and 81.2 ppm (**4**) [$J_{C,H}$ = 149 Hz (av.)], attributed to the C_β resonance, in the ^{13}C NMR spectra. Furthermore, the apical μ_3-carbon appears as a singlet at δ = 380.1 (**3**) and 377.3 ppm (**4**), which is shifted to high field with respect to complex **1** [$\delta(\mu_3\text{-}\mathit{C}Me)$ = 401.7 ppm].[1a] These data are in agreement with the rotation of the organometallic ligand around the alkaline-earth metal center, analogously to the situation found in other similar compounds,[7] and with removal of the proton of the starting μ_3-ethylidyne group. The molecular structure of these derivatives was confirmed by an X-ray single crystal structure analysis of **3** (see Figure 1). Selected bond lengths and angles for **3** are included in Table 1.

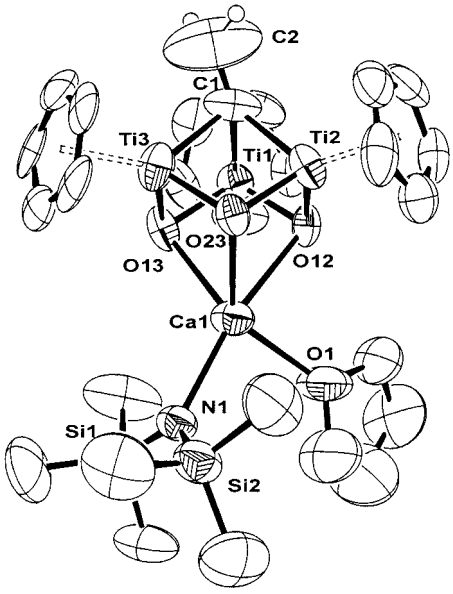


Figure 1. Molecular structure of **3** in the crystal. Hydrogen atoms and the methyl groups of the rings have been omitted for clarity.

Table 1. Selected bond lengths and angles for complex **3**.

Ca(1)–N(1)	2.314(9)	Ca(1)–O(1)	2.424(11)
Ca(1)–O av.	2.444(8)	Ti···Ca av.	3.243(3)
Ti···Ti av.	2.832(3)	Ti–C(1) av.	2.088(15)
C(1)–C(2)	1.23(2)	Ti–O av.	1.901(8)
Si–N(1) av.	1.685(10)	Si–C av.	1.872(15)
Ca–Si av.	3.423(5)	Ti–Cp* av.	2.069
Cp*–Ti–C(1) av.	129.0	C(1)–Ti–O av.	88.9(5)
Ti–O–Ti av.	96.4(3)	O–Ti–O av.	95.7(3)
Ti–O–Ca av.	95.7(3)	O–Ca–O(1) av.	113.0(3)
O–Ca–O av.	70.4(2)		

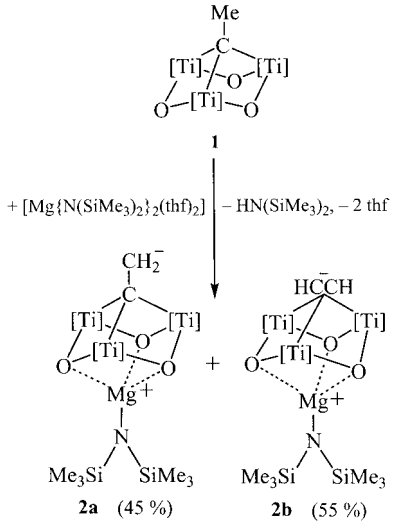
The crystal structure of compound **3** reveals a cubic core where the $[CaN(SiMe_3)_2(thf)]$ moiety occupies the free vertex of the incomplete cube-type complex **1**, being linked through the three oxygen atoms. The calcium atom adopts a distorted trigonal bipyramid geometry constituted by the three oxygen atoms of the organometallic oxide, the oxygen of the tetrahydrofuran molecule and the nitrogen atom of the bis(trimethylsilyl)amide ligand, in a similar way to that found for the calcium atom of the previously reported compound $[\{(thf)(Me_3Si)_2NCa\}(\mu_3\text{-}O)_3\{Ti_3Cp^*_3(\mu_3\text{-}C)\}]$.[8] The axial positions of this bipyramid in complex **3** are occupied by the N(1) and O(12) atoms.

The $[CaN(SiMe_3)_2(thf)]$ fragment presents similar bond lengths and angles to other calcium complexes containing

this unit.[9] Also, the distances from calcium to the oxygen atoms of the organometallic oxide are in the range 2.421(8)–2.488(8) Å, and the longest is that corresponding to the *trans* position to the bis(trimethylsilyl)amide ligand. Both the amide and the tetrahydrofuran fragments are located in an alternate position with respect to the pentamethylcyclopentadienyl rings to minimize the steric repulsion.

The incorporation of the alkaline earth atom into the organometallic ligand **1** does not produce significant variations in the $[CTi_3O_3]$ core, although it leads to a significant shortening of the C(1)–C(2) length, from 1.514(7) Å[1] in **1** to 1.23(2) Å in **3**. At the same time the C(1)–C(2) bond, which is perpendicular to the plane formed by the three titanium atoms in **1**, now forms an angle of 64.1(1)°.[10] This arrangement contrasts with that found for the complex $[(thf)_2Cs(\mu_3\text{-}O)_3\{Ti_3Cp^*_3(\mu_3\text{-}CCH_2)\}]$, where the spatial disposition of the deprotonated ethylidyne is also perpendicular and the carbon–carbon distance is 1.528(11) Å.[6]

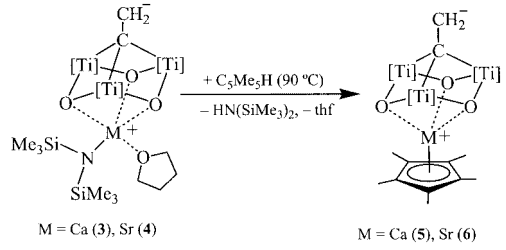
Interestingly, the reaction of **1** with the magnesium amide $[Mg\{N(SiMe_3)_2\}_2(thf)_2]$, in hexane at 180 °C, takes place with deprotonation of the μ_3-ethylidyne group and formation of two compounds, **2a** and **2b**, in approximately a 45:55 ratio (Scheme 3). Both species co-crystallize as red crystals that are soluble in the usual solvents (toluene, hexane...) and are highly air-sensitive. Attempts to separate these compounds were unsuccessful.



Scheme 3. Reaction of **1** with magnesium bis(trimethylsilyl)amide. [Ti] = Ti(η^5-C_5Me_5).

Compounds **2a** and **2b** were characterized by standard analytical and spectroscopic techniques. The most notable features in the ^1H and ^{13}C NMR spectra of $[\{(Me_3Si)_2NMg\}(\mu_3\text{-}O)_3\{Ti_3Cp^*_3(\mu_3\text{-}CCH_2)\}]$ (**2a**) are the resonances for the μ_3-CCH_2^- group. The ^1H NMR spectrum displays a singlet at δ = 2.95 ppm and the ^{13}C NMR spectrum reveals a triplet at δ = 85.1 ppm ($J_{C,H}$ = 151 Hz), assigned to the β-carbon atom, and the α-carbon atom resonance at δ = 384.3 ppm, similar to the values found for the calcium (**3**) and strontium (**4**) derivatives. $[\{(Me_3Si)_2NMg\}(\mu_3\text{-}O)_3\{Ti_3Cp^*_3(\mu_3\text{-}\eta^2\text{-}CHCH)\}]$ (**2b**) exhibits a singlet at δ = 6.55 ppm in the ^1H NMR spectrum and a doublet of doublets at δ = 206.2 ppm ($J_{C,H}$ = 156, $^2J_{C,H}$ = 5.1 Hz) in the ^{13}C NMR spectrum for the μ_3-η^2-$CHCH^-$ group. Furthermore, the presence of single signals at δ = 1.86 ppm for the methyl group, δ = 119.9 ppm for the ring carbons, and δ = 12.5 ppm for the methyl carbons of the Cp* ligands in these spectra suggest a dynamic behavior for compound **2b**. An analogous situation has been reported[11] for the complex $[Rh_3Cp^*_3(\mu_3\text{-}\eta^2\text{-}C_2H_2)(\mu_3\text{-}S)]^{2+}$, where the authors suggest that the cavity constructed by the three Cp* ligands and the metal atoms is big enough to allow the movement of the hydrocarbon ligand μ_3-η^2-CHCH.

The reaction of **2**–**4** with protic reagents such as pentamethylcyclopentadiene (C_5Me_5H) and the alcohol Ph_3COH led to the metathesis of the amide group in a regioselective way, although, surprisingly, the μ_3-ethylidyne group was not regenerated. C_5Me_5H reacts with complexes **3** and **4** at about 90 °C to give the derivatives $[Cp^*M(\mu_3\text{-}O)_3\{Ti_3Cp^*_3(\mu_3\text{-}CCH_2)\}]$ [M = Ca (**5**), Sr (**6**); see Scheme 4]. However, it does not react with the magnesium complexes **2a** and **2b**, probably due to the steric hindrance and low acidity of the pentamethylcyclopentadiene. Compounds **5** and **6** were isolated as brown solids in good yields and characterized by standard analytical and spectroscopic techniques.



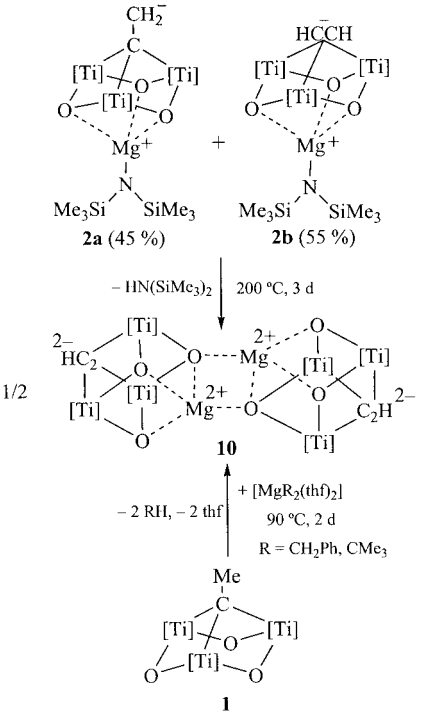
Scheme 4. Reactivity of **3** and **4** with pentamethylcyclopentadiene. [Ti] = Ti(η^5-C_5Me_5).

The NMR spectroscopic data are consistent with the structure shown in Scheme 4, thus confirming the existence of the Cp* group at the coordination sphere of the alkaline-earth elements and revealing the presence of the fragment μ_3-CCH_2^- [$\delta(CCH_2)$ = 2.64 (**5**) and 2.55 ppm (**6**) (s); $\delta(CCH_2)$ = 82.5 (**5**) and 81.3 ppm (**6**) (t, $J_{C,H} \approx$ 150 Hz); $\delta(CCH_2)$ = 378.2 (**5**) and 375.6 ppm (**6**)].

The reactions of the alcohol Ph_3COH with complexes **2**–**4** were carried out in NMR tubes in [D_6]benzene as solvent at room temperature (see Experimental Section). In all cases the elimination of the amide group as free amine was detected and the complexes $[(Ph_3COMg)(\mu_3\text{-}O)_3\{Ti_3Cp^*_3(\mu_3\text{-}C_2H_2)\}]$ (**7a**,**b**) and $[(Ph_3COM)(\mu_3\text{-}O)_3\{Ti_3Cp^*_3(\mu_3\text{-}CCH_2)\}]$ [M = Ca (**8**) and Sr (**9**)] characterized.

Once the displacement of the amide group by several reagents had been established, we wondered what would happen if compounds **2**–**4** were treated with the starting complex **1** as organometallic tridentate ligand. The oxometallocubanes **2a**,**b** did not react with **1** at room temperature. However, when the solution was heated for several days at

about 200 °C and then slowly cooled, an insoluble microcrystalline red solid **10** was isolated in high yield. Curiously, the same result was obtained when complexes **2a**,**b** were heated at that temperature in the absence of **1** (see Scheme 5). Furthermore, compound **10** also resulted from the combination of equimolecular amounts of **1** and the dialkylmagnesiums $[MgR_2(thf)_2]$ (R = CH_2Ph, CMe_3). Solid **10** proved to be stable under argon at room temperature and insoluble in most common solvents (toluene, hexane, THF...). The new complex was characterized by elemental analysis, IR spectroscopy, and by single-crystal X-ray diffraction.



Scheme 5. Thermal treatment of complexes **2a**,**b** and reaction of **1** with dialkylmagnesiums. [Ti] = Ti(η^5-C_5Me_5).

The molecular structure of **10** is shown in Figure 2, while selected bond lengths and angles are included in Table 2. The crystallographic study of **10** revealed the presence of two $[MgO_3Ti_3C_2]$ cores directly linked by two Mg–O bonds to form a central planar rhombic Mg_2O_2 moiety. The alkaline-earth atoms are located in the vacant vertex of the preorganized organometallic oxide **1** and present a tetracoordinate environment. The pentamethylcyclopentadienyl rings of the cubes adopt an alternate configuration to minimize steric hindrance. The disposition of the core in complex **10** is similar to that reported for $[Li(\mu_4\text{-}O)(\mu_3\text{-}O)_2\{Ti_3Cp^*_3(\mu_3\text{-}C)\}]_2$,[12] and confirms the ability of **1** to encapsulate magnesium atoms.

The magnesium···magnesium distance [2.765(4) Å] is shorter than those found in the literature for other complexes containing Mg_2O_2 units,[13] and even shorter than the sum of the Van der Waals radii (3.40 Å).[14] This shortening could be due to the geometry of the molecule itself and the steric hindrance of the ligands around the magnesium

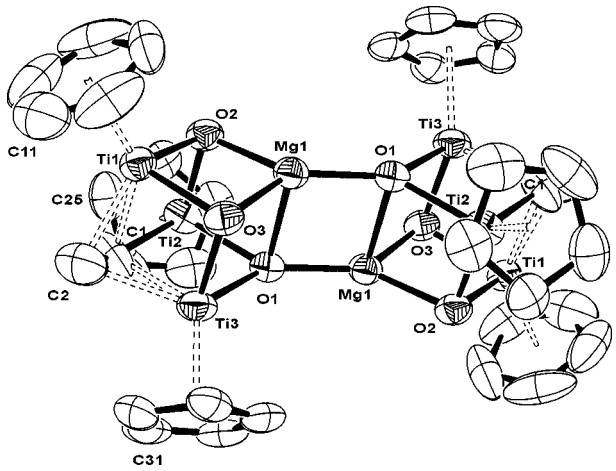


Figure 2. Molecular structure of **10**. The methyl groups of the Cp* rings and hydrogen atoms have been omitted for clarity.

Table 2. Selected bond lengths and angles for complex **10**.

C(1)–C(2)	1.297(12)	C(1)–Ti(1)	2.147(7)
C(1)–Ti(2)	1.956(7)	C(1)–Ti(3)	2.068(9)
C(2)–Ti(1)	2.094(9)	C(2)–Ti(3)	2.239(10)
Mg(1)···Mg(1)	2.765(4)	Mg(1)–O(1)	2.149(4)
Mg(1)–O(2)	1.986(5)	Mg(1)–O(3)	1.985(4)
Mg(1)–O(1)[a]	1.929(4)	O(1)–Ti(2)	2.053(4)
O(1)–Ti(3)	2.115(4)	O(2)–Ti(1)	2.010(4)
O(2)–Ti(2)	1.909(4)	O(3)–Ti(1)	1.985(4)
O(3)–Ti(3)	1.930(4)	Ti(1)···Ti(3)	2.801(2)
Ti(1)···Ti(2)	2.819(2)	Ti(2)···Ti(3)	2.870(2)
C(2)–C(1)–Ti(2)	155.6(6)	C(2)–C(1)–Ti(3)	79.8(6)
Ti(2)–C(1)–Ti(3)	90.8(3)	C(2)–C(1)–Ti(1)	70.0(5)
Ti(2)–C(1)–Ti(1)	86.6(3)	Ti(3)–C(1)–Ti(1)	83.3(3)
C(1)–C(2)–Ti(1)	74.4(5)	C(1)–C(2)–Ti(3)	65.4(5)
Ti(1)–C(2)–Ti(3)	80.5(3)	O(1)[a]–Mg(1)–O(3)	134.3(2)
O(1)[a]–Mg(1)–O(2)	137.1(2)	O(3)–Mg(1)–O(2)	88.4(2)
O(1)[a]–Mg(1)–O(1)	94.8(2)	O(3)–Mg(1)–O(1)	83.7(2)
O(2)–Mg(1)–O(1)	84.2(2)	Ti(2)–O(1)–Ti(3)	86.9(2)
Mg(1)–O(1)–Mg(1)	85.2(2)	Ti(2)–O(1)–Mg(1)	88.9(2)
Ti(3)–O(1)–Mg(1)	89.8(2)	Ti(2)–O(2)–Mg(1)	98.1(2)
Ti(2)–O(2)–Ti(1)	91.9(2)	Mg(1)–O(2)–Ti(1)	90.9(2)
Ti(3)–O(3)–Ti(1)	91.4(2)	Ti(3)–O(3)–Mg(1)	100.5(2)
Ti(1)–O(3)–Mg(1)	91.6(2)	O(3)–Ti(1)–O(2)	87.7(2)
O(3)–Ti(1)–C(2)	88.3(3)	O(2)–Ti(1)–C(2)	121.8(3)
O(3)–Ti(1)–C(1)	90.5(3)	O(2)–Ti(1)–C(1)	86.4(2)
O(2)–Ti(2)–C(1)	95.0(2)	O(2)–Ti(2)–O(1)	88.8(2)
C(1)–Ti(2)–O(1)	93.4(3)	O(3)–Ti(3)–C(1)	94.4(2)
O(3)–Ti(3)–O(1)	85.9(2)	C(1)–Ti(3)–O(1)	88.5(2)
O(3)–Ti(3)–C(2)	85.7(3)	O(1)–Ti(3)–C(2)	121.3(3)

[a] Intercube.

atoms, giving rhombic and not square arrangements. The distance between the magnesium atom and the closer oxygen atom of the other cube Mg(1)–O(1) [1.929(4) Å] is similar to those to O(2) and O(3) of the same cube, while the distance with respect to O(1) of the same cube [2.149(4) Å] is clearly longer and allows us to describe the environment of each magnesium atom as a trigonal pyramid instead of tetrahedral. The sum of the angles in the base of that pyramid is 359.8(2)°.

Complex **10** presents narrower Ti–O–Ti and O–Ti–O angles (10° and 16.5° respectively) and Ti–O distances up to 0.28 Å longer than those found in **1**. However, the Ti···Ti

distances stay in the same range [2.819(1) Å in **1** and an average value of 2.830(2) Å in **10**].

The main feature of the solid-state structure of complex **10** is undoubtedly the relative disposition of the hydrocarbyl unit that is formed as a result of the double deprotonation of the μ_3-CCH_3 group with respect to the Ti_3O_3 surface (see Figure 3). The C(1)–C(2) bond length of 1.297(12) Å is similar to that found in compound **3** but now the Ti–C(1) lengths are quite different, with values ranging from 1.956(7) Å for Ti(2)–C(1) to 2.147(7) Å for Ti(1)–C(1). This means that C(1) is no longer equidistant to the three titanium atoms, being closer to Ti(2). Simultaneously, C(2) shows shorter distances to the titanium atoms [Ti(1)–C(2) = 2.094(9) and Ti(3)–C(2) = 2.239(10) Å] than those found in complex **3**.[15] All this leads to the fact that the C(1)–C(2) line forms an angle of only 20.5° with respect to the plane constituted by the three titanium atoms. The different dispositions of the C(1)–C(2) bond with respect to the Ti_3 plane in complexes **1**, **3**, and **10** are represented in Scheme 6.

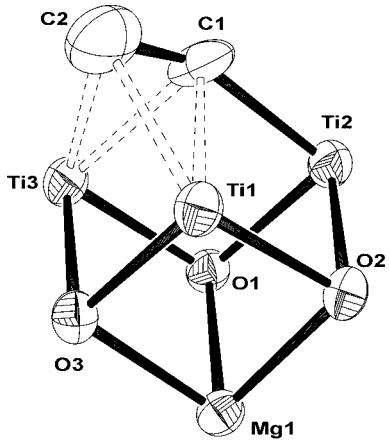
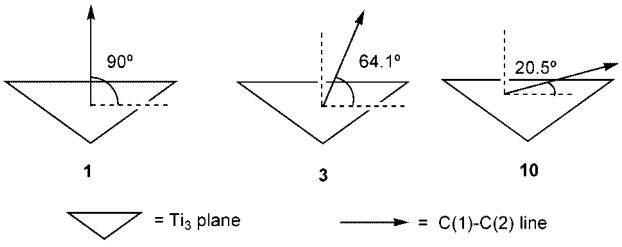


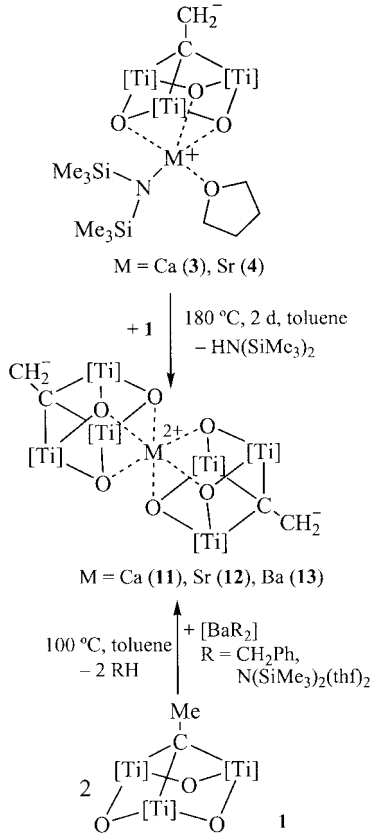
Figure 3. View of the $[MgO_3Ti_3C_2]$ core in complex **10**.



Scheme 6. Disposition of the C(1)–C(2) bond with respect to the Ti_3 plane in **1**, **3**, and **10**.

Complexes **1**, **3**, and **10** present an organic ligand supported on an organometallic oxide containing titanium atoms in their higher oxidation state. The electronic deficiency of the titanium centers of **3** and **10** can be alleviated, at least partially, by the donation of electron density from the respective carbanions μ_3-CCH_2^- and μ-CCH^{2-}, which bends the C(1)–C(2) bond towards the titanium atoms.

In the case of the calcium and strontium complexes, the addition of **1** to toluene solutions of **3** or **4** and heating to 180 °C for several days afforded the corner-shared double cubane compounds $[M\{(\mu_3\text{-}O)_3Ti_3Cp^*_3(\mu_3\text{-}CCH_2)\}_2]$ [M = Ca (**11**), Sr (**12**)] as dark-red, microcrystalline solids that are insoluble in the usual solvents (toluene, hexane, tetrahydrofuran,...). The IR spectra, elemental analysis, and an X-ray diffraction study of **11** confirmed the structures proposed in Scheme 7.



Scheme 7. Formation of calcium, strontium, and barium oxoheterometallodicubanes.

Repeated attempts to obtain crystals of complex **11** failed and only once did we succeed in performing an X-ray diffraction study. The crystals were obtained from a toluene solution at –20 °C, but unfortunately their quality was very poor and the results[16] prevent us from making a detailed discussion of the structure. However, it can be established that **11** shows a double cube $[C_2Ti_6O_6Ca]$ core with the calcium atom located at the shared vertex of a distorted octahedral environment formed by the oxygen atoms of both preorganized ligands (Figure 4) in a similar way to other already reported double cube complexes.[8]

The analogous barium complex $[Ba\{(\mu_3\text{-}O)_3Ti_3Cp^*_3(\mu_3\text{-}CCH_2)\}_2]$ (**13**) can be obtained by treatment of $[BaR_2]$ [R = $N(SiMe_3)_2$, CH_2Ph] with the μ_3-ethylidyne complex **1** (see Scheme 7). Both reactions occur with formation of the complex, after heating [R = $N(SiMe_3)_2$, 100 °C, 2 days; R = CH_2Ph, 90 °C, one night], to give a red microcrystalline insoluble solid in 77–87% yield. The new complex was characterized by elemental analysis and IR spectroscopy.

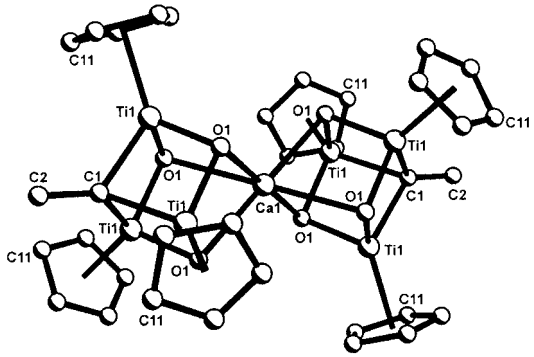


Figure 4. Molecular structure of compound **11**.

Conclusions

This work is part of an ongoing effort to study the peculiar chemical behavior exhibited by the μ_3-ethylidyne complex [{TiCp*(μ-O)}$_3$(μ_3-CMe)] (**1**). Treatment of this molecular model with alkaline-earth metal amides and alkyls produces the deprotonation of the μ_3-ethylidyne fragment to give μ_3-CCH_2^-, μ_3-$CHCH^-$, or μ_3-CCH^{2-} carbanions. The interaction of these fragments with the titanium atoms increases with a higher charge of the carbanion. Simultaneously, the alkaline-earth cation is incorporated through the oxygen atoms to build new cage structures.

Experimental Section

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

[{TiCp*(μ-O)}$_3$(μ_3-CMe)] (**1**) was synthesized according to the published procedure.[1] [$MgR_2(thf)_2$] (R = CH_2Ph,[17] CMe_3[18]), [$Ba(CH_2Ph)_2$],[19] and [M{$N(SiMe_3)_2$}$_2$(thf)$_2$], (M = Mg,[20] Ca,[21] Sr,[21] Ba[21]) were prepared following the literature methods. Pentamethylcyclopentadiene was purchased from Aldrich and Ph_3COH from Fluka and sublimed before use.

Elemental analyses (C, H, N) were performed with a Heraeus CHN-O-RAPID and/or Perkin–Elmer 2400-Serie II C, H, N, S/O. IR spectra were obtained in KBr pellets with a FT-IR Perkin–Elmer SPECTRUM 2000 spectrophotometer. NMR spectra were recorded on Varian NMR System spectrometers: Gemini-200, Unity-300, or Mercury-VX. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to TMS. Thermal reactions were carried out in a Roth autoclave model III (300 mL), with heater model 30S (20–300 °C) and temperature regulator model DR 500.

Preparation of [{$(Me_3Si)_2NMg$}(μ_3-O)$_3${$Ti_3Cp^*_3$(μ_3-C_2H_2)}] (2a,b): A 100-mL Carius tube was charged with [{TiCp*(μ-O)}$_3$(μ_3-CMe)] (**1**; 0.30 g, 0.48 mmol), [Mg{$N(SiMe_3)_2$}$_2$(thf)$_2$] (0.24 g, 0.48 mmol), and hexane (30 mL) and then sealed under vacuum. This solution was heated in an autoclave at 180 °C for one day. The Carius tube was opened in a glovebox and the solution concentrated and cooled to –40 °C to give a clean mixture of products which contained complexes **2a** and **2b** in approximately a 45:55 ratio (yield: 0.32 g, 82%). IR (KBr): $\tilde{\nu}$ = 2945 cm^{-1} (s), 2911 (vs), 2859 (s), 1492 (w), 1433 (m), 1377 (s), 1242 (s), 1180 (w), 997 (vs), 931 (w), 888 (s), 843 (s), 829 (s), 752 (m), 669 (m), 543 (s), 576 (s), 513 (m), 476 (m), 429 (m). $C_{38}H_{65}MgNO_3Si_2Ti_3$ (807.91): calcd. C 56.48, H 8.11, N 1.73; found C 56.12, H 8.37, N 1.38.

2a: ^{1}H NMR (300 MHz, [D_6]benzene, 20 °C, TMS): δ = 0.46 [s, 18 H, N(SiMe_3)$_2$], 1.91 (s, 45 H, C_5Me_5), 2.95 (s, 2 H, μ_3-CCH_2) ppm. ^{13}C{^{1}H} NMR (75 MHz, [D_6]benzene, 20 °C, TMS): δ = 7.4 [N(SiMe_3)$_2$], 12.1 (C_5Me_5), 85.1 (μ_3-CCH_2), 120.0 (C_5Me_5), 384.3 (μ_3-CCH_2) ppm.

2b: ^{1}H NMR (300 MHz, [D_6]benzene, 20 °C, TMS): δ = 0.45 [s, 18 H, N(SiMe_3)$_2$], 1.86 (s, 45 H, C_5Me_5), 6.55 (s, 2 H, μ_3-η^2-*H*C*C*H) ppm. ^{13}C{^{1}H} NMR (75 MHz, [D_6]benzene, 20 °C, TMS): δ = 7.2 [N(SiMe_3)$_2$], 12.5 (C_5Me_5), 119.9 (C_5Me_5), 206.2 (μ_3-η^2-H*C*CH) ppm.

Preparation of [{(thf)$(Me_3Si)_2NM$}(μ_3-O)$_3${$Ti_3Cp^*_3$(μ_3-CCH_2)}] [M = Ca (3), Sr (4)]: The preparation of **3** or **4** was performed in a similar fashion to **2**. Complex **1** (0.4 g, 0.64 mmol) was treated with [Ca{$N(SiMe_3)_2$}$_2$(thf)$_2$] (0.32 g, 0.64 mmol) or [Sr{$N(SiMe_3)_2$}$_2$(thf)$_2$] (0.33 g, 0.64 mmol) in hexane (50 mL) at 140 °C for 4 d to afford **3** as red crystals (0.51 g, 88%) or at 100 °C for two days to give **4** as a bright red solid (0.50 g, 83%).

3: ^{1}H NMR (300 MHz, [D_6]benzene, 20 °C, TMS): δ = 0.37 [s, 18 H, N(SiMe_3)$_2$], 1.41 [m, 4 H, O(CH_2CH_2)$_2$], 1.99 (s, 45 H, C_5Me_5), 2.82 (s, 2 H, μ_3-CCH_2), 3.87 [m, 4 H, O(CH_2CH_2)$_2$] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D_6]benzene, 20 °C, TMS): δ = 6.2 [N(SiMe_3)$_2$], 11.7 (C_5Me_5), 25.5 [O(CH_2CH_2)$_2$], 69.6 [O(CH_2CH_2)$_2$], 82.3 (μ_3-CCH_2), 117.9 (C_5Me_5), 380.1 (μ_3-CCH_2) ppm. IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1} (s), 2908 (vs), 2857 (s), 1493 (w), 1437 (m), 1377 (s), 1254 (s), 1179 (m), 1055 (vs), 1031 (vs), 931 (m) 879 (s), 820 (vs),762 (w), 618 (s), 584 (s), 520 (m), 415 (s). $C_{42}H_{73}CaNO_4Si_2Ti_3$ (895.82): calcd. C 56.31, H 8.21, N 1.56; found C 56.17, H 8.58, N 1.18.

4: ^{1}H NMR (300 MHz, [D_6]benzene, 20 °C, TMS): δ = 0.35 [s, 18 H, N(SiMe_3)$_2$], 1.37 [m, 4 H, O(CH_2CH_2)$_2$], 2.00 (s, 45 H, C_5Me_5), 2.72 (s, 2 H, μ_3-CCH_2), 3.62 [m, 4 H, O(CH_2CH_2)$_2$] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D_6]benzene, 20 °C, TMS): δ = 5.8 [N(SiMe_3)$_2$], 11.6 (C_5Me_5), 25.3 [O(CH_2CH_2)$_2$], 69.4 [O(CH_2CH_2)$_2$], 81.2 (μ_3-CCH_2), 117.5 (C_5Me_5), 377.3 (μ_3-CCH_2) ppm. IR (KBr): $\tilde{\nu}$ = 2911 cm^{-1} (vs), 2858 (s), 1493 (w), 1435 (s), 1376 (s), 1244 (s), 1178 (w), 1077 (vs), 1033 (s), 932 (m), 879 (s), 819 (vs), 758 (s), 645 (s), 623 (s), 584 (s), 391 (s). $C_{42}H_{73}NO_4Si_2SrTi_3$ (943.34): calcd. C 53.47, H 7.80, N 1.48; found C 53.22, H 7.75, N 1.43.

Preparation of [Cp*Ca(μ_3-O)$_3${$Ti_3Cp^*_3$(μ_3-CCH_2)}] (5): Pentamethylcyclopentadiene (53 μL, 0.34 mmol) was added to a solution of **3** (0.30 g, 0.33 mmol) in hexane (40 mL) and the reaction mixture was heated at 90 °C for 6 h to afford a dark-red solution. The solvent was removed in vacuo and the product was isolated in a 75% yield (0.20 g). ^{1}H NMR (300 MHz, [D_6]benzene, 20 °C, TMS): δ = 1.90 (s, 45 H, TiC_5Me_5), 2.22 (s, 15 H, CaC_5Me_5) 2.64 (s, 2 H, μ_3-CCH_2) ppm. ^{13}C{^{1}H} NMR (75 MHz, [D_6]benzene, 20 °C, TMS): δ = 11.4 (TiC_5Me_5), 11.4 (CaC_5Me_5), 114.0 (CaC_5Me_5), 118.1 (TiC_5Me_5), 82.5 (μ_3-CCH_2), 378.2 (μ_3-CCH_2) ppm. IR (KBr): $\tilde{\nu}$ = 2962 cm^{-1} (m), 2910 (s) 2857 (m), 1495 (w), 1438 (m), 1377 (m), 1088 (m), 1022 (m), 791 (vs), 675 (s), 617 (m), 579 (m), 420 (m). $C_{42}H_{62}CaO_3Ti_3$ (798.64): calcd. C 63.16, H 7.82; found C 63.09, H 8.11.

Preparation of [Cp*Sr(μ_3-O)$_3${$Ti_3Cp^*_3$(μ_3-CCH_2)}] (6): Complex **4** (0.30 g, 0.32 mmol) was dissolved in toluene (40 mL) in a 100-mL Carius tube fitted with a Young valve and pentamethylcyclopentadiene (50 μL, 0.32 mmol) was added. The reaction mixture was heated at 90 °C for 6 h. After that, the solution was filtered and the solvent was removed to yield **6** (0.20 g, 74% yield). ^{1}H NMR (300 MHz, [D_6]benzene, 20 °C, TMS): δ = 1.90 (s, 45 H, TiC_5Me_5),

2.20 (s, 15 H, SrC_5Me_5) 2.55 (s, 2 H, μ_3-CCH_2) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 11.0 (SrC_5Me_5), 11.3 (TiC_5Me_5), 81.3 (μ_3-CCH_2), 113.7 (SrC_5Me_5), 117.6 (TiC_5Me_5), 375.6 (μ_3-CCH_2) ppm. IR (KBr): $\tilde{\nu}$ = 2956 cm^{-1} (m), 2908 (s), 2856 (s), 1494 (w), 1437 (m), 1375 (m), 1082 (m), 1024 (m), 791 (vs), 680 (s), 619 (m), 582 (m), 390 (m). $C_{42}H_{62}O_3SrTi_3$ (846.16): calcd. C 59.61, H 7.38; found C 60.26, H 7.70.

Reaction of [{(Me$_3$Si)$_2$NMg}(μ_3-O)$_3${Ti$_3$Cp*$_3$(μ_3-C$_2$H$_2$)}] (2a,b) with Ph$_3$COH: Complexes **2a**,**b** (22 mg, 0.027 mmol) and Ph_3COH (ca. 7 mg, 0.027 mmol) were dissolved in [D$_6$]benzene (1.0 mL). The mixture reaction was transferred to a 5-mm NMR tube and once **2a**,**b** had been consumed at room temperature, the solvent and most of the amine formed, [NH(SiMe$_3$)$_2$], were removed under vacuum. The solid was then dissolved in [D$_6$]benzene and the solution was checked by ^{1}H and ^{13}C NMR spectroscopy allowed us to characterize the products as [(Ph_3COMg)(μ_3-O)$_3${Ti$_3$Cp*$_3$(μ_3-C$_2$H$_2$)}] (**7a**,**b**).

7a: ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 1.87 (s, 45 H, C_5Me_5), 2.82 (s, 2 H, μ_3-CCH_2), 6.9–7.5 (m, $OCPh_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 11.8 (C_5Me_5), 83.7 (μ_3-CCH_2), 120.0 (C_5Me_5), 125.0–155.0 ($OCPh_3$), 379.1 (μ_3-CCH_2) ppm.

7b: ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 1.80 (s, 45 H, C_5Me_5), 6.18 (s, 2 H, μ_3-η^2-$CHCH$), 6.9–7.5 (m, $OCPh_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 12.2 (C_5Me_5), 120.2 (C_5Me_5), 125.0–150.0 ($OCPh_3$), 200.8 (μ_3-η^2-$CHCH$) ppm.

Reaction of [{(thf)(Me$_3$Si)$_2$NCa}(μ_3-O)$_3${Ti$_3$Cp*$_3$(μ_3-CCH$_2$)}] (3) with Ph$_3$COH: In a similar fashion to **7**, complex **3** (21 mg, 0.023 mmol) and Ph_3COH (ca. 6 mg, 0.023 mmol) were dissolved in [D$_6$]benzene (1.0 mL). After thirty minutes at room temperature, the solvent and most of the amine formed were removed under vacuum and the solid was dissolved in [D$_6$]benzene. The NMR spectra allowed us to characterize the product as [(Ph_3COCa)(μ_3-O)$_3${Ti$_3$Cp*$_3$(μ_3-CCH$_2$)}] (**8**). ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 1.98 (s, 45 H, C_5Me_5), 2.80 (s, 2 H, μ_3-CCH_2), 6.9–7.7 (m, $OCPh_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 12.0 (C_5Me_5), 81.3 (μ_3-CCH_2), 117.8 (C_5Me_5), 125.0–155.0 ($OCPh_3$), 378.6 (μ_3-CCH_2) ppm.

Reaction of [{(thf)(Me$_3$Si)$_2$NSr}(μ_3-O)$_3${Ti$_3$Cp*$_3$(μ_3-CCH$_2$)}] (4) with Ph$_3$COH: The preparation was similar to that for **8**, but with **4** (22 mg, 0.023 mmol) and Ph_3COH (ca. 6 mg, 0.023 mmol) in [D$_6$]benzene (1.0 mL). The NMR spectra of the resulting solution allowed us to characterize the product as [(Ph_3COSr)(μ_3-O)$_3${Ti$_3$Cp*$_3$(μ_3-CCH$_2$)}] (**9**). ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 2.03 (s, 45 H, C_5Me_5), 2.78 (s, 2 H, μ_3-CCH_2), 6.9–7.7 (m, $OCPh_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 11.6 (C_5Me_5), 80.5 (μ_3-CCH_2), 82.6 ($OCPh_3$), 117.0 (C_5Me_5), 125.0–155.0 ($OCPh_3$), 377.7 (μ_3-CCH_2) ppm.

Preparation of [Mg(μ_4-O)(μ_3-O)$_2${Ti$_3$Cp*$_3$(μ_3-CCH)}]$_2$ (10). Method A: [{TiCp*(μ-O)}$_3$(μ_3-CMe)] (**1**; 0.20 g, 0.32 mmol), [Mg{N(SiMe$_3$)$_2$}$_2$(thf)$_2$] (0.16 g, 0.32 mmol), and hexane (30 mL) were placed in a 100-mL Carius tube. The pressure of the argon atmosphere was reduced and the reaction mixture was heated at 200 °C for four days. Slow crystallization of the solution at room temperature afforded **10** as red crystals suitable for an X-ray diffraction analysis. The isolated compound was obtained in 82% (0.17 g) yield.

Method B: Complex **1** (0.20 g, 0.32 mmol) and [Mg(CH$_2$Ph)$_2$(thf)$_2$] (0.112 g, 0.32 mmol) or [Mg(CMe$_3$)$_2$(thf)$_2$] (0.091 g, 0.32 mmol) were placed in a 100-mL Carius tube fitted with a Young valve and dissolved in toluene (30 mL). The mixture was heated at 90 °C for two days. The reddish solution was filtered, concentrated until 15 mL, and, finally, cooled to –40 °C to give a dark-red microcrystalline solid with a yield of 77% (0.16 g) from [Mg(CH$_2$Ph)$_2$(thf)$_2$] and 82% (0.17 g) from [Mg(CMe$_3$)$_2$(thf)$_2$]. IR (KBr): $\tilde{\nu}$ = 2906 cm^{-1} (vs), 2855 (s), 1489 (w), 1437 (s), 1373 (s), 1023 (m), 793 (m), 645 (vs), 534 (s), 492 (s), 454 (m), 403 (m). $C_{64}H_{92}Mg_2O_6Ti_6$ (1293.3): calcd. C 59.44, H 7.17; found C 59.29, H 7.52.

Preparation of [Ca{(μ_3-O)$_3$Ti$_3$Cp*$_3$(μ_3-CCH$_2$)}$_2$] (11): Compound **11** was prepared by heating **3** (0.15 g, 0.17 mmol) and **1** (0.104 g, 0.17 mmol) in toluene (20 mL) at 180 °C for two days. The Carius tube was opened in a glovebox and the solution was concentrated and cooled (–20 °C) to yield **11** as a dark-red, microcrystalline solid (0.19 g, 88%). IR (KBr): $\tilde{\nu}$ = 2907 cm^{-1} (vs), 2857 (s), 1492 (w), 1437 (m), 1375 (s), 1023 (m), 793 (m, br), 615 (vs), 518 (m), 472 (w), 418 (s), 387 (s). $C_{64}H_{94}CaO_6Ti_6$ (1286.8): calcd. C 59.74, H 7.36; found C 60.03, H 7.52.

Preparation of [Sr{(μ_3-O)$_3$Ti$_3$Cp*$_3$(μ_3-CCH$_2$)}$_2$] (12): Similarly to the preparation of **11**, **4** (0.15 g, 0.16 mmol) and **1** (99 mg, 0.16 mmol) were heated in toluene (20 mL) at 180 °C for two days to afford **12** as a red, microcrystalline solid (0.16 g, 75%). IR (KBr): $\tilde{\nu}$ = 2908 cm^{-1} (vs), 2857 (s), 1493 (w), 1435 (m), 1375 (s), 1023 (m), 793 (vs), 664 (m), 615 (vs), 528 (m), 416 (m), 389 (m). $C_{64}H_{94}O_6SrTi_6$ (1334.29): calcd. C 57.61, H 7.10; found C 57.70, H 7.20.

Preparation of [Ba{(μ_3-O)$_3$Ti$_3$Cp*$_3$(μ_3-CCH$_2$)}$_2$] (13): The thermal treatment of a mixture of **1** and BaR_2 [R = N(SiMe$_3$)$_2$, CH_2Ph] led to the formation of compound **13**. Thus, a solution of **1** (0.40 g, 0.64 mmol) and [Ba{N(SiMe$_3$)$_2$}$_2$(thf)$_2$] (0.183 g, 0.32 mmol) in toluene (40 mL), in a 100-mL Carius tube sealed under vacuum by flame, was heated in an autoclave at 100 °C for 2 d. When using [Ba(CH$_2$Ph)$_2$] (0.077 g, 0.24 mmol) and **1** (0.30 g, 0.48 mmol), the solution was heated at 90 °C for one night. After that, the Carius tube was opened in a glovebox and the solution concentrated and cooled to –40 °C to yield a dark-red, microcrystalline solid, which was identified as **13**, in a yield of 86% (0.38 g) for the reaction with [Ba{N(SiMe$_3$)$_2$}$_2$(thf)$_2$] and 78% (0.26 g) with [Ba(CH$_2$Ph)$_2$]. IR (KBr): $\tilde{\nu}$ = 2911 cm^{-1} (vs), 2858 (s), 1493 (w), 1436 (s), 1377 (s), 1103 (m), 1023 (m), 795 (vs), 668 (m), 616 (s), 543 (m), 486 (w), 394 (m). $C_{64}H_{94}BaO_6Ti_6$ (1384.0): calcd. C 55.54, H 6.85; found C 55.02, H 6.97.

X-ray Structure Determinations of 3 and 10: Crystals of **3** were grown from a hexane solution at –20 °C. Crystals of **10** were grown as described in the Experimental Section using Method A. Crystals were mounted in a glass capillary in a random orientation and transferred to an Enraf–Nonius CAD4 diffractometer for characterization and data collection at room temperature. Table 3 provides a summary of the crystal data, data collection, and refinement parameters for both complexes.

Intensity measurements were performed by ω–2θ scans in the range $3° < 2\theta < 46°$ for **3**. Of the 15341 measured reflections, 7387 were independent; R_1 = 0.083 and wR_2 = 0.219 [for 2706 reflections with $F > 4\sigma(F)$]. The values of R_1 and wR_2 are defined as: $R_1 = \Sigma||F_o| - |F_c||/[\Sigma|F_o|]$; $wR_2 = \{[\Sigma w(F_o^2 - F_c^2)^2] / [\Sigma w(F_o^2)^2]\}^{1/2}$.

Intensity measurements were performed by ω–2θ scans in the range $3.6° < 2\theta < 46°$ for **10**. Of the 4721 measured reflections, 4472 were independent; R_1 = 0.074 and wR_2 = 0.198 [for 3174 reflections with $F > 4\sigma(F)$].

The structures were solved, using the WINGX package,[22] by direct (**3**) and Patterson (**10**) methods (SHELXS-97)[23] and refined by least-squares against F^2 (SHELXL-97).[23] Complex **3** crys-

Table 3. Crystal data and structure refinement for **3** and **10**.

	3	**10**
Empirical formula	$C_{42}H_{73}CaNO_4Si_2Ti_3 \cdot 1/2C_6H_{14}$	$C_{64}H_{92}Mg_2O_6Ti_6$
Formula weight	939.06	1293.40
Temperature [K]	293(2)	293(2)
Wavelength (Mo-K_α) [Å]	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	11.622(3)	11.705(5)
b [Å]	21.314(5)	20.419(6)
c [Å]	24.260(5)	15.567(7)
β [°]	118.0(1)	119.7(1)
V [Å^3]; Z	5307(2); 4	3233(2); 2
$\rho_{calcd.}$ [g cm^{-3}]	1.175	1.329
μ [mm^{-1}]	0.619	0.772
F(000)	2012	1360
Crystal size [mm]	0.35 × 0.28 × 0.24	0.40 × 0.25 × 0.22
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Scan mode; θ range	ω–2θ; 1.35 to 23.00°	ω–2θ; 1.81 to 22.96°
Index ranges	–12 to 0, –23 to 23, –23 to 26	–12 to 0, –22 to 0, –14 to 17
Collected reflections	15341	4721
Independent reflections	7387 [R_{int} = 0.176]	4472 [R_{int} = 0.103]
Goodness-of-fit on F^2	0.939	1.032
Final R indices [$F > 4\sigma(F)$]	R_1 = 0.083; wR_2 = 0.219	R_1 = 0.074; wR_2 = 0.198
R indices (all data)	R_1 = 0.251; wR_2 = 0.331	R_1 = 0.110; wR_2 = 0.225
Largest diff. peak/hole [e Å^{-3}]	0.680 and –0.631	0.789 and –0.611

tallized with half a molecule of hexane. All non-hydrogen atoms of **3** were refined anisotropically, except those of the solvent, and the hydrogen atoms positioned geometrically and refined by using a riding model in the last cycles of refinement.

Compound **10** showed disorder in the pentamethylcyclopentadienyl linked to Ti(1) and also in C(2). Both disorders were treated conventionally by using the PART command of the SHELXL[23] program and allowing free refinement of the occupancy factors with the FVAR command. The final values were 70% of occupancy for C(2) and 53% for the C(11)–C(20) ring. All non-hydrogen atoms, except those of the disordered pentamethylcyclopentadienyl fragment, were refined anisotropically. All the hydrogen atoms were positioned geometrically and refined by using a riding model in the last cycles of refinement.

CCDC-296004 (for **3**) and -296005 (for **10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

The authors wish to acknowledge the financial support of the Spanish Ministerio de Ciencia y Tecnología (BQU2001-1499), the Comunidad de Madrid (07N/0091/2002), and the Universidad de Alcalá.

[1] a) R. Andrés, M. Galakhov, A. Martín, M. Mena, C. Santamaría, *Organometallics* **1994**, *13*, 2159–2163; b) R. Andrés, M. Galakhov, A. Martín, M. Mena, C. Santamaría, *J. Chem. Soc., Chem. Commun.* **1995**, 551–552.

[2] a) R. Andrés, M. V. Galakhov, M. P. Gómez-Sal, A. Martín, M. Mena, C. Santamaría, *Chem. Eur. J.* **1998**, 1206–1213; b) M. V. Galakhov, M. Mena, C. Santamaría, *Chem. Commun.* **1998**, 691–692; c) P. Gómez-Sal, A. Martín, M. Mena, M. C. Morales, C. Santamaría, *Chem. Commun.* **1999**, 1839–1840; d) R. Andrés, M. V. Galakhov, M. P. Gómez-Sal, A. Martín, M. Mena, M. C. Morales-Varela, C. Santamaría, *Chem. Eur. J.* **2002**, 805–811.

[3] a) G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis*, John Wiley and Sons, New York, **1994**, p. 400; b) B. C. Gates, *Catalytic Chemistry*, John Wiley and Sons, New York, **1992**; c) F. Zaera, *Chem. Rev.* **1995**, *95*, 2651–2693; d) B. E. Bent, *Chem. Rev.* **1996**, *26*, 1361–1390; e) H. H. Kung, *Transition Metal Oxides: Surface Chemistry and Catalysis*, Elsevier Science Publishers, Amsterdam, The Netherlands, **1989**; f) M. A. Barteau, *Chem. Rev.* **1996**, *96*, 1413–1430; g) P. M. Maitlis, H. C. R. Long Quyoum, M. L. Turner, Z.-Q. Wang, *Chem. Commun.* **1996**, 1–8; h) F. Zaera, *Catal. Lett.* **2003**, *91*, 1–10; i) H. H. Hwu, J. G. Chen, *Chem. Rev.* **2005**, *105*, 185–212.

[4] a) M. M. Hills, J. E. Parmeter, W. H. Weinberg, *J. Am. Chem. Soc.* **1987**, *109*, 597–599; b) A. J. Slavin, B. E. Bent, C.-T. Kao, G. A. Somorjai, *Surf. Sci.* **1988**, *206*, 124–144; c) C.-H. Hwang, C.-W. Lee, H. Kang, C. M. Kim, *Surf. Sci.* **2001**, *490*, 144–152; d) L. M. Ilharco, A. R. García, R. Brito de Barros, *Surf. Sci.* **2002**, *516*, 85–94; e) H. Kang, C. W. Lee, C. H. Hwang, C. M. Kim, *Appl. Surf. Sci.* **2003**, *203–204*, 842–846; f) M. Sock, A. Eichler, S. Surnev, J. N. Andersen, B. Klötzer, K. Hayek, M. G. Ramsey, F. P. Netzer, *Surf. Sci.* **2003**, *545*, 122–136; g) R. Deng, E. Herceg, M. Trenary, *Surf. Sci.* **2004**, *573*, 310–319.

[5] H. H. Hwu, J. G. Chen, *Surf. Sci.* **2004**, *557*, 144–158.

[6] O. González-del Moral, A. Martín, M. Mena, M. C. Morales-Varela, C. Santamaría, *Chem. Commun.* **2005**, 3682–3684.

[7] A. Abarca, M. V. Galakhov, J. Gracia, A. Martín, M. Mena, J.-M. Poblet, J. P. Sarasa, C. Yélamos, *Chem. Eur. J.* **2003**, *9*, 2337–2346.

[8] A. Martín, M. Mena, M. C. Morales-Varela, C. Santamaría, *Eur. J. Inorg. Chem.* **2004**, 1914–1921.

[9] a) D. J. Burkey, E. K. Alexander, T. P. Hanusa, *Organometallics* **1994**, *13*, 2773–2786; b) M. Westerhausen, M. Hartmann, N. Makropoulos, B. Wieneke, M. Wieneke, W. Schwarz, D. Stalke, *Z. Naturforsch., Teil B* **1998**, *53*, 117–125; c) M. Westerhausen, S. Schneiderbauer, A. N. Kneifel, Y. Soltl, P. Mayer, H. Noth, Z. Zhong, P. J. Dijkstra, J. Feijen, *Eur. J. Inorg. Chem.* **2003**, 3432–3439.

[10] PARST a) M. Nardelli, *Comput. Chem.* **1983**, *7*, 95–97; b) M. Nardelli, *J. Appl. Crystallogr.* **1995**, *28*, 659.

[11] T. Nishioka, K. Isobe, I. Kinoshita, Y. Ozawa, A. V. de Miguel, T. Nakai, S. Miyajima, *Organometallics* **1998**, *17*, 1637–1639.
[12] J. Gracia, A. Martín, M. Mena, M. C. Morales-Varela, J.-M. Poblet, C. Santamaría, *Angew. Chem.* **2003**, *115*, 957–960; *Angew. Chem. Int. Ed.* **2003**, *42*, 927–930.
[13] a) J. Calabrese, M. A. Cushing, S. D. Ittel, *Inorg. Chem.* **1988**, *27*, 867–870; b) C.-C. Chang, W.-H. Lee, T.-Y. Her, G.-H. Lee, S.-M. Peng, Y. Wang, *J. Chem. Soc., Dalton Trans.* **1994**, 315–322; c) P. Ghosh, G. Parkin, *Inorg. Chem.* **1996**, *35*, 1429–1430; d) C. A. Zechmann, T. J. Boyle, M. A. Rodriguez, R. A. Kemp, *Inorg. Chim. Acta* **2001**, *319*, 137–146.
[14] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441–451.
[15] 2.68(2) Å is the shortest distance between the C(2) and titanium atoms in complex **3**.
[16] X-ray data for complex **14**: $C_{64}H_{94}CaO_6Ti_6$, M = 1286.87, trigonal, $R\bar{3}$, a = 19.434(4), b = 19.434(3), c = 14.544(2) Å, U = 4751.6(12) Å^3, Z = 3, ρ_{calc} = 1.349 g cm^{-3}, μ = 0.849 mm^{-1}, F(000) = 2034. 8744 reflections collected at 200 K, 2398 [R_{int} = 0.114] independent, final R indices [$I > 2\sigma(I)$] R_1 = 0.165, wR_2 = 0.358. Largest diff. peak and hole 0.800 and –0.759 e Å^{-3}.
[17] R. R. Schrock, *J. Organomet. Chem.* **1976**, *122*, 209–225.
[18] G. E. Coates, J. A. Heslop, *J. Chem. Soc. A* **1968**, 514–518.
[19] A. Weeber, S. Harder, H. H. Brintzinger, K. Knoll, *Organometallics* **2000**, *19*, 1325–1332.
[20] K. W. Henderson, J. F. Allan, A. R. Kennedy, *Chem. Commun.* **1997**, 1149–1150.
[21] D. C. Bradley, M. B. Hursthouse, A. A. Ibrahim, K. M. A. Malik, M. Motevalli, R. Möseler, H. Powell, J. D. Runnades, A. C. Sullivan, *Polyhedron* **1990**, *9*, 2959–2964.
[22] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.
[23] *SHELX-97: Programs for Crystal Structure Analysis* (release 97-2), G. M. Sheldrick, University of Göttingen, Germany, **1998**.

Received: January 26, 2006
Published Online: April 18, 2006

