Deprotonation of μ_3-Methylidyne Groups on a Ti_3O_3 Support: A Way to Build Oxotitanocubanes Containing Alkali and Alkaline-Earth Metals

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The μ_3-methylidyne group of the complex $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}CH)]$ (**1**) ($Cp^* = \eta^5\text{-}C_5Me_5$) was deprotonated by amides of the group 1 elements, $[MN(SiMe_3)_2]$ (M = Li, Na, K, Rb, Cs) to form the oxoheterometallocubane complexes $[M(\mu_3\text{-}O)_3\{Ti_3Cp^*{}_3(\mu_3\text{-}C)\}]$ [M = Li (**3**), Na (**4**), K (**5**), Rb (**6**), Cs (**7**)]. Similar treatments of **1** with the alkaline-earth amides $[M\{N(SiMe_3)_2\}_2(thf)_2]$ (M = Mg, Ca, Sr) afforded the heterometallocubane derivatives $[\{(thf)_x(Me_3Si)_2NM\}(\mu_3\text{-}O)_3\{Ti_3Cp^*{}_3(\mu_3\text{-}C)\}]$ [M = Mg, x = 0, (**8**); Ca, x = 1, (**9**); Sr, x = 1, (**10**)] in high yields. The addition of ligands such as cyclopentadiene (C_5H_6) or pentamethylcyclopentadiene (C_5Me_5H) to the compounds **3**–**7** allowed recovery of the μ_3-methylidyne oxocomplex **1**. The analogous reaction of **8**–**10** with C_5H_6 caused the displacement of the amide fragment to give the heterometallocubanes $[(CpM)(\mu_3\text{-}O)_3\{Ti_3Cp^*{}_3(\mu_3\text{-}C)\}]$ [M = Mg (**11**), Ca (**12**), Sr (**13**)], while C_5Me_5H reacts only with **9** and **10** to give the compounds $[(Cp^*M)(\mu_3\text{-}O)_3\{Ti_3Cp^*{}_3(\mu_3\text{-}C)\}]$ [M = Ca (**14**), Sr (**15**)]. Furthermore, heating of the species **8**–**10** in the presence of the starting complex **1** produced amine elimination and afforded the corner-shared heterometallodicubanes $[M\{(\mu_3\text{-}O)_3Ti_3Cp^*{}_3(\mu_3\text{-}C)\}_2]$ [M = Mg (**16**), Ca (**17**), Sr (**18**)]. Treatment of **1** with the amide $[Ba\{N(SiMe_3)_2\}_2(thf)_2]$ or dialkyl derivatives of magnesium $[MgR_2(thf)_2]$ (R = CH_2Ph, *t*Bu) and barium $[Ba(CH_2Ph)_2]$ provided the corner-shared metallodicubanes $[M\{(\mu_3\text{-}O)_3Ti_3Cp^*{}_3(\mu_3\text{-}C)\}_2]$ [M = Mg(**16**), Ba(**19**)]. The molecular structures of complexes **9**, **16**, **17** and **18** have been established by single-crystal X-ray analyses.

Introduction

Our efforts to explore the behavior of alkylidyne groups on a trinuclear support in the complexes $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}CR)]$ [R = H (**1**), Me (**2**)],[1] as a molecular approach to hydrocarbon-metal(oxo) surface interactions, have revealed surprising and unprecedented chemical reactivity. Thus, we have shown that metal carbonyl hydrides,[2] carbon monoxide,[3] isocyanides,[3] ketones,[4] *N*-benzylidene(phenyl)amine,[5] amines, diamines and the imine $Ph_2C{=}NH$[6] are incorporated into the Ti_3O_3 core by transformation of the alkylidyne units. In these systems, the role of the oxygen atoms is considerable, bridging the titanium atoms firmly and enhancing the cooperative effect between them but we do not have evidence for its direct participation in those processes. Furthermore, in the course of our studies we have discovered other kinds of reactivity for the complexes $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}CR)]$ [R = H (**1**), Me (**2**)] as preorganized neutral tridentate six electron donor ligands without implication of the alkylidyne groups.[7] In fact, they provide an effective route to heterometallocubanes upon treatment with appropriate metal carbonyl complexes, where the metal carbonyl fragment shares electron density with the titanium atoms. Therefore the $[(\mu_3\text{-}CR)Ti_3Cp^*{}_3(\mu_3\text{-}O)_3M(CO)_n]$ cores of these oxoheterometallocubanes are discrete models for studying the oxide-to-metal catalyst-support interaction.

Recently, we have communicated the intercalation of alkali metal ions into layered organometallic titanium oxides by treatment of the complex $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}CH)]$ (**1**) with alkali metal (Li, Na, K) alkyls and amides.[8] This process takes place with the incorporation of the alkali metal at the free vertex of the incomplete cube-type core Ti_3O_3C and the deprotonation of the μ_3-methylidyne ligand. Consequently, the active cooperation between the oxo and alkylidyne groups is possible in the singular chemistry of the complexes $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}CR)]$.

We have expanded this preliminary study and herein we describe the behavior of the complex $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}CH)]$ (**1**) towards alkali and alkaline-earth dialkylamides and alkyls.

Results and Discussion

When the complex $[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}CH)]$ (**1**) was treated with the alkyl derivatives [MR] (M = Li, R = CH_2SiMe_3, CH_2CMe_3, *n*Bu; M = Na, K, R = *t*Bu) at room temperature or with the amides $[MN(SiMe_3)_2]$ (M = Li,

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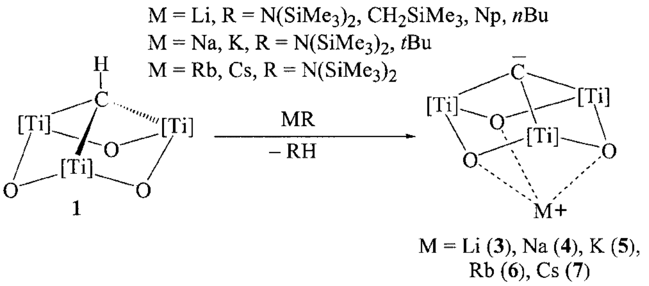
Na, K), at 60 °C overnight in a 1:1 ratio in toluene or hexane, the compounds **3−5** were obtained (70−90%) (see Scheme 1). On the other hand, the amides $[MN(SiMe_3)_2]$ (M = Rb, Cs), react with complex **1** in a 1:1 ratio at 60 °C in tetrahydrofuran to give the derivatives **6** and **7** in high yields (70−80%). The isolated solids were found to be stable under argon at room temperature and practically insoluble in common solvents such as toluene, hexane and dichloromethane, with the exception of tetrahydrofuran, which allowed their NMR spectroscopic characterization.



Scheme 1. Reaction of **1** with alkaline amide and alkyl reagents. [Ti] = Ti(η^5-C_5Me_5)

The ^1H and ^{13}C NMR spectra in [D$_8$]tetrahydrofuran, of these species, show signals assignable to equivalent η^5-C_5Me_5 groups and singlets for the apical μ_3-carbon atoms in the range 577−587 ppm, consistent with symmetrical structures in solution and the removal of the protons of the μ_3-methylidyne fragments.

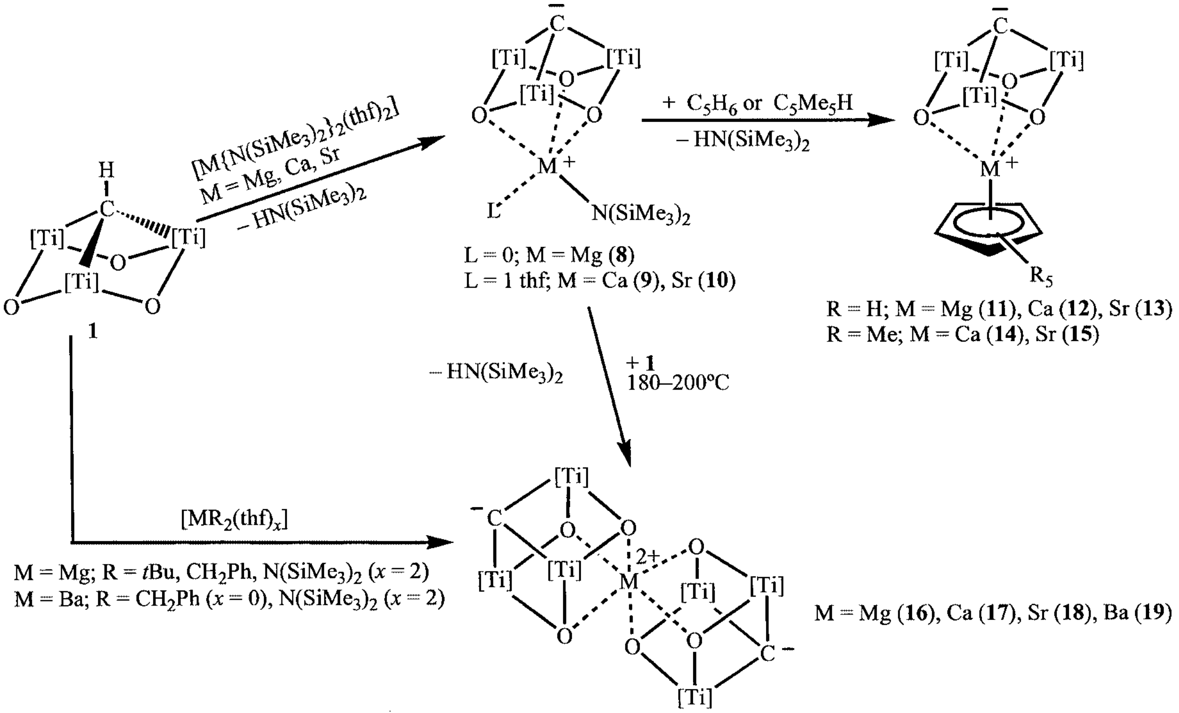
To unequivocally probe the existence of the μ_3-carbido group, the reactions of **3−7** with MeI in [D$_6$]benzene were performed, which slowly yielded the μ_3-ethylidyne complex $[Ti_3Cp^*_3(\mu_3\text{-}O)_3(\mu_3\text{-}CMe)]$ (**2**). In a similar way, addition of ligands with acidic protons such as C_5H_6 or C_5Me_5H to the compounds **3−7** in [D$_6$]benzene caused the protonation of the carbide species and recovery of the μ_3-methylidyne complex **1**.

The X-ray diffraction study of **3** was reported in a previous communication and showed a dimeric structure in the solid state.[8] The lithium atoms are incorporated at the free vertex of the deprotonated oxoalkylidyne **1** derivative and two cube-type cores LiO_3Ti_3C are directly linked through two Li−O bonds.

In an attempt to extend our studies on the incorporation of s-block metals into the preorganized structure of **1**, we have also designed reactions with alkaline-earth derivatives. With this aim, we chose as starting reagents the dialkylamides $[M\{N(SiMe_3)_2\}_2(thf)_2]$ (M = Mg, Ca, Sr, Ba) and the dialkyls $[MgR_2(thf)_2]$ (R = CH_2Ph, *t*Bu) and $[Ba(CH_2Ph)_2]$.

The reactions of **1** with equimolecular amounts of $[M\{N(SiMe_3)_2\}_2(thf)_2]$ (M = Mg, Ca, Sr) also appeared to take place through the deprotonation of the μ_3-methylidyne group and amine elimination, to give soluble green microcrystalline solids of the complexes **8−10** in high yields (82−95%). The X-ray diffraction study of **9** and the analytical and spectroscopic data of all compounds support the structures shown in Scheme 2.

The structure of **9** was determined by a single-crystal X-ray diffraction study (Figure 1). Geometrical parameters



Scheme 2. Reactivity of **1** with alkaline-earth metal reagents. [Ti] = Ti(η^5-C_5Me_5)

are summarized in Table 1. At first sight, the core of the molecular structure can be described as a cube in which the metallic centers alternate their positions with the oxygen and carbon atoms. The titanium atoms exhibit three-legged stool environments, while the calcium atom is five-coordinate with three sites occupied by the tridentate ligand, [{TiCp*(μ-O)}$_3$(μ-C)], and the remainder of the coordination sphere being filled by one amide group and one tetrahydrofuran molecule.

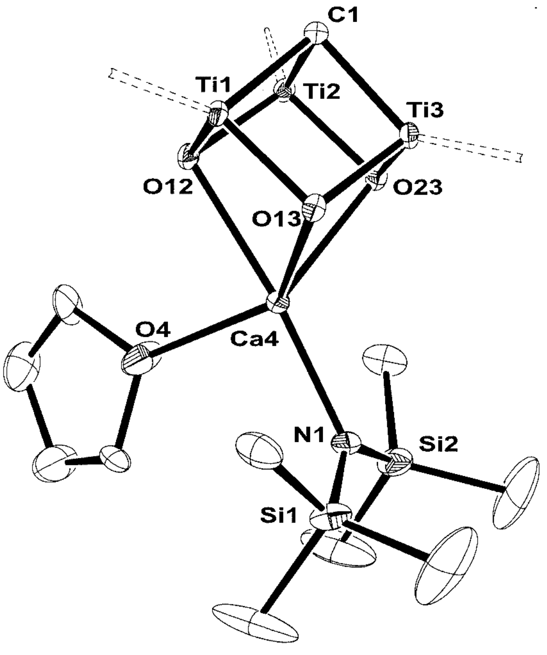


Figure 1. Simplified view of the molecular structure of **9** in the crystal

Table 1. Selected averaged lengths (Å) and angles (°) for complex **9**

Ti−C(1)	1.963(4)	N(1)−Ca(4)	2.291(4)
Ti−O	1.895(3)	O(4)−Ca(4)	2.376(4)
O(13)−Ca(4)	2.427(3)	Ca(4)···Ti	3.232(1)
O(23)−Ca(4)	2.425(3)	Ti···Ti	2.756(1)
O(12)−Ca(4)	2.483(3)	N(1)−Si	1.684(4)
Ti−C(1)−Ti	89.2(2)	Ti−O−Ti	93.3(1)
Ti−O−Ca(4)	95.4(1)	O−Ti−O	96.6(1)
N(1)−Ca(4)−O(4)	92.3(1)	O−Ti−C(1)	88.6(2)
N(1)−Ca(4)−O(23)	114.4(1)	Si(1)−N(1)−Ca(4)	115.1(2)
N(1)−Ca(4)−O(13)	114.4(1)	Si(1)−N(1)−Si(2)	129.7(2)
N(1)−Ca(4)−O(12)	173.8(1)	Si(2)−N(1)−Ca(4)	115.0(2)
O(23)−Ca(4)−O(13)	71.3(1)	O(4)−Ca(4)−O(23)	133.0(2)
O(4)−Ca(4)−O(12)	81.5(1)	O(4)−Ca(4)−O(13)	133.2(2)
O(13)−Ca(4)−O(12)	70.4(1)	O(23)−Ca(4)−O(12)	70.5(1)

Distances from the calcium to the oxygen atoms of the preorganized ligand are in the range of 2.425(3)−2.483(3) Å, the latter corresponding to a *trans* position of the calcium to the amido group. These distances are similar to those seen in other calcium complexes found in the literature with higher coordination numbers.[9] In the same way, the calcium−nitrogen bond length of 2.291(4) Å is close to that found for complexes containing the Ca−N(SiMe$_3$)$_2$ moiety.[10] The Ti−C(1) bond length, 1.963 Å (av.), is shorter than those shown in [{TiCp*(μ-O)}$_3$(μ-CH)] (**1**) [Ti−C(1) = 2.10 Å av.],[1b,1c] **2** [Ti−C(1) = 2.12 Å av.][1a,1c] and the oxoheterometallodicubane [{Li(μ$_3$-O)$_3$[Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ$_3$-C)]}$_2$] (Ti−C$^-$ 2.055 Å av.),[8] and close to that in the zwitterionic derivative [{Ti(η^5-C$_5$Me$_5$)(μ-O)}$_3${μ$_3$-η^2-C$^-$C(Me)N$^+$(2,6-Me$_2$C$_6$H$_3$)}] (Ti−C$^-$ 2.017(5) Å].[3]

The ^{1}H NMR spectra for complexes **8**−**10** in [D$_6$]benzene each show only one signal assignable to the η^5-C$_5$Me$_5$ groups due to the rotation of the organometallic ligand around the metallic center, analogous to the situation found in other similar compounds.[11] In the ^{13}C NMR spectra of these complexes the singlets for the apical carbides at very low field (δ = 588−598 ppm) are particularly noteworthy.

Again, the chemical evidence for the existence of the μ$_3$-carbido groups in **8**−**10** was obtained by their treatment with MeI in [D$_6$]benzene, which quantitatively afforded the μ$_3$-ethylidyne complex [Ti$_3$Cp*$_3$(μ-O)$_3$(μ$_3$-CMe)] (**2**).

Unlike the alkali metal complexes **3**−**7**, the reactions of compounds **8**−**10** with cyclopentadiene (C$_5$H$_6$) did not involve carbide protonation, but led to the metathesis reaction of the amide group to give the new heterometallocubane derivatives [(CpM)(μ$_3$-O)$_3${Ti$_3$Cp*$_3$(μ$_3$-C)}] [M = Mg (**11**), Ca (**12**), Sr (**13**)]. The analogous reaction with pentamethylcyclopentadiene (C$_5$Me$_5$H) afforded the compounds [(Cp*M)(μ$_3$-O)$_3${Ti$_3$Cp*$_3$(μ$_3$-C)}] [M = Ca (**14**), Sr (**15**)]. Pentamethylcyclopentadiene did not react, however, with the magnesium compound **8**, probably due to the steric hindrance and lower acidity of the C$_5$Me$_5$H ligand. The compounds **11**−**15** were isolated as green solids in good yields and the analytical and spectroscopic data are in agreement with the formulations given in Scheme 2.[12]

Compounds **11**, **12**, **13** and **14** are soluble in hydrocarbon and aromatic solvents, which allowed their NMR spectroscopic characterization. The strontium compound **15**, however, is scarcely soluble in benzene, toluene or tetrahydrofuran. The presence of the apical μ$_3$-carbido in all the cases was confirmed by ^{13}C NMR spectroscopy in [D$_6$]benzene, a singlet in the range δ = 580−594 ppm being observed in each case.

On the other hand, the elimination of the amido group could also be achieved by thermal treatment (over 150 °C) of **8**−**10** in toluene with one equivalent of the starting complex [{TiCp*(μ-O)}$_3$(μ$_3$-CH)] (**1**), producing green solids identified as the corner-shared double heterometallocubanes species [M{(μ-O)$_3$Ti$_3$Cp*$_3$(μ$_3$-C)}$_2$] M = Mg (**16**), Ca (**17**), Sr (**18**).[13] These complexes are insoluble in all the usual solvents such as toluene, hexane and even tetrahydrofuran. Fortunately, after numerous trials their solid-state structures were determined by X-ray diffraction (vide infra).

The complex [Mg{(μ-O)$_3$Ti$_3$Cp*$_3$(μ$_3$-C)}$_2$] (**16**) could also be obtained in 80−87% yield by irradiation or heating of a toluene solution of **1** and [Mg(CH$_2$Ph)$_2$(thf)$_2$] or [Mg*t*Bu$_2$(thf)$_2$]. In both cases, the reaction occurred with alkane elimination. Similar thermal treatment of **1** with [Ba{N(SiMe$_3$)$_2$}$_2$(thf)$_2$] in toluene at 100 °C for two days or with [Ba(CH$_2$Ph)$_2$] at 90 °C overnight afforded the oxoheterometallodicubane barium analogue, in good yield

(66−78%), [Ba{(μ-O)$_3$Ti$_3$Cp*$_3$(μ$_3$-C)}$_2$] (**19**), as a microcrystalline green solid, which was insoluble in practically all solvents.

X-ray Crystal Structures of 16, 17 and 18

The solid-state structures of **16**, **17** and **18** determined from X-ray diffraction data are comprised of two trinuclear [Ti$_3$Cp*$_3$O$_3$C] units that are joined to each other by an alkaline-earth metal atom, which lies on the center of symmetry. In this arrangement, the tridentate organometallic ligands are situated in alternate positions relative to the pentamethylcyclopentadienyl groups in each case .

As shown in Figure 2, the geometry around the central metal atom can be described as distorted octahedral in each case. An examination of the values of the bond lengths and angles for these complexes (see Table 2) reveals an increasing distortion from magnesium to strontium, with the latter being best described as a trigonal antiprism with wider O−M−O intercube and closer intracube angles. The distance M−O increases in the same way, in agreement with the increasing size of the atomic radii of the central atom upon descending the group. In the case of calcium [Ca−O = 2.435(4) Å av., **17**], this value is close to that mentioned above for the metallocubane compound **9** [Ca−O = 2.445(3) Å av.]. The M−O bond lengths in the magnesium and strontium derivatives are in the expected ranges for oxocomplexes with high numbers of oxygen atoms.[14]

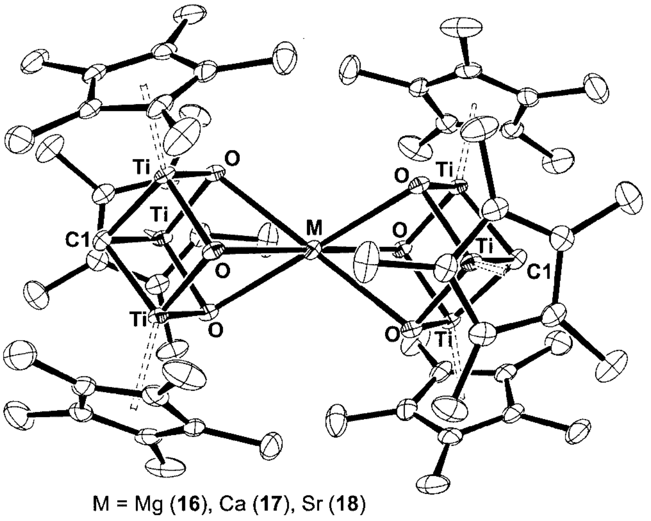


Figure 2. Simplified view of the molecular structures of **16**, **17** and **18**

The Ti−C(1) bond lengths decrease from magnesium to strontium [Mg = 2.020(10) Å av., Ca = 1.990(7) Å av., Sr = 1.970(2) Å av.], consistent with the higher steric requirement of the metal center. In all cases, these bond lengths are slightly shorter than those shown in **1** [Ti−C(1) = 2.10 Å av.][1b,1c] and **2** [Ti−C(1) = 2.12 Å av.],[1a,1c] and in the same range as those found in the zwitterionic derivative [{Ti(η^5-C$_5$Me$_5$)(μ-O)}$_3${μ$_3$-η^2-C$^-$C(Me)N$^+$(2,6-Me$_2$C$_6$H$_3$)}] [Ti−C$^-$ 2.017(5) Å].[3]

Table 2. Selected averaged distances (Å) and angles (°) for **16**, **17** and **18**

	M = Mg, **16**	M = Ca, **17**	M = Sr, **18**
Ti−O	1.905(6)	1.907(4)	1.896(2)
Ti−C(1)	2.020(10)	1.990(7)	1.970(2)
Ti···Ti	2.815(3)	2.780(2)	2.756(1)
M−O	2.174(6)	2.435(4)	2.585(2)
Ti···M	2.995(2)	3.230(2)	3.383(1)
O−Ti−O	92.1(3)	96.2(2)	97.2(1)
Ti−O−Ti	95.2(3)	93.6(2)	93.2(1)
M−O−Ti	94.2(2)	95.4(2)	96.9(1)
Ti−C1−Ti	88.3(4)	88.5(3)	88.1(1)
O−M−O[a]	78.2(3)−101.8(2)	71.2(2)−108.8(2)	66.8(1)−113.2(1)

[a] The narrower values correspond to the O−M−O angles of the same cube.

Conclusion

As outlined in the introduction, the active cooperation between the oxo and methylidyne groups is possible in the singular trinuclear chemistry of titanium. The results presented here demonstrate the peculiar behavior of the μ$_3$-methylidyne complex [{TiCp*(μ-O)}$_3$(μ$_3$-CH)] (**1**) with alkali and alkaline-earth metal amides and alkyls. In all cases, the processes go via the alkylidyne deprotonation and the anchorage of the group 1 or 2 cation metal on the [Ti$_3$O$_3$] system to form heterometallocubane or corner-shared heterometallodicubane species.

Experimental Section

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

[{TiCp*(μ-O)}$_3$(μ$_3$-CH)] (**1**) was synthesized according to the published procedures.[1a,1c] *n*BuLi was purchased from Aldrich as a 1.6 M solution in hexane. [LiCH$_2$SiMe$_3$] and [LiNp] were prepared as described in the literature,[15] as were [Na*t*Bu] and [K*t*Bu].[16] [MN(SiMe$_3$)$_2$] (M = Li, Na, K) were purchased from Aldrich and used as supplied. [MN(SiMe$_3$)$_2$] (M = Rb, Cs),[17] [MgR$_2$(thf)$_2$] (R = CH$_2$Ph,[18] *t*Bu[19]), [Ba(CH$_2$Ph)$_2$],[20] and [M{N(SiMe$_3$)$_2$}$_2$(thf)$_2$], (M = Mg,[21] Ca,[22] Sr,[22] Ba[22]) were prepared following the literature methods. Pentamethylcyclopentadiene and dicyclopentadiene were purchased from Aldrich.

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 instrument. IR spectra were obtained in KBr pellets by using an FT-IR Perkin−Elmer SPECTRUM 2000 spectrophotometer. NMR spectra were recorded with a Varian 300 spectrometer. Chemical shifts are given in ppm (δ) downfield from TMS (δ = 0.0) using the residual protons or carbon atoms of the solvent as an internal reference. 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 $[\mathrm{Li}(\mu_3\text{-O})_3\{\mathrm{Ti}_3\mathrm{Cp}_3^*(\mu_3\text{-C})\}]$ (3): *n*BuLi (0.35 mL, 0.56 mmol) was added to a solution of **1** (0.35 g, 0.57 mmol) in hexane (40 mL) in a 100-mL Carius tube. The reaction mixture was stirred at room temperature overnight. The green solid was then filtered, washed with hexane and vacuum dried to afford 0.33 g of **3** (Yield: 93%). ^{1}H NMR (300 MHz, [D$_8$]tetrahydrofuran, 20 °C, TMS): δ = 1.99 (s, $\mathrm{C_5}Me_5$) ppm. ^{13}C{^{1}H} NMR (300 MHz, [D$_8$]tetrahydrofuran, 20 °C, TMS): δ = 12.0 ($\mathrm{C_5}Me_5$), 115.3 ($C_5\mathrm{Me_5}$), 581.4 (μ_3-C) ppm. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2907 (s), 2856 (vs), 1491 (w), 1437 (s), 1373 (s), 1023 (m), 801 (w), 681 (vs), 616 (vs), 464 (w), 416 (s). $\mathrm{C_{31}H_{45}LiO_3Ti_3}$ (616.27): calcd. C 60.42, H 7.36; found C 60.81, H 7.59.

Preparation of $[\mathrm{Na}(\mu_3\text{-O})_3\{\mathrm{Ti}_3\mathrm{Cp}_3^*(\mu_3\text{-C})\}]$ (4): A 100-mL Carius tube was charged with **1** (0.30 g, 0.49 mmol), $[\mathrm{NaN(SiMe_3)_2}]$ (0.09 g, 0.49 mmol), and hexane (40 mL). The reaction mixture was heated at 60 °C overnight and the red solid formed was filtered, washed with hexane and dried under vacuum to give 0.26 g of **4** (Yield: 83%). ^{1}H NMR (300 MHz, [D$_8$]tetrahydrofuran, 20 °C, TMS): δ = 1.95 (s, $\mathrm{C_5}Me_5$) ppm. ^{13}C{^{1}H} NMR (300 MHz, [D$_8$]tetrahydrofuran, 20 °C, TMS): δ = 11.7 ($\mathrm{C_5}Me_5$), 115.4 ($C_5\mathrm{Me_5}$), 586.7 (μ_3-C) ppm. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2907 (vs), 2850 (vs), 1493 (w), 1437 (s), 1372 (s), 1023 (m), 795 (w), 681 (vs), 621 (vs), 467 (w), 411 (s). $\mathrm{C_{31}H_{45}NaO_3Ti_3}$ (632.32): calcd. C 58.88, H 7.17; found C 58.65, H 7.45.

Preparation of $[\mathrm{K}(\mu_3\text{-O})_3\{\mathrm{Ti}_3\mathrm{Cp}_3^*(\mu_3\text{-C})\}]$ (5): In a similar fashion to **4**, a solution of **1** (0.30 g, 0.49 mmol) and $[\mathrm{KN(SiMe_3)_2}]$ (0.10 g, 0.49 mmol) in hexane (40 mL) was heated at 60 °C overnight. The red solid formed was filtered and dried under vacuum to give 0.23 g of **5** (Yield: 72%). ^{1}H NMR (300 MHz, [D$_8$]tetrahydrofuran, 20 °C, TMS): δ = 1.94 (s, $\mathrm{C_5}Me_5$) ppm. ^{13}C{^{1}H} NMR (300 MHz, [D$_8$]tetrahydrofuran, 20 °C, TMS): δ = 11.5 ($\mathrm{C_5}Me_5$), 115.1 ($C_5\mathrm{Me_5}$), 582.0 (μ_3-C) ppm. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2910 (vs), 2857 (vs), 1597 (w), 1495 (w), 1439 (s), 1375 (s), 1247 (w), 1067 (w), 916 (m), 899 (m), 852 (s), 784 (vs), 680 (s), 624 (m), 573 (m), 411 (s). $\mathrm{C_{31}H_{45}KO_3Ti_3}$ (648.43): calcd. C 57.42, H 6.99; found C 56.99, H 7.10.

Preparation of $[\mathrm{Rb}(\mu_3\text{-O})_3\{\mathrm{Ti}_3\mathrm{Cp}_3^*(\mu_3\text{-C})\}]$ (6): In a 100-mL Carius tube with a valve were placed $[\{\mathrm{TiCp^*}(\mu\text{-O})\}_3(\mu_3\text{-CH})]$ (**1**) (0.50 g, 0.82 mmol), $[\mathrm{RbN(SiMe_3)_2}]$ (0.20 g, 0.82 mmol) and tetrahydrofuran (40 mL). The reaction mixture was heated at 60 °C and stirred overnight. The red solution was then filtered, and the solvent removed under vacuum to afford 0.46 g of **6** (Yield: 81%). ^{1}H NMR (300 MHz, [D$_8$]tetrahydrofuran, 20 °C, TMS): δ = 1.94 (s, $\mathrm{C_5}Me_5$) ppm. ^{13}C{^{1}H} NMR (300 MHz, [D$_8$]tetrahydrofuran, 20 °C, TMS): δ = 11.7 ($\mathrm{C_5}Me_5$), 115.1 ($C_5\mathrm{Me_5}$), 579.5 (μ_3-C) ppm. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2905 (vs), 2854 (s), 1493 (w), 1431 (m), 1375 (s), 1260 (w), 1023 (w), 800 (w), 776 (w), 657 (vs), 630 (vs), 583 (m), 436 (m), 382 (m). $\mathrm{C_{31}H_{45}O_3RbTi_3}$ (694.80): calcd. C 53.59, H 6.53; found C 53.02, H 6.85.

Preparation of $[\mathrm{Cs}(\mu_3\text{-O})_3\{\mathrm{Ti}_3\mathrm{Cp}_3^*(\mu_3\text{-C})\}]$ (7): The preparation was similar to that for **6** from $[\{\mathrm{TiCp^*}(\mu\text{-O})\}_3(\mu_3\text{-CH})]$ (**1**) (0.50 g, 0.82 mmol), $[\mathrm{CsN(SiMe_3)_2}]$ (0.24 g, 0.82 mmol) and tetrahydrofuran (40 mL). The light red solid of **7** was obtained in a 73% yield (0.44 g). ^{1}H NMR (300 MHz, [D$_8$]tetrahydrofuran, 20 °C, TMS): δ = 1.94 (s, $\mathrm{C_5Me_5}$) ppm. ^{13}C{^{1}H} NMR (300 MHz, [D$_8$]tetrahydrofuran, 20 °C, TMS): δ = 11.6 ($\mathrm{C_5}Me_5$), 114.7 ($C_5\mathrm{Me_5}$), 577.3 (μ_3-C) ppm. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2908 (s), 2856 (s), 1494 (w), 1438 (w), 1373 (w), 1261 (w), 1021 (w), 800 (w), 681 (vs), 628 (s), 476 (w), 418 (s). $\mathrm{C_{31}H_{45}CsO_3Ti_3}$ (742.24): calcd. C 50.16, H 6.11; found C 49.08, H 6.45.

Preparation of $[\{(\mathrm{Me_3Si})_2\mathrm{NMg}\}(\mu_3\text{-O})_3\{\mathrm{Ti}_3\mathrm{Cp}_3^*(\mu_3\text{-C})\}]$ (8): A solution of compound **1** (0.20 g, 0.33 mmol) and $[\mathrm{Mg\{N(SiMe_3)_2\}_2(thf)_2}]$ (0.16 g, 0.33 mmol) in toluene (30 mL) was placed in a 100-mL Carius-tube. The ampoule was sealed under vacuum by flame and the reaction mixture was heated at 180 °C for two days. The solution was then filtered, and the solvent removed to afford **8** as a green microcrystalline solid. Yield: 0.21 g, 82%. ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 0.40 [s, 18 H, N(SiMe_3)$_2$], 2.04 (s, 45 H, $\mathrm{C_5}Me_5$); ^{13}C{^{1}H} NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 6.3 [N(SiMe_3)], 11.8 ($\mathrm{C_5}Me_5$), 120.6 ($C_5\mathrm{Me_5}$), 598.3 (μ_3-C) ppm. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2940 (s), 2909 (vs), 2858 (s), 1491 (w), 1435 (m), 1377 (s), 1242 (s), 1001 (vs), 931 (w), 888 (s), 829 (vs), 789 (s), 752 (m), 670 (vs), 610 (vs), 467 (m), 430 (s). $\mathrm{C_{37}H_{63}MgNO_3Si_2Ti_3}$ (794.03): calcd. C 55.97, H 8.00, N 1.76; found C 55.99, H 8.39, N 1.73.

Preparation of $[\{(\mathrm{thf})(\mathrm{Me_3Si})_2\mathrm{NCa}\}(\mu_3\text{-O})_3\{\mathrm{Ti}_3\mathrm{Cp}_3^*(\mu_3\text{-C})\}]$ (9): A solution of **1** (0.50 g, 0.82 mmol) and $[\mathrm{Ca\{N(SiMe_3)_2\}_2(thf)_2}]$ (0.41 g, 0.82 mmol) in hexane (50 mL) was placed in a 100-mL Carius-tube with Young's valve. The reaction mixture was heated at 90 °C for 36 h. The green solution was then filtered, and the solvent was removed under vacuum to give **9** as a green powder (0.68 g, 94%). The slow evaporation of the solvent from a concentrated solution in hexane led to single-crystals of **9** suitable for an X-ray analysis. ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 0.34 [s, 18 H, N(SiMe_3)$_2$], 1.36 (m, 4 H, thf), 2.12 (s, 45 H, $\mathrm{C_5}Me_5$), 3.87 (m, 4 H, thf) ppm. ^{13}C{^{1}H} NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 5.8 [N(SiMe_3)$_2$], 12.1 ($\mathrm{C_5}Me_5$), 24.9 and 70.4 (thf), 118.9 ($C_5\mathrm{Me_5}$), 592.7 (μ_3-C) ppm. IR (KBr): $\tilde{\nu}$ = 2944 (m), 2909 (s), 2856 (m), 1493 (w), 1437 (m), 1376 (m), 1256 (m), 1057 (s), 1027 (s), 931 (w), 879 (m), 793 (s), 675 (vs), 615 (s), 467 (m), 423 (m). $\mathrm{C_{41}H_{71}CaNO_4Si_2Ti_3}$ (881.91): calcd. C 55.84, H 8.12, N 1.59; found C 56.27, H 8.12, N 1.30.

Preparation of $[\{(\mathrm{thf})(\mathrm{Me_3Si})_2\mathrm{NSr}\}(\mu_3\text{-O})_3\{\mathrm{Ti}_3\mathrm{Cp}_3^*(\mu_3\text{-C})\}]$ (10): Compound **10** was prepared similarly to **9** from **1** (0.40 g, 0.66 mmol), $[\mathrm{Sr\{N(SiMe_3)_2\}_2(thf)_2}]$ (0.36 g, 0.66 mmol) and hexane (50 mL). The solution was heated at 90 °C for 36 h. The green solution was filtered, and the solvent was removed to yield 0.58 g (95%) of **10** as a crystalline green solid. ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 0.32 [s, 18 H, N(SiMe_3)$_2$], 1.32 (m, 4 H, thf), 2.13 (s, 45 H, $\mathrm{C_5}Me_5$), 3.77 (m, 4 H, thf) ppm. ^{13}C{^{1}H} NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 5.6 [N(SiMe_3)$_2$], 12.0 ($\mathrm{C_5}Me_5$), 25.0 and 69.8 (thf), 118.5 ($C_5\mathrm{Me_5}$), 588.0 (μ_3-C) ppm. IR (KBr): $\tilde{\nu}$ = 2910 (s), 2860 (s), 1493 (w), 1441 (m), 1377 (m), 1254 (m), 1178 (w), 1037 (m), 932 (w), 818 (s), 678 (vs), 615 (s), 467 (w), 421 (m). $\mathrm{C_{41}H_{71}NO_4Si_2SrTi_3}$ (929.45): calcd. C 52.98, H 7.70, N 1.51; found C 53.24, H 8.10, N 1.32.

Preparation of $[(\mathrm{CpMg})(\mu_3\text{-O})_3\{\mathrm{Ti}_3\mathrm{Cp}_3^*(\mu_3\text{-C})\}]$ (11): Addition of cyclopentadiene (25 µL, 0.38 mmol) to a solution of **8** (0.30 g, 0.38 mmol) and heating in toluene (30 mL) at 70 °C overnight led to the product **11** as a green solid in 73% yield (0.19 g). ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 2.03 (s, 45 H, $\mathrm{C_5}Me_5$), 6.49 (s, 5 H, $\mathrm{C_5}H_5$) ppm. ^{13}C{^{1}H} NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 11.7 ($\mathrm{C_5}Me_5$), 106.3 ($C_5\mathrm{H_5}$), 120.5 ($C_5\mathrm{Me_5}$), 594.3 (μ_3-C) ppm. IR (KBr): $\tilde{\nu}$ = 2909 (s), 2857 (m), 1494 (w), 1435 (m), 1375 (m), 1246 (m), 1025 (w), 789 (vs), 672 (vs), 618 (m), 419 (m). $\mathrm{C_{36}H_{50}MgO_3Ti_3}$ (698.74): calcd. C 61.88, H 7.21; found C 61.10, H 7.75.

Preparation of $[(\mathrm{CpCa})(\mu_3\text{-O})_3\{\mathrm{Ti}_3\mathrm{Cp}_3^*(\mu_3\text{-C})\}]$ (12): Compound **12** was prepared in a similar way to **11** from **9** (0.50 g, 0.57 mmol) and cyclopentadiene (40 µL, 0.60 mmol) in toluene (40 mL) at room temperature. After 2 h, 0.34 g of dark green solid **12** (84% yield) was obtained. ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 2.06 (s, 45 H, $\mathrm{C_5}Me_5$), 6.44 (s, 5 H, $\mathrm{C_5}H_5$) ppm. ^{13}C{^{1}H} NMR

(300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 11.8 (C_5*Me*$_5$), 110.3 (*C*$_5$H$_5$), 119.1 (*C*$_5$Me$_5$), 588.3 (μ_3-*C*) ppm. IR (KBr): ṽ = 3078 (w), 2908 (s), 2857 (m), 1493 (w), 1436 (m), 1375 (m), 1259 (w), 1068 (w), 1024 (m), 788 (vs), 735 (s), 676 (vs), 619 (s), 466 (w), 419 (m), 396 (m). $C_{36}H_{50}CaO_3Ti_3$ (714.51): calcd. C 60.52, H 7.05; found C 60.96, H 7.44.

Preparation of [(CpSr)(μ_3-O)$_3${Ti$_3$Cp$_3$*(μ_3-C)}] (13): Cyclopentadiene (40 μL, 0.60 mmol) was added to a solution of **10** (0.50 g, 0.54 mmol) in toluene (40 mL) and kept at room temperature. After 2 h, **13** was isolated as a green solid in 76% yield (0.31 g) by removing the solvent. ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 2.14 (s, 45 H, C$_5$*Me*$_5$), 6.36 (s, 5 H, C$_5$*H*$_5$) ppm. ^{13}C{^{1}H} NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 12.0 (C$_5$*Me*$_5$), 108.9 (*C*$_5$H$_5$), 117.6 (*C*$_5$Me$_5$), 591.6 (μ_3-*C*) ppm. IR (KBr): ṽ = 2909 (s), 2858 (s), 1493 (w), 1437 (m), 1377 (m), 1259 (w), 1068 (w), 1025 (w), 788 (vs), 735 (s), 675 (vs), 608 (s), 466 (w), 421 (m). $C_{36}H_{50}O_3SrTi_3$ (762.05): calcd. C 56.74, H 6.61; found C 56.76, H 6.88.

Preparation of [(Cp*Ca)(μ_3-O)$_3${Ti$_3$Cp$_3$*(μ_3-C)}] (14): Pentamethylcyclopentadiene (55 μL, 0.35 mmol) was added to a solution of **9** (0.30 g, 0.34 mmol) in hexane (40 mL). The reaction mixture was heated at 90 °C for 6 h to afford a green solution. The solvent was removed under vacuum and the product was isolated in 75% yield (0.20 g). ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 2.04 (s, 45 H, C$_5$*Me*$_5$), 2.21 (s, 15 H, C$_5$*Me*$_5$) ppm. ^{13}C{^{1}H} NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 11.2 and 11.8 (C$_5$*Me*$_5$), 114.3 and 119.4 (*C*$_5$Me$_5$), 588.6 (μ_3-*C*) ppm. IR (KBr): ṽ = 2962 (m), 2910 (s), 2855 (m), 1495 (w), 1438 (m), 1375 (m), 1259 (w), 1084 (m), 1020 (m), 790 (vs), 733 (m), 676 (vs), 615 (m), 467 (m), 420 (m). $C_{41}H_{60}CaO_3Ti_3$ (784.64): calcd. C 62.76, H 7.71; found C 63.07, H 7.96.

Preparation of [(Cp*Sr)(μ_3-O)$_3${Ti$_3$Cp$_3$*(μ_3-C)}] (15): Compound **15** was prepared similarly to **14** from **10** (0.30 g, 0.32 mmol) and C$_5$Me$_5$H (50 μL, 0.32 mmol) in hexane (40 mL). The solution was heated at 90 °C for 6 h to yield 0.22 g of **15** as a green microcrystalline solid (82% yield). ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 2.03 (s, 45 H, C$_5$*Me*$_5$), 2.17 (s, 15 H, C$_5$*Me*$_5$) ppm. ^{13}C{^{1}H} NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 11.5 and 12.4 (C$_5$*Me*$_5$), 114.0 and 118.8 (*C*$_5$Me$_5$), 580.0 (μ_3-*C*) ppm. IR (KBr): ṽ = 2964 (m), 2910 (s), 2586 (m), 1495 (w), 1439 (m), 1375 (m), 1258 (w), 1081 (m), 1022 (m), 790 (vs), 731 (m), 678 (vs), 616 (s), 468 (m), 420 (m). $C_{41}H_{60}O_3SrTi_3$ (832.19): calcd. C 59.18, H 7.27; found C 59.72, H 7.49.

Preparation of [Mg{(μ-O)$_3$Ti$_3$Cp*$_3$(μ_3-C)}$_2$]·C$_7$H$_8$ (16). Method A: [{TiCp*(μ-O)}$_3$(μ_3-CH)] (**1**) (0.50 g, 0.82 mmol), [Mg(CH$_2$Ph)$_2$(thf)$_2$] (0.14 g, 0.41 mmol) or [Mg*t*Bu$_2$(thf)$_2$] (0.12 g, 0.41 mmol) and toluene (50 mL) were placed in a Carius tube with Young's valve. The argon atmosphere pressure was reduced and the reaction mixture was irradiated with an ultraviolet lamp for 2 days. The green solution was then filtered and cooled to 4 °C to afford **16** as green crystals suitable for an X-ray diffraction analysis. After several crystallizations the isolated product was dried under vacuum giving a total yield of 80% (0.44 g) in the reaction with [Mg(CH$_2$Ph)$_2$(thf)$_2$] and 87% (0.48 g) with [Mg*t*Bu$_2$(thf)$_2$]. **Method B:** In a 100-mL Carius tube **1** (0.12 g, 0.19 mmol) and **8** (0.15 g, 0.19 mmol) were dissolved in toluene (20 mL) and then the ampoule was sealed under vacuum by flame. The solution was heated at 200 °C for 2 days. Slow crystallization led to green needles of **16** (0.20 g, 79%) which were vacuum dried. IR (KBr, cm^{-1}): ṽ = 2906 (vs), 2848 (vs), 1494 (m), 1437 (s), 1374 (s), 1261 (w), 1023 (m), 858 (s), 786 (s), 729 (s), 676 (m), 607 (vs), 464 (w), 424 (s). $C_{69}H_{98}MgO_6Ti_6$ (1335.12): calcd. C 62.07, H 7.40; found C 62.28, H 7.57.

Preparation of [{M{(μ_3-O)$_3$Ti$_3$Cp*$_3$(μ_3-C)}$_2$] [M = Ca (17), Sr (18)]: The preparations of **17** and **18** were similar to that of **16**. **1** (0.10 g, 0.17 mmol) and **9** (0.15 g, 0.17 mmol) or **10** (0.15 g, 0.16 mmol) in toluene (20 mL) react at 180 °C over 36 h to afford **17** or **18**, respectively, as green needles (Yields: 0.18 g, 84% **17**; 0.15 g, 71% **18**).

17: IR (KBr): ṽ = 2908 (s), 2858 (s), 1489 (w), 1437 (m), 1384 (m), 1376 (m), 1257 (w), 1025 (w), 790 (m), 675 (vs), 606 (s), 464 (m), 425 (m). $C_{62}H_{90}CaO_6Ti_6$ (1258.75): calcd. C 59.16, H 7.21; found C 59.58, H 7.20.

18: IR (KBr): ṽ = 2908 (s), 2857 (m), 1492 (w), 1439 (m), 1376 (m), 1025 (w), 790 (w), 675 (vs), 608 (vs), 467 (m), 426 (s). $C_{62}H_{90}O_6SrTi_6$ (1306.29): calcd. C 57.01, H 6.94; found C 57.07, H 6.95.

Preparation of [Ba{(μ_3-O)$_3$Ti$_3$Cp*$_3$(μ_3-C)}$_2$] (19): This complex can be synthesized either by thermal treatment at 100 °C for two days of a solution of [{TiCp*(μ-O)}$_3$(μ_3-CH)] (**1**) (0.40 g, 0.65 mmol) and [Ba{N(SiMe$_3$)$_2$}$_2$(thf)$_2$] (0.20 g, 0.33 mmol) in toluene (50 mL) or by heating at 90 °C overnight a solution of **1** (0.30 g, 0.49 mmol) and [Ba(CH$_2$Ph)$_2$] (0.08 g, 0.24 mmol). Following this, the reaction mixture was repeatedly concentrated, cooled and filtered to afford a green microcrystalline solid identified as **19** (Yield: 0.22−0.35 g, 66−78%). IR (KBr): ṽ = 2911 (vs), 2858 (s), 1493 (w), 1436 (m), 1377 (s), 1262 (w), 1103 (m), 1023 (m), 795 (vs), 668 (m), 616 (s), 394 (m). $C_{62}H_{90}BaO_6Ti_6$ (1356.00): calcd. C 54.92, H 6.69; found C 54.40, H 6.96.

X-ray Crystallographic Studies of Complexes 9, 16, 17 and 18

X-ray quality crystals of **16** were grown as described in the Exp. Sect. Crystals were mounted in glass capillaries in a random orientation and transferred to an Enraf−Nonius CAD4 diffractometer for characterization and data collection at room temperature. Crystals of complexes **9**, **17** and **18** were grown as described in the Exp. Sect., removed from the Schlenk vessels 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 100 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[23] by direct methods (SHELXS-97) and refined by least-squares against F^2 (SHELXL-97).[24]

Complex **9** exhibited severe disorder both in the pentamethylcyclopentadienyl rings and in the coordinated THF molecule, two sites with 50% occupancy were found for all the disordered atoms. Only the carbon atoms of the C31−C40 pentamethylcyclopentadienyl ring were isotropically refined, the rest of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were not added.

All non-hydrogen atoms of **16**, except the methyl carbon atoms C14, C15 and C16 of one pentamethylcyclopentadienyl ring and those of the disordered solvent, were anisotropically refined. Only the hydrogen atoms of the pentamethylcyclopentadienyl rings were included, positioned geometrically and refined by using a riding model.

Complex **17** also exhibited disorder in both molecules of the solvent and C16, all these atoms were refined with 50% of occupan-

Table 3. Crystal data and structure refinement for **9**, **16**, **17** and **18**

Compound	**9**	**16**	**17**	**18**
Empirical formula	$C_{41}H_{71}CaNO_4Si_2Ti_3$	$C_{62}H_{90}MgO_6Ti_6{\cdot}2C_7H_8$	$C_{62}H_{90}O_6CaTi_6{\cdot}2\ C_7H_8$	$C_{62}H_{90}O_6SrTi_6$
Molecular mass	881.95	1427.32	1443.09	1306.36
Temperature [K]	100(2)	293(2)	100(2)	100(2)
Wavelength (Mo-K_α)	0.71073 Å	0.71073	0.71073	0.71073
Crystal system	triclinic	orthorhombic	orthorhombic	monoclinic
Space group	$P\bar{1}$	*Pnnm*	*Pnmn*	*C*2/*c*
a (Å); α (°)	11.310(1); 89.97(1)	14.409(5)	14.508(4)	19.707(2)
b (Å); β (°)	12.729(1); 89.95(1)	15.099(7)	15.2028(4)	14.026(3); 95.886(10)
c (Å); γ (°)	16.223(2); 88.85(1)	16.640(8)	16.421(4)	22.539(4)
Volume [Å^3]; Z	2335.0(4); 2	3620(3); 2	3621.9(13); 2	6197.2(18); 4
$\rho_{calcd.}$ [g·cm^{-3}]	1.254	1.309	1.323	1.400
μ(Mo-K_α) [mm^{-1}]	0.699	0.688	0.750	1.635
F(000)	940	1508	1524	2720
Crystal size [mm]	0.441 × 0.267 × 0.150	0.24 × 0.22 × 0.18	0.65 × 0.50 × 0.27	0.34 × 0.30 × 0.28
Diffractometer	Bruker−Nonius KappaCCD	Enraf−Nonius CAD4	Bruker−Nonius KappaCCD	Bruker−Nonius KappaCCD
θ Range	5.03 to 27.50	3.05 to 25.03°	4.85 to 29.79°	5.08 to 27.51°
Index ranges	$-14 \leq h \leq 14$ $-16 \leq k \leq 16$ $0 \leq l \leq 21$	$-17 \leq h \leq 0$ $0 \leq k \leq 17$ $-19 \leq l \leq 0$	$-18 \leq h \leq 18$ $-21 \leq k \leq 21$ $-19 \leq l \leq 18$	$-25 \leq h \leq 25$ $-18 \leq k \leq 18$ $-29 \leq l \leq 29$
Collected reflections	47913	3583	48804	50676
Independent reflections	10507 [*R*(int) = 0.001]	3307 [*R*(int) = 0.001]	4286 [*R*(int) = 0.2009]	7091 [*R*(int) = 0.1071]
Observed data [$I > 2\sigma(I)$]	6700	1788	3044	5829
Goodness-of-fit on F^2	0.939	1.135	1.101	1.094
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.071$, $wR2 = 0.178$	$R1 = 0.108$, $wR2 = 0.291$	$R1 = 0.095$, $wR2 = 0.242$	$R1 = 0.035$, $wR2 = 0.079$
R indices (all data)	$R1 = 0.125$, $wR2 = 0.212$	$R1 = 0.190$, $wR2 = 0.350$	$R1 = 0.132$, $wR2 = 0.274$	$R1 = 0.052$, $wR2 = 0.086$
Largest diff. peak and hole [e·Å^{-3}]	1.879 and −0.992	0.992 and −0.827	1.292 and −1.378	0.490 and −0.476

cies. All the hydrogen atoms were included, positioned geometrically and refined by using a riding model except those linked to disordered atoms.

Complex **18** crystallized without solvent molecules. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were directly located in the difference Fourier maps and isotropically refined.

CCDC-223163 to -223166 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] [1a] R. Andrés, M. Galakhov, A. Martín, M. Mena, C. Santamaría, *Organometallics* **1994**, *13*, 2159−2163. [1b] R. Andrés, M. Galakhov, A. Martín, M. Mena, C. Santamaría, *J. Chem. Soc., Chem. Commun.* **1995**, 551−552. [1c] R. Andrés, PhD thesis, Universidad de Alcalá, Madrid (Spain), **1995**.

[2] R. Andrés, M. Galakhov, A. Martín, M. Mena, C. Santamaría, *J. Chem. Soc., Chem. Commun.* **1995**, 551−552.

[3] R. Andrés, M. Galakhov, M. P. Gómez-Sal, A. Martín, M. Mena, C. Santamaría, *Chem. Eur. J.* **1998**, *4*, 1206−1213.

[4] M. Galakhov, M. Mena, C. Santamaría, *Chem. Commun.* **1998**, 691−692.

[5] M. P. Gómez-Sal, A. Martín, M. Mena, M. C. Morales, C. Santamaría, *Chem. Commun.* **1999**, 1839−1840.

[6] R. Andrés, M. Galakhov, M. P. Gómez-Sal, A. Martín, M. Mena, M. C. Morales-Varela, C. Santamaría, *Chem. Eur. J.* **2002**, *8*, 805−811.

[7] A. Abarca, M. Galakhov, P. Gómez-Sal, A. Martín, M. Mena, J. M. Poblet, C. Santamaría, J. P. Sarasa, *Angew. Chem.* **2000**, *112*, 544−547; *Angew. Chem. Int. Ed.* **2000**, *39*, 534−537.

[8] 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.

[9] See as a few examples: [9a] K. Kubo, E. Yamamoto, N. Kato, A. Mori, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1999**, *55*, 1819−1821. [9b] M. Westerhausen, S. Schneiderbauer, H. Piotrowski, M. Suter, H. Noth, *J. Organomet. Chem.* **2002**, *643*, 189−193. [9c] K. Kunze, L. Bihry, P. Atanasova, M. J. Hampden-Smith, E. N. Duesler, *Chem. Vap. Deposition* **1996**, *2*, 105.

[10] [10a] M. Westerhausen, M. Hartmann, N. Makropoulos, B. Wieneke, M. Wieneke, W. Schwarz, D. Stalke, *Z. Naturforsch., Teil B* **1998**, *53*, 117−125. [10b] M. Westerhausen, R. Low, W. Schwarz, *J. Organomet. Chem.* **1996**, *513*, 213−229. [10c] D. J. Burkey, E. K. Alexander, T. P. Hanusa, *Organometallics* **1994**, *13*, 2773−2786. More examples can be found in the Cambridge Crystallographic Data Base: F. H. Allen, *Acta Crystallogr., Sect. B* **2002**, *58*, 380−388.

[11] 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.

[12] The compounds **14** and **15** were also detected by ^{1}H NMR in the thermolysis of solutions of **9** and **10**, respectively.

[13] Also, complexes **16−18** can be obtained in lower yield by thermal treatment (170−200 °C) of compounds **8−10**.

[14] For magnesium: [14a] S. Chadwick, U. Englich, K. Ruhlandt-Senge, *Inorg. Chem.* **1999**, *38*, 6289−6293. [14b]A. D. Bond, R. A. Layfield, J. A. MacAllister, M. McPartlin, J. M. Rawson, D. S. Wright, *Chem. Commun.* **2001**, 1956−1957. For strontium: [14c] W. Paw, T. H. Baum, Kin-Chung Lam, A. L. Rheingold, *Inorg. Chem.* **2000**, *39*, 2011−2014. [14d] S. R. Drake, S. A. S. Miller, M. B. Hursthouse, K. M. A. Malik, *Polyhedron* **1993**, *12*, 1621−1634. More examples can be found in the Cambridge Crystallographic Data Base: F. H. Allen, *Acta Crystallogr. Sect. B* **2002**, *58*, 380−388.

[15] C. Tessiers-Youngs, O. T. Beachley Jr., *Inorg. Synth.* **1986**, *24*, 95−97.

[16] C. Schade, W. Bauer, P. von R. Schleyer, *J. Organomet. Chem.* **1985**, *295*, C25−C28.

[17] F. T. Edelmann, F. Pauer, M. Wedler, D. Stalke, *Inorg. Chem.* **1992**, *31*, 4143−4146.

[18] R. R. Schrock, *J. Organomet. Chem.* **1976**, *122*, 209−225.

[19] [19a] G. E. Coates, J. A. Heslop, *J. Chem. Soc., Chem. Commun.* **1968**, *A*, 514. [19b] C. W. Kamienski, J. F. Eastham, *J. Organomet. Chem.* **1967**, *8*, 535−541.

[20] A. Weeber, S. Harder, H. H. Brintzinger, K. Knoll, *Organometallics* **2000**, *19*, 1325−1332.

[21] K. W. Henderson, J. F. Allan, A. R. Kennedy, *Chem. Commun.* **1997**, 1149−1150.

[22] 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.

[23] L. J. Farrugia, WinGX.-A Windows Program for Crystal Structure Analysis, University of Glasgow, Glasgow, **1998**.

[24] G. M. Sheldrick, SHELX97, Program for Crystal Structure Analysis (Release 97−2), University of Göttingen, Germany, **1998**.

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