Synthesis and Characterization of New Polynuclear Titanium(IV) Oxo Alkyls: $[Cp^*TiR(\mu\text{-}O)]_3$ and $[Cp^*Ti(\mu\text{-}O)]_3ClR_2$. Thermolysis of $[Cp^*TiEt(\mu\text{-}O)]_3$ and the Crystal Structure of the First (μ_3-Ethylidyne)titanium Complex, $[Cp^*Ti(\mu\text{-}O)]_3(\mu_3\text{-}CMe)$[†]

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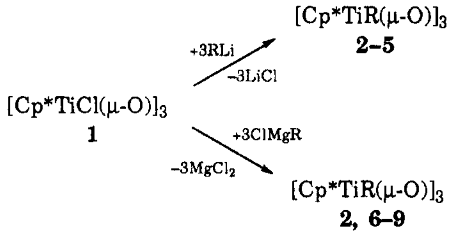
The oxo trimer $[Cp^*TiCl(\mu\text{-}O)]_3$ (1) ($Cp^* = \eta^5\text{-}C_5Me_5$) reacts with organolithium LiR (R = Me, Ph, $p\text{-}MeC_6H_4$, C≡CPh) or Grignard reagents ClMgR (R = Me, Et, Pr, CH_2Ph, C≡CH) to give the new alkyl oxo trimers $[Cp^*TiR(\mu\text{-}O)]_3$ (**2–9**) and $[Cp^*Ti(\mu\text{-}O)]_3ClR_2$ (**10–12**) in good yield. In the case of $[Cp^*TiEt_3(\mu\text{-}O)]_3$ (**6**), the thermal decomposition at temperatures in the range of 195–200 °C leads to the preparation of the first example of a d^0 (μ_3-alkylidyne) complex, $[Cp^*Ti(\mu\text{-}O)]_3(\mu_3\text{-}CMe)$ (**13**). The structure of this complex has been proved unequivocally by X-ray diffraction studies (space group *Pnma*, $a = 12.104(6)$ Å, $b = 19.404(5)$ Å, $c = 13.744(1)$ Å, $Z = 4$, $R = 0.046$, and $R_w = 0.050$). The oxo cluster core of **13** can be described like a six membered ring, Ti_3O_3, where the three titanium atoms form an almost perfect equilateral triangle capped by a μ_3-ethylidyne ligand, with short nonbonded Ti···Ti contacts (average value of 2.82 Å).

In recent years organometallic oxides (OMO) have received considerable interest as hydrocarbon-soluble models for metal oxide surfaces and thus help to provide a basic understanding of catalyst-to-support interactions in heterogeneous catalytic processes.[1] We have previously described a variety of titanium cluster oxides benefiting from the highly solubilizing pentamethylcyclopentadienyl ligand,[2] and we have found that trimer $[Cp^*TiCl(\mu\text{-}O)]_3$ (1) is a versatile starting material for the preparation of many interesting complexes containing the "Cp*TiO" moiety.

Results and Discussion

Complex 1 can be easily alkylated in a conventional way by using stoichiometric amounts of the corresponding organolithium or Grignard reagents in diethyl ether or tetrahydrofuran to give the novel trinuclear complexes $[Cp^*TiR(\mu\text{-}O)]_3$ (**2–9**) [R = Me (**2**), Ph (**3**), $p\text{-}MeC_6H_4$ (**4**), C≡CPh (**5**), Et (**6**), Pr (**7**), CH_2Ph (**8**), C≡CH (**9**)] in high yields (eq 1).



(1)

R = Me (**2**), Ph (**3**), $p\text{-}MeC_6H_4$ (**4**), C≡CPh (**5**), Et (**6**), Pr (**7**), CH_2Ph (**8**), C≡CH (**9**)

Alkyl trimers **2–9** are air sensitive both in solution and in the solid state. They dissolve readily in common organic solvents, and such solutions are stable at room temperature. These complexes were characterized by elemental analysis, IR, NMR spectroscopy, and mass spectrometry (see Experimental Section).

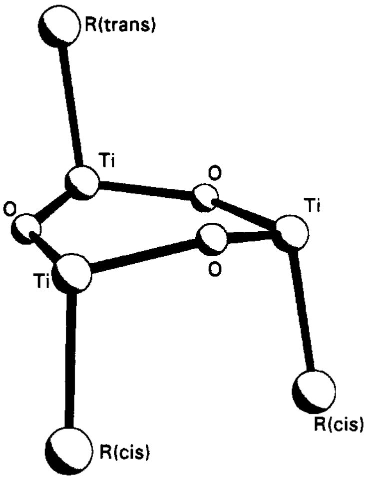


Figure 1. Structure for $[Cp^*TiR(\mu\text{-}O)]_3$ (Cp* rings omitted for clarity).

The ^1H and ^{13}C NMR spectra demonstrate the presence of nonequivalent Cp* and R groups in a 2:1 ratio, that is consistent with structures containing two geometrically different types of R and pentamethylcyclopentadienyl groups. The three $Cp^*R(\mu\text{-}O)Ti$ units are linked and form an almost planar Ti_3O_3 six membered ring with two Cp* groups and one R (trans) situated above the plane, while the other Cp* and two R (cis) lie below it (Figure 1), as

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[†] Dedicated to Professor Ricardo Serrano, deceased on 30 January 1992, whom we remember with affection.

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we have found previously in $[Cp^*TiMe(\mu\text{-}O)]_3$.[3]

The ^1H NMR spectra of **6**–**8** clearly indicate that the CH_2 (cis) protons of these complexes are diastereotopic and give rise to ABC_3, $ABCDK_3$, and AB spin–spin systems, respectively.

$[Cp^*TiCl(\mu\text{-}O)]_3$ can also be partially alkylated just by using the stoichiometric amount of the corresponding organolithium or -magnesium reagents (eqs 2 and 3). The compounds **10**–**12** were characterized by elemental analysis and ^1H and ^{13}C NMR spectroscopy (see Experimental Section).

$$\underset{\mathbf{1}}{[Cp^*TiCl(\mu\text{-}O)]_3} + 2LiR \xrightarrow[-2LiCl]{THF/0\ ^\circ C} [Cp^*Ti(\mu\text{-}O)]_3ClR_2 \quad (2)$$

$$R = Me\ (\mathbf{10}),\ Ph\ (\mathbf{11})$$

$$\underset{\mathbf{1}}{[Cp^*TiCl(\mu\text{-}O)]_3} + 2ClMgEt \xrightarrow[-2MgCl_2]{THF/-78\ ^\circ C} \underset{\mathbf{12}}{[Cp^*Ti(\mu\text{-}O)]_3ClEt_2} \quad (3)$$

We are investigating the reactivity and stability[4] of these electron-deficient metal centers connected by oxo groups, and here we report the results of the thermolysis of **6** to give a Ti_3O_3 cluster where a CMe group is capping the triangle containing the three titanium atoms. Similar μ_3-alkylidyne structures are known for trinuclear middle/late transition metal clusters with a metal–metal bond and/or carbonyl species in low oxidation states[5] and have been detected by high resolution electron energy loss spectroscopy (HREELS) and low energy electron diffraction (LEED) on transition-metal surfaces, including Pt, Pd, and Ni, after the adsorption and rearrangement of alkenes;[6] but the metals involved in all these situations never belong to the early transition groups.

When a toluene solution of **6** was heated at 195 °C for 12 h (eq 4), the color of the solution changed from yellow to dark orange. At the same time, the reaction was monitored by ^1H NMR spectroscopy in a sealed NMR

$$\underset{\mathbf{6}}{[Cp^*TiEt(\mu\text{-}O)]_3} \xrightarrow[-2C_2H_6]{Tol/195\ ^\circ C/12\ h} \underset{\mathbf{13}}{[Cp^*Ti(\mu\text{-}O)]_3(\mu_3\text{-}CMe)} \quad (4)$$

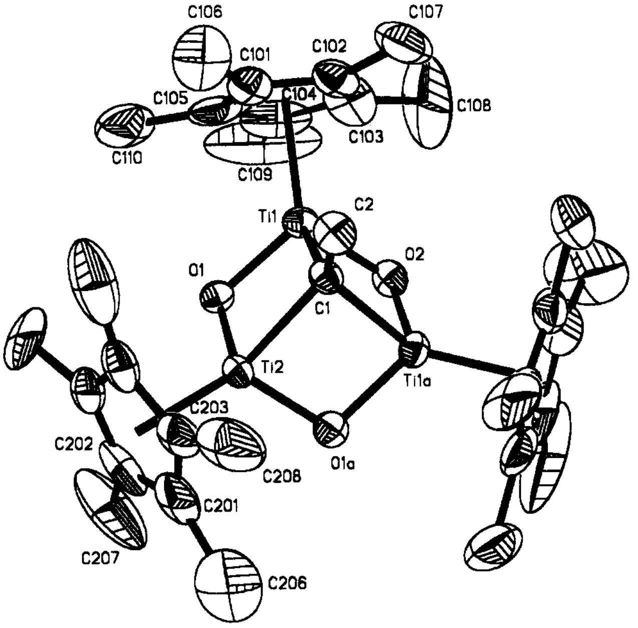

Figure 2. ORTEP representation of $[Cp^*Ti(\mu\text{-}O)]_3(\mu_3\text{-}CMe)$ (**13**). The thermal ellipsoids correspond to 40% probability.

Table 1. Details of the X-ray Diffraction Study for $(Cp^*TiO)_3(\mu_3\text{-}CMe)$ (13)

molecular formula	$C_{32}H_{48}O_3Ti_3$
space group	*Pnma*
unit cell vol, Å^3	3228.2(19)
a, Å	12.104(6)
b, Å	19.404(5)
c, Å	13.744(1)
Z	4
calcd dens, g·cm^{-3}	1.289
cryst dimens, mm	0.35 × 0.28 × 0.25
abs coeff, cm^{-1}	7.5
2θ range, deg	4–52
total no. of reflns measd	3551
no. of reflns measd with $F \geq 4\sigma(F)$	1923
no. of params	181
scan type	ω–θ
p	0.04
R	0.046
R_w	0.050
final residual, e Å^{-3}	0.328/–0.258
GOF	1.40

tube in benzene-d_6 and only ethane was evolved and detected. Removal of solvent yielded **13** in quantitative yield and analytically high purity.

Compound **13** is an orange, crystalline solid very soluble in common organic solvents. The C_{3v} symmetry of the molecular structure of **13** was confirmed by means of ^1H and ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum revealed a quadruplet at a very low field (δ 401.7 ppm, $^2J_{CH}$ = 6.4 Hz) for the CCH_3 ethylidyne carbon.

Structural Study of $[Cp^*Ti(\mu\text{-}O)]_3(\mu_3\text{-}CMe)$

Red crystals of $[Cp^*Ti(\mu\text{-}O)]_3(\mu_3\text{-}CMe)$ (**13**) were obtained from a toluene solution at −10 °C. Figure 2 shows the molecular structure and Tables 1 and 2 summarize crystal and structural data, while selected bond lengths and angles appear in Table 3. There are no intermolecular contact distances which could be considered to imply a bonding interaction.

In complex **13**, one of the planes of the C_{3v} symmetry coincides with the crystallographic symmetry plane which contains C(1), C(2), O(2), Ti(2) and bisects a C_5Me_5 ring. The bridging oxygens [O(1),O(1a)], titaniums [Ti(1),Ti(1a)], and the other C_5Me_5 groups lie on either side of this plane.

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Table 2. Positional Parameters and Their Estimated Standard Deviations for Compound 13

atom	*x*	*y*	*z*	*B* (Å^2)
Ti(1)	0.31048(6)	0.17735(3)	0.58477(5)	2.84(1)
Ti(2)	0.15253(8)	0.25000	0.47365(7)	2.68(2)
O(1)	0.1631(2)	0.1751(1)	0.5541(2)	3.20(5)
O(2)	0.3219(3)	0.25000	0.6691(2)	3.32(8)
C(1)	0.3283(4)	0.25000	0.4710(4)	2.7(1)
C(2)	0.4053(5)	0.25000	0.3843(4)	3.6(1)
C(101)	0.4084(3)	0.0816(2)	0.5146(3)	4.3(1)
C(102)	0.4849(4)	0.1179(2)	0.5710(3)	4.6(1)
C(103)	0.4514(4)	0.1144(3)	0.6681(3)	6.4(1)
C(104)	0.3532(4)	0.0764(2)	0.6703(3)	7.2(1)
C(105)	0.3280(4)	0.0558(2)	0.5758(4)	6.2(1)
C(106)	0.4213(5)	0.0661(3)	0.4077(4)	7.3(1)
C(107)	0.5921(4)	0.1490(3)	0.5354(5)	7.9(2)
C(108)	0.5063(6)	0.1465(4)	0.7551(4)	15.8(2)
C(109)	0.2864(6)	0.0581(4)	0.7597(5)	17.9(2)
C(110)	0.2287(6)	0.0124(3)	0.5453(7)	12.5(3)
C(201)	0.0258(4)	0.3075(3)	0.3701(3)	5.9(1)
C(202)	−0.0263(5)	0.25000	0.4080(5)	6.1(2)
C(203)	0.1132(4)	0.2859(2)	0.3093(3)	4.6(1)
C(206)	−0.0061(6)	0.3820(3)	0.3894(5)	13.0(2)
C(207)	−0.1200(7)	0.25000	0.4832(8)	14.0(5)
C(208)	0.1862(5)	0.3319(3)	0.2503(4)	9.4(2)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound 13

Ti(1)–O(1)	1.834	Ti(1)–O(2)	1.830(2)
Ti(1)–C(1)	2.117(4)	Ti(1)–Cp1[a]	2.068
Ti(2)–O(1)	1.831(2)	Ti(2)–C(1)	2.127(5)
Ti(2)–Cp2[a]	2.064	C(1)–C(2)	1.514(7)
Ti(1)–O(1)–Ti(2)	100.8(1)	Ti(1)–O(2)–Ti(1a)	100.8
O(1)–Ti(1)–O(2)	103.7(1)	O(1)–Ti(2)–O(1a)	105.1
Cp1–Ti(1)–O(1)	122.9	Cp1–Ti(1)–O(2)	122.1
Cp1–Ti(1)–C(1)	124.7	Cp2–Ti(2)–O(1)	121.7
Cp2–Ti(2)–C(1)	125.9	Ti(1)–C(1)–Ti(2)	83.4(2)
Ti(1)–C(1)–C(2)	130.1(2)	Ti(1)–C(1)–Ti(1a)	83.6
Ti(2)–C(1)–C(2)	129.0(4)		

[a] Cp1 and Cp2 are the centroids of the corresponding C_5Me_5 rings.

The three titanium atoms are the apices of a hypothetical equilateral triangle (angles Ti–Ti–Ti = 60°) capped by a μ_3-ethylidyne ligand and bridged by three oxygens to form a six membered Ti_3O_3 ring in a chair conformation (O–Ti–O = 103.7°, average) with angles Ti–O–Ti (100.8°, average) clearly smaller than those found for $[Cp^*TiMe(\mu\text{-}O)]_3$ (Ti–O–Ti = 132.9°, average), $(Cp^*Ti)_4(\mu\text{-}O)_6$ (Ti–O–Ti = 122.9°, average), and $[Cp^*TiCl(\mu\text{-}O)]_3$ (Ti–O–Ti = 133.9°, average).[2,7]

Ti–Ti distances, 2.82 Å, are very short compared with 3.35 Å found in $[Cp^*TiCl(\mu\text{-}O)]_3$,[7] 3.34 Å in $[Cp^*TiMe(\mu\text{-}O)]_3$,[2] 3.23 Å in $(Cp^*Ti)_4(\mu\text{-}O)_6$,[2] 2.96 Å in TiO_2,[8] 2.94 Å in the metallic titanium,[8] or even in cases where a Ti–Ti bond is proposed (2.83–3.00 Å).[9] Nevertheless, still shorter distances have been reported where a metal–metal interaction is not possible and is a consequence of bridging ligands, 2.72 Å in $\{(Cp^*Ti)_2[\mu\text{-}\eta^1{:}\eta^5\text{-}C_5(CH_3)_4CH_2](\mu\text{-}O)_2\}$[10] and 2.80 Å in $\{[Cp^*Ti(NH)]_3N\}$.[11]

Distances from titanium atoms to the ethylidyne C(1), 2.117(4) and 2.127(5) Å, are in the range of those observed for Ti–C(sp^3) bonds in mono(pentamethylcyclopentadienyl)titanium alkyls.[2,12] Thus the bridgehead carbon atom may be viewed essentially as an sp^3-hybridized alkylidyne carbon (Figure 3; model I) with the "internal" angles Ti–C(1)–Ti considerably smaller (average 83.5°) than the "external" angles Ti–C(1)–C(2) (average 129.5°). A similar geometry is also typical of the related alkylidyne cobalt of the well-known $[Co_3(\mu_3\text{-}CR)(CO)_9]$,[13] although in these cases an sp-hybridized alkylidyne carbon (Figure 3; model II) is consistent with all experimental evidence.[14]

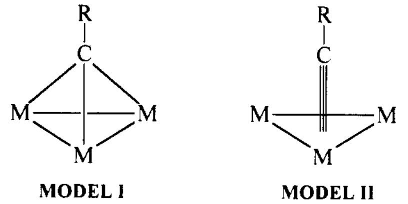

Figure 3. Carbyne-type resonance structures.

The Ti–ring centroid distances are all comparable to those in other titanium organometallic oxides,[2,7] and the Cp* rings are tilted slightly toward the apical carbon atom of the ethylidyne group, forming dihedral angles of 76.4(1)° [Cp*(1), Cp*(1a)] and 77.3(1)° [Cp*(2)] with the Ti_3 plane.

Further studies aimed at extending the range of this alkylidyne/oxide cluster, elucidating the mode of its formation and reactivity are underway and will be reported in due course.

Experimental Section

Reagents and Solvents. All operations were performed under rigorous exclusion of air and moisture (oxygen-free argon; Schlenk technique or MBraun glovebox). Solvents (reagent grade) were carefully dried over sodium–potassium alloy (pentane, hexane, toluene, diethyl ether, tetrahydrofuran) and distilled under argon immediately before use. Oven-dried glassware was repeatedly evacuated on a pumping system (ca. 1 × 10^{-3} mmHg) and subsequently filled with inert gas.

$[Cp^*TiCl(\mu\text{-}O)]_3$ (1) was synthesized by hydrolysis of Cp^*TiCl_3[15] in refluxing acetone on a 10-g scale according to the published procedure[7,16] and was dried in vacuo at 100 °C for 10 h. LiR (R = Ph, $p\text{-}MeC_6H_4$, C≡CPh) were prepared in hexane, as free solvent solids, from PhI, $p\text{-}MeC_6H_4I$, HC≡CPh, and *n*-buthyllithium (Aldrich, 1.6 M in hexane). Grignard reagents were purchased from Aldrich as THF or diethyl ether solutions (ClMgMe, 3 M in THF; ClMgEt, 2 M in THF; ClMgPr 2 M in diethyl ether; $ClMgCH_2Ph$, 2 M in THF; ClMgC≡CH, 0.5 M in THF). LiMe was purchased from Aldrich as a 1.6 M solution in diethyl ether.

Analyses and Physical Measurements. C and H microanalyses were performed with a Perkin-Elmer 240B microanalyzer. ^1H NMR and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Unity-300 spectrometer, and chemical shifts are referenced to residual protons or carbon of the solvent or to TMS. The ^1H NMR spectra of 6 and 7 were recorded on a Varian Unity-500 Plus spectrometer and calculated with a Varian spin

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simulation program (RMS = 0.01 Hz). IR spectra were taken with a Perkin-Elmer 883 spectrophotometer using KBr pellets or Nujol mulls. Electron impact (EI) mass spectra were recorded at 70 eV on a Hewlett-Packard 5988 spectrometer. Thermal decompositions were performed in a Roth autoclave Model III (300 mL), with heater Model 30S (20–300 °C) and temperature regulator Model DR 500.

Preparation of $[Cp^*TiR(\mu\text{-}O)]_3$ [R = Me (2), Ph (3), $p\text{-}MeC_6H_4$ (4), C≡CPh (5), Et (6), Pr (7), CH_2Ph (8), C≡CH (9)]. All these compounds were prepared by the same procedure (method A), by adding a solution of the alkylating agent diluted in THF to a solution of $[Cp^*TiCl(\mu\text{-}O)]_3$ in THF at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed under reduced pressure, and the solid obtained was extracted with hexane or a hexane/toluene (5:1) mixture. The combined extracts were dried in vacuo to give the corresponding products in good yield (80–90%) and high purity (>95% by ^1H NMR).

We describe the preparation of $[Cp^*TiEt(\mu\text{-}O)]_3$ (6) as an example of method A.

Preparation of $[Cp^*TiEt(\mu\text{-}O)]_3$ (6). ClMgEt (4.26 mL of a 2 M solution in THF, 8.52 mmol) diluted in 15 mL of THF was slowly added from a dropping funnel over a solution of $[Cp^*TiCl(\mu\text{-}O)]_3$ (2.00 g, 2.84 mmol) in THF (50 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed in vacuo and the solid residue extracted with 50 mL of hexane. The solution was filtered and the solvent removed to afford 1.65 g of 6 as a yellow solid in 85% yield (97% pure by ^1H NMR). ^1H NMR (C_6D_6, 20 °C, δ): 1.995 (s, 30H, $C_5\mathit{Me}_5$), 1.993 (s, 15H, $C_5\mathit{Me}_5$), 1.50 (ABC_3 spin syst, ^2J = −11.4, ^3J = 7.32, 7.20 Hz, 10H, $C_2\mathit{H}_5$), 1.55 (t, ^3J = 7.5 Hz, 3H, $C_2\mathit{H}_5$), 1.17 (q, ^3J = 7.5 Hz, 2H, C_2H_5). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, δ): 121.4 (C_5Me_5), 121.2 (C_5Me_5), 11.7 ($C_5\mathit{Me}_5$), 11.5 ($C_5\mathit{Me}_5$), 59.8 ($\mathit{C}H_2Me$), 57.9 ($\mathit{C}H_2Me$), 18.2 ($CH_2\mathit{C}H_3$), 17.2 ($CH_2\mathit{C}H_3$). MS (EI, *m/z*, rel inten): 655 [(M^+ − Et), 7%]. IR (KBr, cm^{-1}): 2911, (vs, b), 770, (vs, vb), 622, (s), 472 (s). Anal. Calcd for $C_{36}H_{60}O_3Ti_3$ (M_r = 684.50): C, 63.17; H, 8.83. Found: C, 63.15; H, 8.76.

$[Cp^*TiMe(\mu\text{-}O)]_3$ (2). $[Cp^*TiCl(\mu\text{-}O)]_3$ (1.00 g, 1.42 mmol) and ClMgMe (1.42 mL of a 3 M solution in THF, 4.26 mmol) were used to yield 0.75 g of a yellow solid (83% yield). ^1H NMR (C_6D_6, 20 °C, δ): 1.94 (s, 15H, $C_5\mathit{Me}_5$), 1.93 (s, 30H, $C_5\mathit{Me}_5$), 0.77 (s, 6H, Ti*Me*), 0.51 (s, 3H, Ti*Me*). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, δ): 121.6 (C_5Me_5), 121.3 (C_5Me_5), 44.1 (Ti*Me*), 40.3 (Ti*Me*), 11.7 ($C_5\mathit{Me}_5$), 11.5 ($C_5\mathit{Me}_5$). MS (EI, *m/z*, rel inten): 642 [(M^+), 2%]. IR (KBr, cm^{-1}): 2948 (s, b), 1374 (s), 784 (vs, vb), 391 (s). Anal. Calcd for $C_{33}H_{54}O_3Ti_3$ (M_r = 642.43): C, 61.70; H, 8.47. Found: C, 61.82; H, 8.73.

$[Cp^*TiPh(\mu\text{-}O)]_3$ (3). From 0.50 g (0.71 mmol) of $[Cp^*TiCl(\mu\text{-}O)]_3$ and 0.18 g (2.13 mmol) of LiPh, 0.47 g of 3 as a yellow solid (80% yield) was isolated. ^1H NMR (C_6D_6, 20 °C, δ): 1.85 (s, 30H, $C_5\mathit{Me}_5$), 1.79 (s, 15H, $C_5\mathit{Me}_5$), 7.68 (m, 2H, $C_6\mathit{H}_5$), 7.35 (m, 4H, $C_6\mathit{H}_5$); 7.24 (m, 3H, $C_6\mathit{H}_5$), 7.01 (m, 6H, $C_6\mathit{H}_5$). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, δ): 124.5 (C_5Me_5), 123.8 (C_5Me_5), 12.6 ($C_5\mathit{Me}_5$), 12.4 ($C_5\mathit{Me}_5$), 192.7 (ipso-C_6H_5), 190.9 (ipso-C_6H_5), 137.7 (C_6H_5), 136.2 (C_6H_5), 125.7 (C_6H_5), 125.5 (C_6H_5), 125.8 (C_6H_5), 126.3 (C_6H_5). MS (EI, *m/z*, rel inten): 617 [M^+ − (Cp*Ph), 14%]. IR (KBr, cm^{-1}): 3050 (m), 2909 (s, b), 764 (vs, vb), 720 (s). Anal. Calcd for $C_{48}H_{60}O_3Ti_3$ (M_r = 828.64): C, 69.57; H, 7.30. Found: C, 69.49; H, 7.24.

$[Cp^*Ti(p\text{-}MeC_6H_4)(\mu\text{-}O)]_3$ (4). From $[Cp^*TiCl(\mu\text{-}O)]_3$ (0.50 g, 0.71 mmol) and Li($p\text{-}MeC_6H_4$) (0.21 g, 2.13 mmol), 0.52 g of yellow solid (84% yield) was obtained. ^1H NMR (C_6D_6, 20 °C, δ): 1.89 (s, 30H, $C_5\mathit{Me}_5$), 1.83 (s, 15H, $C_5\mathit{Me}_5$), [7.63 (2H), 7.28 (4H), 7.10 (2H), 6.83 (4H), $p\text{-}CH_3C_6\mathit{H}_4$], 2.27 (s, 3H, $p\text{-}C\mathit{H}_3C_6H_4$), 2.18 (s, 6H, $p\text{-}C\mathit{H}_3C_6H_4$). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, δ): 123.5 (C_5Me_5), 124.7 (C_5Me_5), 12.6 ($C_5\mathit{Me}_5$), 12.5 ($C_5\mathit{Me}_5$), 21.6 ($p\text{-}\mathit{C}H_3C_6H_4$), 21.7 ($p\text{-}\mathit{C}H_3C_6H_4$), 189.7 [ipso-($p\text{-}Me\mathit{C}_6H_4$)], 187.6 (ipso-($p\text{-}Me\mathit{C}_6H_4$)], 137.8 ($p\text{-}Me\mathit{C}_6H_4$), 136.3 ($p\text{-}Me\mathit{C}_6H_4$), 135.2 ($p\text{-}Me\mathit{C}_6H_4$), 134.4 ($p\text{-}Me\mathit{C}_6H_4$), 126.4 ($p\text{-}Me\mathit{C}_6H_4$), 126.2 ($p\text{-}Me\mathit{C}_6H_4$). IR (KBr, cm^{-1}): 2913 (s, b), 767 (vs, vb), 618 (m). Anal. Calcd for $C_{51}H_{66}O_3Ti_3$ (M_r = 870.70): C, 70.35; H, 7.64. Found: C, 70.27; H, 7.58.

$[Cp^*Ti(C{\equiv}CPh)(\mu\text{-}O)]_3$ (5). A 0.50-g (0.71-mmol) sample of $[Cp^*TiCl(\mu\text{-}O)]_3$ and 0.23 g (2.13 mmol) of Li(C≡CC_6H_5) were used to yield 0.55 g of an orange yellow solid (86%). ^1H NMR (C_6D_6, 20 °C, δ): 2.20 (s, 30H, $C_5\mathit{Me}_5$), 2.28 (s, 15H, $C_5\mathit{Me}_5$), 7.65 (m, 4H, $C_6\mathit{H}_5$), 7.50 (m, 5H, $C_6\mathit{H}_5$), 6.95 (m, 6H, $C_6\mathit{H}_5$). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, δ): 125.8 (C_5Me_5), 126.5 (C_5Me_5), 12.7 ($C_5\mathit{Me}_5$), 12.5 ($C_5\mathit{Me}_5$), 149.2 (*C*≡CPh), 145.7 (*C*≡CPh), 107.1 (C≡*C*Ph), 107.7 (C≡*C*Ph), 132.2 (C≡$C\mathit{C}_6H_5$), 131.8 (C≡$C\mathit{C}_6H_5$), 128.6 (C≡$C\mathit{C}_6H_5$), 128.3 (C≡$C\mathit{C}_6H_5$), 126.8 (C≡$C\mathit{C}_6H_5$), 125.7 (C≡$C\mathit{C}_6H_5$). IR (KBr, cm^{-1}): 2910 (m, b), 2082 (s), 1483 (s), 772 (vs, vb). Anal. Calcd for $C_{54}H_{60}O_3Ti_3$ (M_r = 900.70): C, 72.01; H, 6.71. Found: C, 72.05; H, 6.72.

$[Cp^*TiPr(\mu\text{-}O)]_3$ (7). $[Cp^*TiCl(\mu\text{-}O)]_3$ (0.50 g, 0.71 mmol) and $ClMg(CH_2Ph)$ (1.06 mL of a 2 M solution in THF, 2.13 mmol) were used to yield 1.80 g of a yellow solid (87%). ^1H NMR ($CDCl_3$, 20 °C, δ): 1.95 (s, 30H, $C_5\mathit{Me}_5$), 1.93 (s, 15H, $C_5\mathit{Me}_5$), [1.77 (Δν = 16 Hz), 1.46 (Δν = 8 Hz), 1.14 ($C\mathit{H}_2C\mathit{H}_2C\mathit{H}_3$, 14H, $ABCDK_3$ spin syst, $^2J_{AB}$ = −11.9 Hz, $^2J_{CD}$ = −14.7 Hz, ^3J = 5.8, 8.8, 13.9, 5.6 Hz)], [1.70, 1.18, 1.10 ($C\mathit{H}_2C\mathit{H}_2C\mathit{H}_3$, 7H, $AA'BB'K_3$ spin syst, $^2J_{AA'}$ = −11.2 Hz, $^2J_{BB'}$ = −13.0 Hz, ^3J = 3.9, 10.1, 15.8, 4.0 Hz)]. $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, δ): 121.4 (C_5Me_5), 121.2 (C_5Me_5), 11.8 ($C_5\mathit{Me}_5$), 11.5 ($C_5\mathit{Me}_5$), 71.6 ($\mathit{C}H_2CH_2CH_3$), 69.9 ($\mathit{C}H_2CH_2CH_3$), 26.8 ($CH_2CH_2CH_3$), 25.8 ($CH_2CH_2CH_3$), 21.4 ($CH_2CH_2CH_3$), 20.9 ($CH_2CH_2CH_3$). MS (EI, *m/z*, rel inten): 684 [(M^+ − Pr), 13%]. IR (KBr, cm^{-1}): 2917 (vs, b), 1374 (s), 776 (vs, vb), 538 (s), 417 (s). Anal. Calcd for $C_{39}H_{66}O_3Ti_3$ (M_r = 726.59): C, 64.47; H, 9.16. Found: C, 64.43; H, 9.12.

$[Cp^*Ti(CH_2Ph)(\mu\text{-}O)]_3$ (8). $[Cp^*TiCl(\mu\text{-}O)]_3$ (0.50 g, 0.71 mmol) and $ClMg(CH_2Ph)$ (1.06 mL of a 2 M solution in THF, 2.13 mmol) were used to give 0.43 g of an orange solid (70% yield). ^1H NMR (C_6D_6, 20 °C, δ): 1.91 (s, 30H, $C_5\mathit{Me}_5$), 1.86 (s, 15H, $C_5\mathit{Me}_5$), [3.07, 2.89 (AB spin syst, ^2J = 10.5 Hz, 4H, $C\mathit{H}_2Ph$)], 2.80 (s, 2H, $C\mathit{H}_2Ph$), 7.21 (m, 15H, $CH_2\mathit{Ph}$). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, δ): 123.7 (C_5Me_5), 123.3 (C_5Me_5), 12.0 ($C_5\mathit{Me}_5$), 11.7 ($C_5\mathit{Me}_5$), 70.0 ($\mathit{C}H_2Ph$), 67.0 ($\mathit{C}H_2Ph$), 148.9 [ipso-($CH_2\mathit{C}_6H_5$)], 148.3 [ipso-($CH_2\mathit{C}_6H_5$)], 129.5 ($CH_2\mathit{C}_6H_5$), 129.2 ($CH_2\mathit{C}_6H_5$), 128.5 ($CH_2\mathit{C}_6H_5$), 127.8 ($CH_2\mathit{C}_6H_5$), 122.9 ($CH_2\mathit{C}_6H_5$), 122.7 ($CH_2\mathit{C}_6H_5$). MS (EI, *m/z*, rel inten): 780 [(M^+ − CH_2Ph), 1%]. IR (KBr, cm^{-1}): 2910 (m, b), 757 (vs, vb), 697 (m). Anal. Calcd for $C_{51}H_{66}O_3Ti_3$ (M_r = 870.72): C, 70.35; H, 7.64. Found: C, 70.29; H, 7.60.

$[Cp^*Ti(C{\equiv}CH)(\mu\text{-}O)]_3$ (9). $[Cp^*TiCl(\mu\text{-}O)]_3$ (0.50 g, 0.71 mmol) and ClMg(C≡CH) (4.26 mL of a 0.5 M solution in THF, 2.13 mmol) were used to yield 0.36 g of a brown yellow product (75%). ^1H NMR (C_6D_6, 20 °C, δ): 2.23 (s, 30H, $C_5\mathit{Me}_5$), 2.15 (s, 15H, $C_5\mathit{Me}_5$), 2.65 (s, 2H, C≡C*H*), 2.55 (s, 1H, C≡C*H*). ^{13}C NMR (C_6D_6, 20 °C δ): 127.0 (m, C_5Me_5), 126.2 (m, C_5Me_5), 12.7 (q, ^1J = 127.1 Hz, $C_5\mathit{Me}_5$), 12.5 (q, ^1J = 127.3 Hz, $C_5\mathit{Me}_5$), 139.9 (d, ^2J = 34.8 Hz, *C*≡CH), 136.8 (d, ^2J = 34.8 Hz, *C*≡CH), 94.5 (d, ^1J = 224.0 Hz, C≡*C*H), 94.3 (d, ^1J = 224.4 Hz, C≡*C*H). IR (KBr, cm^{-1}): 3284 (w), 3232 (w), 2910 (m, b), 1948 (m), 784 (vs, vb). Anal. Calcd for $C_{36}H_{48}O_3Ti_3$ (M_r = 672.41): C, 64.30; H, 7.20. Found: C, 64.26; H, 7.19.

An alternative route (method B) was used to obtain $[Cp^*TiMe(\mu\text{-}O)]_3$ (2) and $[Cp^*Ti(CH_2Ph)(\mu\text{-}O)]_3$ (8) by hydrolysis of the corresponding Cp^*TiR_3 (R = Me, CH_2Ph) complexes.[17]

Preparation of $[Cp^*TiMe(\mu\text{-}O)]_3$ (2) (Method B). H_2O (79 μL, 4.38 mmol) in a small volume of THF (ca. 0.5 mL) was added via syringe over a solution of Cp^*TiMe_3 (1.00 g, 4.38 mmol) in 50 mL of hexane and the mixture cooled to 0 °C. The reaction mixture was slowly warmed to room temperature, and effervescence of methane was observed. The solution was allowed to stir overnight[18] and then filtered and the solvent removed in vacuo to obtain 0.89 g of yellow crystals of 2 (95% yield, 96% pure by ^1H NMR).

Preparation of $[Cp^*TiCH_2Ph(\mu\text{-}O)]_3$ (8) (Method B). A 1.00-g (2.19-mmol) sample of $Cp^*Ti(CH_2Ph)_3$ was dissolved in

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[17] Mena, M.; Royo, P.; Serrano, R.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* **1989**, *8*, 476.

[18] If D_2O is used, the reaction is stirred for 24 h at room temperature.

50 mL of a 0.1% water solution in acetonitrile at 0 °C. An orange precipitate of 8 was formed in a few minutes. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. The precipitate was collected by filtration and dried in vacuo to yield 0.60 g of product (95%, 93% pure by ^{1}H NMR).

Preparation of $(Cp^*Ti)_3Me_2Cl(\mu\text{-}O)_3$ (10). A solution of $[Cp^*TiCl(\mu\text{-}O)]_3$ (0.50 g, 0.71 mmol) in 50 mL of toluene was cooled to −45 °C. LiMe (0.88 mL of a 1.6 M solution in diethyl ether, 1.42 mmol) diluted in 10 mL of diethyl ether was slowly added from a dropping funnel. The reaction mixture was allowed to stir for 2 days and then filtered, and the solvent was removed under reduced pressure; 0.32 g (70% yield) of a yellow solid was obtained. ^{1}H NMR (C_6D_6, 20 °C, δ): 2.03 (s, 15H, C_5Me_5), 1.97 (s, 30H, C_5Me_5), 0.82 (s, 6H, Ti*Me*). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, δ): 126.2 (C_5Me_5), 122.6 (C_5Me_5), 12.0 (C_5Me_5), 11.7 (C_5Me_5), 45.6 (Ti*Me*). MS (EI, *m/z*, rel inten): 648 [(M^+ − Me), 47%]. IR (KBr, cm^{-1}): 2914 (s, b), 1375 (m), 783 (vs, vb). Anal. Calcd for $C_{32}H_{51}ClO_3Ti_3$ (M_r = 662.84): C, 57.98; H, 7.76. Found: C, 57.88; H, 7.67.

Preparation of $(Cp^*Ti)_3Et_2Cl(\mu\text{-}O)_3$ (11). A 0.71-mL aliquot of ClMgEt (2 M solution in THF, 1.42 mmol) diluted in 10 mL of THF was slowly added from a dropping funnel to a solution of $[Cp^*TiCl(\mu\text{-}O)]_3$ (0.50 g, 0.71 mmol) in 50 mL of THF. After stirring for 3 h, the solvent was removed and the residue extracted with 70 mL of hexane. Crystalline yellow product (0.31 g, 65% yield) was obtained upon removing the solvent in vacuo. ^{1}H NMR (C_6D_6, 20 °C, δ): 2.07 (s, 15H, C_5Me_5), 2.00 (s, 30H, C_5Me_5), 1.51 (m, 10H, C_2H_5). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, δ): 125.9 (C_5Me_5), 122.4 (C_5Me_5), 12.1 (C_5Me_5), 11.8 (C_5Me_5), 61.4 (CH_2CH_3), 17.3 (CH_2CH_3). MS (EI, *m/z*, rel inten): 662 [(M^+ − Et), 8%]. IR (KBr, cm^{-1}): 2912 (m, b), 767 (vs, vb). Anal. Calcd for $C_{34}H_{55}ClO_3Ti_3$ (M_r = 690.90): C, 59.11; H, 8.02. Found: C, 58.92; H, 7.93.

Preparation of $(Cp^*Ti)_3Ph_2Cl(\mu\text{-}O)_3$ (12). LiPh (0.12 g, 1.42 mmol) was dissolved in 10 mL of THF and the solution slowly added from a dropping funnel to an ice bath cooled solution of $[Cp^*TiCl(\mu\text{-}O)]_3$ (0.50 g, 0.71 mmol) in 50 mL of THF. The reaction mixture was allowed to warm to room temperature and stirred overnight. Solvent was then removed in vacuo and the residue extracted with 50 mL of a toluene/hexane (3:2) mixture. The resulting solution was evaporated in vacuo to yield 0.41 g of yellow 12 (75%). ^{1}H NMR (C_6D_6, 20 °C, δ): 1.99 (s, 15H, C_5Me_5), 1.90 (s, 30H, C_5Me_5), 7.12 (m, 5H, C_6H_5), 6.89 (m, 5H, C_6H_5). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, δ): 127.1 (C_5Me_5), 124.4 (C_5Me_5), 12.4 (C_5Me_5), 12.3 (C_5Me_5), 194.0 (ipso-C_6H_5), 135.4 (C_6H_5), 125.9 (C_6H_5), 125.7 (C_6H_5). Anal. Calcd for $C_{42}H_{55}ClO_3Ti_3$ (M_r = 786.98): C, 64.10; H, 7.04. Found: C, 63.71; H, 6.89.

Preparation of $[Cp^*Ti(\mu\text{-}O)]_3(\mu_3\text{-}CMe)$ (13). A solution of $[Cp^*TiEt(\mu\text{-}O)]_3$ (2.00 g, 3.08 mmol) in 60 mL of toluene was transferred via cannula into a Carius tube (120 mL of capacity) ready to be sealed by flame in vacuo. This solution was heated, in an autoclave, at 195 °C for 12 h. The Carius tube was opened into a glovebox and the solvent removed in vacuo to yield 1.90 g of a dark red solid (99%). ^{1}H NMR (C_6D_6, 20 °C, δ): 1.95 (s, 45H, C_5Me_5), 2.81 (s, 3H, CCH_3). ^{13}C NMR (C_6D_6, 20 °C, δ): 119.5 (m, C_5Me_5), 11.3 (q, ^1J = 125 Hz, C_5Me_5), 401.7 (q, ^2J = 6.4 Hz, CCH_3), 39.1 (q, ^1J = 126 Hz, CCH_3). MS (EI, *m/z*, rel inten): 624 (M^+, 100%, correct isotope distribution), 597 [$(Cp^*TiO)_3^+$, 24%]. IR (KBr, cm^{-1}): 2913 (s, b), 1430 (m, b), 1374 (m, n), 1023 (w, b), 788 (m, b), 664 (vs, b), 629 (s, n), 425 (s, n), 384 (m, n). Anal. Calcd for $C_{32}H_{48}O_3Ti_3$ (M_r = 624.37): C, 61.56; H, 7.75. Found: C, 61.41; H, 7.70.

X-ray Structure Determination of $[Cp^*Ti(\mu\text{-}O)]_3(\mu_3\text{-}CCH_3)$ (13). Data collection was performed at 20 °C using an Enraf-Nonius CAD4 diffractometer. The structure was solved by a combination of direct methods and Fourier synthesis and refined by full-matrix least-squares techniques. All the non-hydrogen atoms were refined anisotropically. In the later stages of refinement H(22), H(23), H(24), and H(25) were located in difference Fouriers and refined in x, y, z and U_{iso}; other H atoms were included in calculated positions with thermal parameters equivalent to those of the atoms to which they are attached. Positional and thermal parameters of all H atoms were fixed in the last cycle of refinement. Final values of R = 0.046 and R_w = 0.050 (non-Poisson weighting scheme for all observed reflections) were obtained.

Anomalous dispersion corrections and atomic scattering factors were taken from ref 19. Calculations were performed with the SDP package[20] and the programs MULTAN[21] and DIRDIF[22] on a Microvax II computer.

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Supplementary Material Available: Tables of positional parameters, bond distances and angles, and thermal parameters (5 pages). Ordering information is given on any current masthead page.

OM940048J

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