New Organometallic Heteronuclear μ-Oxo Complexes. X-ray Structure of $[Cp^*{}_3Ti_3Cl(\mu\text{-}O_2SO_2)](\mu\text{-}O)_3\cdot C_6H_5CH_3$

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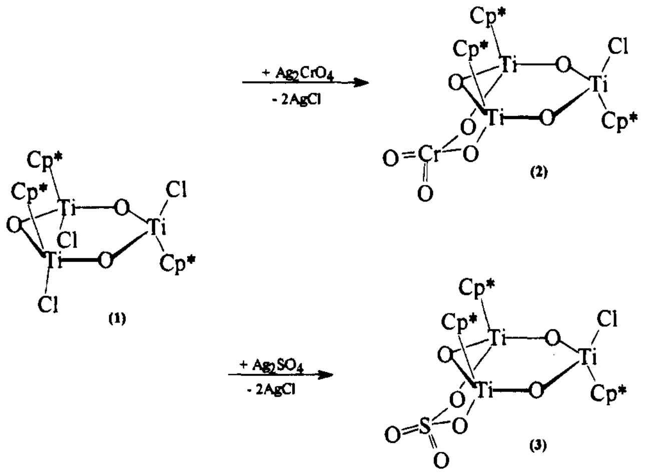
The reaction of $[Cp^*TiCl(\mu\text{-}O)]_3$ (**1**) ($Cp^* = \eta^5\text{-}C_5Me_5$) with anhydrous silver salts of a variety of oxyanions (SO_4^{2-}, CrO_4^{2-}, NO_3^-, and ReO_4^-) in organic solvents leads to the isolation of the compounds $[Cp^*{}_3Ti_3(EO_4)_xCl_y](\mu\text{-}O)_3$ [$x = y = 1$, E = Cr (**2**), S (**3**); $x = 3$, $y = 0$, E = Re (**4**)], $[Cp^*{}_3Ti_3(NO_3)_xCl_{3-x}](\mu\text{-}O)_3$ [$x = 1$ (**5**), 3 (**6**)], and $[Cp^*{}_3Ti_3(CrO_4)L](\mu\text{-}O)_3$ [L = NO_3 (**7**), ReO_4 (**8**)]. The crystal structure of $[Cp^*{}_3Ti_3Cl(\mu\text{-}SO_4)](\mu\text{-}O)_3$ (**3**) determined by X-ray analysis shows that the complex crystallizes solvated with one molecule of toluene in the space group $P\bar{1}$; $a = 8.943(2)$ Å, $b = 11.912(2)$ Å, $c = 19.259(4)$ Å, $\alpha = 72.74(3)°$, $\beta = 89.57(3)°$, $\gamma = 89.62(3)°$, $Z = 2$, $R = 0.078$, and $R_w = 0.105$. The molecule contains a Ti_3O_3 core where a $\mu\text{-}O_2SO_2$ ligand bridges two titanium atoms separated by 3.182(2) Å, a distance substantially shorter than the other two, 3.317(2) and 3.304(3) Å respectively.

Introduction

The chemistry of organometallic oxo complexes is currently an area of high interest due to the relevance of these compounds to metal-catalyzed oxo transfer reactions,[1] as models for studies of metal-support interactions and the transformation of the hydrocarbons on metal or metal oxide surfaces.[2] On the other hand, organometallic oxides can be used as precursors to prepare mono- and multicomponent oxides without the very severe conditions of the traditional ceramics preparation techniques.[3] The syntheses of many mononuclear and dinuclear oxide complexes have appeared in the literature, and their extension to polynuclear systems is particularly interesting because the latter may provide a direct link between the so-called organometallic oxides[4] and the inorganic oxides[3] or polyoxoanions.[5] Nearly all the known oxo-bridged compounds of the transition elements contain identical metal centers (M–O–M), and a much smaller number having two different metals (M–O–M′) have been prepared.[6] We report here the syntheses of the first organometallic heteropolynuclear μ-oxo complexes containing titanium and rhenium/chromium atoms bonded to oxygen. Also we describe in this paper the characterization of some new examples of the unusual organometallic titanium compounds with sulfate[7] or nitrate[8] ligands.

Scheme 1



Results and Discussion

The oxo trichloride $[Cp^*TiCl(\mu\text{-}O)]_3$ (**1**) reacts with anhydrous silver salts of diverse oxoanions with precipitation of silver chloride. Thus, reaction with silver chromate gives the chromate complex **2** and reaction with silver sulfate gives the sulfate complex **3** (Scheme 1).

Perrhenate and nitrate derivatives are also easily prepared from **1** and the appropriate silver salts. Three equivalents of $AgReO_4$ reacts with **1** to form **4** as indicated by eq 1; however, when lower ratios (2:1 or 1:1) of salt are employed, a mixture of complexes containing three, two, or one perrhenate ligands and **1** is obtained. Under similar conditions, the reactions of

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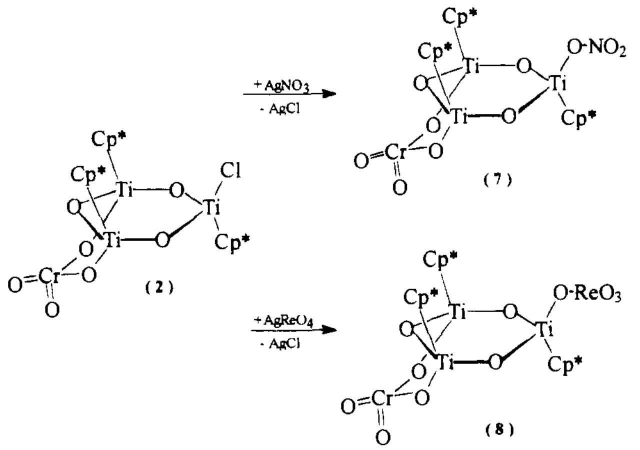
Scheme 2



$AgNO_3$ with **1** in ratios 1:1 and 3:1 led to the formation of the oxo complexes **5** and **6**, respectively (eq 2).

$$\begin{array}{lll} & + 3\,AgReO_4 \xrightarrow{THF\,/\,-\,3\,AgCl} [Cp^*{}_3Ti_3(ReO_4)_3(\mu\text{-}O)_3] & (1) \\ [Cp^*TiCl]_3(\mu\text{-}O)_3 & \qquad\qquad\qquad\qquad (\mathbf{4}) & \\ \quad (1) & + x\,AgNO_3 \xrightarrow{THF\,/\,-\,x\,AgCl} [Cp^*{}_3Ti_3(NO_3)_xCl_{3\text{-}x}(\mu\text{-}O)_3] & (2) \\ & \qquad\qquad\qquad x = 1\ (\mathbf{5}),\ 3\ (\mathbf{6}) & \end{array}$$

On the other hand, treatment of $[Cp^*{}_3Ti_3Cl(\mu\text{-}CrO_4)](\mu\text{-}O)_3$ with $AgNO_3$ and $AgReO_4$ leads to the preparation of $[Cp^*{}_3Ti_3(NO_3)(\mu\text{-}CrO_4)](\mu\text{-}O)_3$ (**7**) and $[Cp^*{}_3Ti_3(ReO_4)(\mu\text{-}CrO_4)](\mu\text{-}O)_3$ (**8**), respectively (see Scheme 2).

All of the products illustrated have been isolated in high yield (70−95%) as microcrystalline solids and characterized by elemental analysis and spectroscopic methods (see Experimental Section).

NMR Spectra. The ^1H and ^{13}C NMR spectra of the complexes **2**−**4** show the clear presence of two inequivalent types of Cp* groups in a 2:1 ratio, in agreement with the structure suggested for them in Scheme 1. Analogous spectral situations have been reported for other complexes containing the "$[Cp^*Ti(\mu\text{-}O)]_3$" moiety: $[Cp^*Ti(\mu\text{-}O)]_3R_2Cl$ (R = Me, Et, Ph) and $[Cp^*TiR(\mu\text{-}O)]_3$ (R = Me, Ph, *p*-MeC_6H_4, C≡CPh, Et, Pr, CH_2Ph, C≡CH, NMe_2).[9] Similar spectral situations should be found for complexes **6**−**8**, Cp* moieties in a 2:1 ratio; however, in these compounds the three Cp* groups give rise to single signals both in ^1H and ^{13}C NMR.

The ^1H and ^{13}C NMR spectra of **5** prove the existence of three different types of Cp* ligands consistent with the substitution of one of the two chlorides in the cis position, at the less crowded side of **1**.

IR Spectra. The IR spectra of complexes **2**−**8** show the characteristic Cp* and Ti−O−Ti absorptions;[10] also the corresponding bands for bidentate SO_4 (**3**) and CrO_4 (**2**, **7**, **8**) ligands are found[11] (see Experimental Section).

Remarkable features in the IR spectra of complexes **5**−**7** are the bands assignable to coordinated nitrato ligands with $\Delta\nu$ 282, 271, and 290 cm^{-1}, respectively. $\Delta\nu$ has been defined as the separation between the two highest energy bands corresponding to the nitrato ligand in similar complexes,[11a] and it is expected to be larger in the case of bidentate $[Ti(O_2NO)_4]$,[12] 405 cm^{-1}; $Sn(O_2NO)_4$,[13] 379 cm^{-1}; $Cp^*Ti(O_2NO)_3$,[14] 364 cm^{-1}] rather than monodentate structures $[Cp_2Ti(ONO_2)_2$,[8a] 240 cm^{-1}], confirming the presence of monodentate oxoanion ligands in the mentionated complexes **5**−**7**.

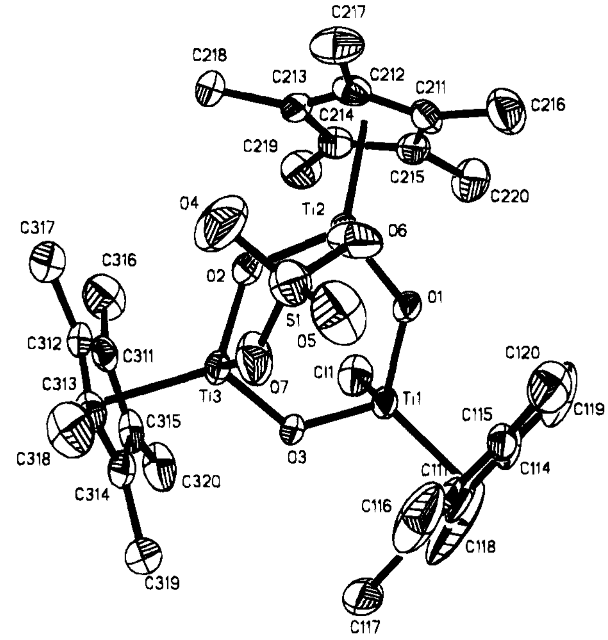


Figure 1. ORTEP plot of $[Cp^*{}_3Ti_3Cl(\mu\text{-}O_2SO_2)](\mu\text{-}O)_3$ (**3**) giving the crystallographic atom numbering. The thermal ellipsoids correspond to 50% probability. The solvent molecule is omitted for clarity.

The IR spectra of **4** and **8** show ν(Re−O) absorptions bands within the 950−880 cm^{-1} range which can be reasonably explained, but not firmly, in terms of presence of monodentate perrhenates.[15]

Thermal Analyses. Thermogravimetric analyses (TGA), under air and nitrogen atmospheres, in the temperature range 25−1100 °C, have been carried out for the organometallic oxides **2**−**4** and **8**. The thermogravimetric analyses of complexes **3** and **4** show decomposition at ca. 100 °C that is essentially complete by 850 °C. Above this temperature, no further weight loss occurs, resulting in ceramic residues, 31% and 19% of the original material for **3** and **4**, respectively. The TGA plots corresponding to complexes **2** and **8** show weight loss in the ranges 200−1000 °C (100−500 °C if the pyrolysis is effected in air) for complex **2** and 175−750 °C for **8** to afford ceramic residues, 41% (**2**) and 53% (**8**) of the original material.

Structural Study of $[Cp^*{}_3Ti_3Cl(\mu\text{-}O_2SO_2)](\mu\text{-}O)_3$ (3). An X-ray diffraction study of **3** reveals the presence of two clusters per unit cell along with two toluene molecules of crystallization. An ORTEP drawing of this oxocluster is shown in Figure 1, and important crystallographic parameters are given in Tables 1−3. Cluster **3** consists of an isosceles triangle of Cp*Ti units [Ti(1)−Ti(2) = 3.317(2) Å, Ti(1)−Ti(3) = 3.304(3) Å, and Ti(2)−Ti(3) = 3.182(2) Å] with each edge bridged by an oxide ligand. At one side of the Ti_3 plane, two of the titanium atoms are bridged by a μ_2-O_2SO_2 ligand while the third has a terminal chlorine atom on the opposite side.

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Table 1. Data for Crystal Structure Analysis of $[Cp^*_3Ti_3Cl(\mu\text{-}O_2SO_2)](\mu\text{-}O)_3$ (**3**)

formula	$C_{37}H_{53}ClO_7STi_3$
crystal habit	prism
λ, Å	0.710 73
temp, K	290
crystal dimens	0.23 × 0.31 × 0.35
fw	821.0
space group	$P\bar{1}$
a, b, c, Å	8.943(2), 11.912(2), 19.259(4)
α, β, γ, deg	72.74(3), 89.57(3), 89.62(3)
Z; V, Å^3	2; 1959.2(19)
D_{calc}, g cm^{-3}	1.392
μ(Mo Kα), cm^{-1}	7.63
index ranges	$-9 \le h \le 9$ $-12 \le k \le 12$ $0 \le l \le 20$
indep reflns	5062
transm factors: max, min	0.342, 0.303
R,[a] R_w[b]	0.078, 0.105

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \sum w^{1/2}(|F_o| - |F_c|)/\sum w^{1/2}|F_o|$; $w^{-1} = \sigma^2(F) + 0.003F^2$.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $[Cp^*_3Ti_3Cl(\mu\text{-}O_2SO_2)](\mu\text{-}O)_3$ (**3**)

	x	y	z	U(eq)
Ti(1)	2504(2)	4423(1)	2155(1)	32(1)
Ti(2)	2145(2)	7294(1)	1374(1)	32(1)
Ti(3)	2165(2)	6315(1)	3101(1)	31(1)
S(1)	4631(3)	8104(2)	2247(1)	48(1)
Cl(1)	99(3)	3872(2)	2049(1)	48(1)
O(1)	2617(7)	5794(4)	1415(3)	36(2)
O(2)	1278(7)	7138(5)	2248(3)	42(2)
O(3)	2517(6)	4882(5)	2978(3)	34(2)
O(4)	3994(10)	9158(7)	2331(5)	83(4)
O(5)	6204(8)	8063(8)	2207(4)	74(4)
O(6)	4099(9)	7936(5)	1535(4)	65(3)
O(7)	4087(8)	7071(6)	2879(4)	58(3)
C(111)	4941(12)	3714(10)	2450(6)	55(5)
C(112)	3916(16)	2768(11)	2786(7)	74(5)
C(113)	3192(13)	2474(8)	2232(8)	65(5)
C(114)	3716(11)	3169(8)	1586(5)	46(4)
C(115)	4771(10)	3948(7)	1700(5)	34(3)
C(116)	5999(15)	4325(14)	2810(9)	115(9)
C(117)	3738(21)	2206(14)	3587(7)	163(10)
C(118)	2166(16)	1477(10)	2371(12)	164(13)
C(119)	3153(12)	3180(12)	826(7)	81(6)
C(120)	5620(13)	4854(10)	1122(7)	67(5)
C(211)	2130(10)	8272(8)	117(4)	35(3)
C(212)	1761(10)	9105(7)	485(5)	34(3)
C(213)	417(10)	8774(7)	852(4)	33(3)
C(214)	−66(9)	7724(7)	722(5)	32(3)
C(215)	1005(11)	7426(7)	265(5)	37(3)
C(216)	3498(11)	8290(10)	−339(6)	58(4)
C(217)	2645(12)	10189(8)	451(6)	54(4)
C(218)	−383(12)	9426(8)	1309(5)	49(4)
C(219)	−1430(11)	7037(8)	1022(6)	51(4)
C(220)	906(13)	6374(9)	−18(6)	59(4)
C(311)	−41(9)	6475(8)	3723(4)	33(3)
C(312)	944(10)	7326(8)	3818(4)	35(3)
C(313)	2180(10)	6748(8)	4207(5)	41(4)
C(314)	1958(11)	5521(8)	4365(5)	38(3)
C(315)	605(10)	5352(8)	4054(5)	35(3)
C(316)	−1495(11)	6716(10)	3329(6)	61(5)
C(317)	742(12)	8631(8)	3544(5)	54(4)
C(318)	3514(12)	7287(10)	4437(6)	61(5)
C(319)	2994(13)	4554(9)	4775(5)	61(4)
C(320)	−100(12)	4166(9)	4092(6)	55(4)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Cp^*_3Ti_3Cl(\mu\text{-}O_2SO_2)](\mu\text{-}O)_3$ (**3**)

Ti(1)−O(1)	1.823(5)	Ti(1)−O(3)	1.825(6)
Ti(1)−Cl(1)	2.281(3)	Ti(1)−Cp*1	2.027
Ti(2)−O(1)	1.812(6)	Ti(2)−O(2)	1.808(6)
Ti(2)−O(6)	1.975(8)	Ti(2)−Cp*2	2.009
Ti(3)−O(2)	1.828(6)	Ti(3)−O(3)	1.817(6)
Ti(3)−O(7)	1.932(7)	Ti(3)−Cp*3	2.005
S(1)−O(4)	1.427(9)	S(1)−O(5)	1.410(7)
S(1)−O(6)	1.522(8)	S(1)−O(7)	1.531(7)
Ti(1)−O(1)−Ti(2)	131.6(4)	Ti(1)−O(3)−Ti(3)	130.3(3)
Ti(2)−O(2)−Ti(3)	122.2(4)	Ti(2)−O(6)−S(1)	126.0(4)
Ti(3)−O(7)−S(1)	132.1(4)	Cp*1−Ti(1)−Cl(1)	116.1
Cp*1−Ti(1)−O(1)	115.5	Cp*1−Ti(1)−O(3)	112.9
Cp*2−Ti(2)−O(1)	117.2	Cp*2−Ti(2)−O(2)	117.3
Cp*2−Ti(2)−O(6)	114.7	Cp*3−Ti(3)−O(2)	117.9
Cp*3−Ti(3)−O(3)	115.1	Cp*3−Ti(3)−O(7)	119.2
O(4)−S(1)−O(5)	116.3(6)	O(4)−S(1)−O(6)	109.4(5)
O(4)−S(1)−O(7)	108.2(5)	O(5)−S(1)−O(6)	104.7(5)
O(5)−S(1)−O(7)	109.1(4)	O(6)−S(1)−O(7)	109.0(4)

[a] Cp*1, Cp*2, and Cp*3 are the centroids of the corresponding C_5Me_5 rings.

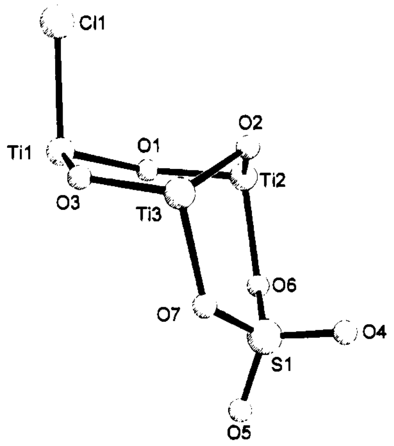

Figure 2. Drawing showing the ring arrangement of the Ti_3O_5S core of $[Cp^*_3Ti_3Cl(\mu\text{-}O_2SO_2)](\mu\text{-}O)_3$ (**3**) (Cp* rings omitted for clarity).

The $Ti_3(\mu_2\text{-}O)_3$ core of the cluster is not planar with a pseudoboat conformation, as is particularly well illustrated by the drawing shown in Figure 2. Bond lengths corresponding to Ti−Cp* (2.01 Å average), Ti−Cl [2.281(3) Å], and Ti−O−Ti bridges of 1.82 Å (average) are within the values found in other structurally characterized oxotitanium complexes.[10,16] The Ti(1)−O(1)−Ti(2) [131.6(4)°] and Ti(1)−O(3)−Ti(3) [130.3(3)°] angles are also within the normal range in titanium oxo trimers,[10] while the corresponding Ti(2)−O(2)−Ti(3) angle [122.2(4)°] is smaller, due to the bridging sulfate ligand, and comparable to those containing an adamantane-like Ti_4O_6 core: $(Cp^*Ti)_4(\mu\text{-}O)_6$ (122.9° average)[16a,b] and $[Ti_4(C_6H_{15}N_3)_4(\mu\text{-}O)_6]Br_4{\cdot}4H_2O$ (125.6° average).[17]

The sulfate ligand lies in nearly symmetrical syn/syn coordination with Ti−O(sulfate) distances 1.932(7) and 1.975(8) Å, similar to those found for strong metal−oxygen bonds between first-row transition metals and oxyanions $(XO_n)^{m-}$ as ligands (1.9−2.2 Å).[11b]

The sulfur−oxygen bond lengths of the sulfate moiety differ as expected from those of the free tetrahedral ion [d(S−O) = 1.49 Å],[18] being shorter for the terminal S−O bonds, 1.410(7) and 1.427(9) Å, but longer for the bridging ones, 1.522(8) and 1.531(7) Å.[19] On the other hand, the short angles Ti(2)−O(6)−S(1), 126.0(4)°, and Ti(3)−O(7)−S(1), 132.1(4)°, which imply an almost sp^2 hybridization for the oxygen atoms, make the

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internal angle O(6)−S(1)−O(7), 109.0(4)°, smaller than the external O(4)−S(1)−O(5), 116.3(6)°.

Experimental Section

Reagents, Solvents, and General Methods. All reactions were performed in Schlenk-type flasks under argon. Solvents were dried under argon by conventional methods.[20] Ag_2SO_4, $AgNO_3$, and deuterated solvents ($CDCl_3$, C_6D_6, CD_2Cl_2) were purchased from commercial sources and used without further purification. $[Cp^*TiCl]_3(\mu\text{-}O)_3$,[9a] Ag_2CrO_4,[21] and $AgReO_4$[21] were prepared according to published procedures. All the silver salts were dried at 100 °C in vacuo (10^{-4} mmHg) for 12 h prior to use.

NMR spectra were recorded on a Varian Unity FT-300 NMR spectrometer. ^1H and ^{13}C shifts are reported in ppm downfield from Me_4Si with residual solvent protons used as an internal reference. IR spectra were recorded on a Perkin-Elmer 883 infrared spectrophotometer using KBr pellets. Electron Impact (EI) mass spectra were recorded at 70 eV on a Hewlett-Packard 5988 spectrometer. C, H, and N analyses were carried out with a Perkin-Elmer 240B microanalyzer, Cr by atomic absorption spectrometry with a Perkin-Elmer 1100B spectrometer, and Cl by volumetric analysis. Thermal analyses were carried out on Dupont-951 and Cahn D-200 thermoanalyzers; samples of 2−5 mg were placed on platinum sample holders, and runs were performed under a nitrogen stream (100−120 mL/min) or still air, using heating rates of 10 °C/min from room temperature to 1100 °C.

Preparation of $[Cp^*_3Ti_3Cl(\mu\text{-}CrO_4)](\mu\text{-}O)_3$ (2). A suspension of $[Cp^*TiCl]_3(\mu\text{-}O)_3$ (2.00 g, 2.84 mmol) and Ag_2CrO_4 (0.94 g, 2.84 mmol) in 400 mL of THF was stirred for ca. 24 h at room temperature in the dark. The color changed slowly from yellow to black. The solution was filtered to remove the AgCl, and the filtrate was evaporated and recrystallized in toluene to obtain **2** as black crystals, yield 95%. ^1H NMR ($CDCl_3$, 20 °C, δ): 2.09 (s, 15H, C_5Me_5); 2.05 (s, 30H, C_5Me_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C, δ): 128.1, 127.8 (C_5Me_5); 12.0, 11.4 (C_5Me_5). IR (KBr, cm^{-1}): 2915 vs; 1486 m; 1428 s; 1377 s; 1073 m; 974 s; 950 s; 840−740 vs, vb; 428 s; 365 m. Anal. Calcd for $C_{30}H_{45}Ti_3ClCrO_7$: C, 48.12; H, 6.06; Cl, 4.73; Cr, 6.94. Found: C, 47.96; H, 6.07; Cl, 4.47; Cr, 6.92.

Preparation of $[Cp^*_3Ti_3Cl(\mu\text{-}O_2SO_2)](\mu\text{-}O)_3$ (3). This complex was obtained similarly to **2**, from 1.00 g (1.42 mmol) of $[Cp^*TiCl]_3(\mu\text{-}O)_3$, 0.44 g (1.42 mmol) of Ag_2SO_4, and THF (250 mL), as a crystalline orange solid, yield 92%. ^1H NMR (CD_2Cl_2, 20 °C, δ): 2.13 (s, 30H, C_5Me_5); 2.10 (s, 15H, C_5Me_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C, δ): 130.3, 130.0 (C_5Me_5); 12.4, 11.9 (C_5Me_5). IR (KBr, cm^{-1}): 2916 s; 1490 w; 1430 m; 1379 s; 1310 vs; 1157 vs; 1027 w; 939 s; 900 vs; 770−725 vs, vb; 446 s, 350 s. MS, m/z [assignment, rel intens. %]: 594 [$(M - Cp^*)^+$, 58]. Anal. Calcd for $C_{30}H_{45}Ti_3ClSO_7$: C, 49.44; H, 6.22. Found: C, 49.53; H, 6.11.

Preparation of $[Cp^*_3Ti_3(ReO_4)_3](\mu\text{-}O)_3$ (4). This compound was prepared similarly to **2**, from $[Cp^*TiCl]_3(\mu\text{-}O)_3$ (0.60 g, 0.85 mmol) and $AgReO_4$ (0.92 g, 2.56 mmol) in 150 mL of THF. The orange solid **4** was obtained in 80% yield. ^1H NMR (C_6D_6, 20 °C, δ): 1.90 (s, 15H, C_5Me_5); 1.88 (s, 30H, C_5Me_5). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, δ): 130.8, 130.1 (C_5Me_5); 11.3, 11.2 (C_5Me_5). IR (KBr, cm^{-1}): 2917 m; 1432 m; 1379 m; 944 vs; 920 s; 879 vs; 761−730 vs, vb; 446 s. Anal. Calcd for $C_{30}H_{45}Ti_3\ Re_3O_{15}$: C, 26.73; H, 3.36. Found: C, 26.69; H, 3.35.

Preparation of $[Cp^*_3Ti_3Cl_2(NO_3)](\mu\text{-}O)_3$ (5). $AgNO_3$ (0.24 g, 1.42 mmol) was added at room temperature to a solution of $[Cp^*TiCl]_3(\mu\text{-}O)_3$ (1.00 g, 1.42 mmol) in 200 mL of THF. After the mixture was stirred for 40 h, the solvent was removed under vacuum; the residue was extracted with toluene and then crystallized at −40 °C for 24 h. Yellow crystals of **5** (70% yield) were collected. ^1H NMR (C_6D_6, 20 °C, δ): 2.07 (s, 15H, C_5Me_5); 2.04 (s, 15H, C_5Me_5); 1.94 (s, 15H, C_5Me_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C, δ): 129.0, 128.3, 127.7 (C_5Me_5); 12.2, 12.0, 11.8 (C_5Me_5). IR (KBr, cm^{-1}): 2915 vs; 1549 vs; 1491 m; 1431 s; 1380 s; 1267 s; 1020 m; 800−750 vs, vb; 446 s; 355 s. MS, m/z [assignment, rel intens. %]: 594 [$(M - Cp^*)^+$, 2]. Anal. Calcd for $C_{30}H_{45}Ti_3Cl_2NO_6{\cdot}C_7H_8$ (toluene): C, 54.04; H, 6.50; N, 1.70. Found: C, 54.26; H, 6.57; N, 1.82.

Preparation of $[Cp^*_3Ti_3(NO_3)_3](\mu\text{-}O)_3$ (6). This preparation was carried out as described for **5**, from $[Cp^*TiCl]_3(\mu\text{-}O)_3$ (1.00 g, 1.42 mmol) and $AgNO_3$ (0.72 g, 4.26 mmol). The yield of orange **6** was ca. 80%. ^1H NMR (C_6D_6, 20 °C, δ): 1.90 (s, C_5Me_5). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, δ): 128.6 (C_5Me_5); 11.7 (C_5Me_5). IR (KBr, cm^{-1}): 2917 vs; 1547 vs; 1495 m; 1430 s; 1381 s; 1276 s; 1021 m; 801−730 vs, vb; 446 s. MS, m/z [assignment, rel intens. %]: 648 [$(M - Cp^*)^+$, 14]. Anal. Calcd for $C_{30}H_{45}Ti_3N_3O_{12}{\cdot}C_7H_8$ (toluene): C, 50.76; H, 6.10; N, 4.80. Found: C, 50.87; H, 5.93; N, 4.76.

Preparation of $[Cp^*_3Ti_3(NO_3)(\mu\text{-}CrO_4)](\mu\text{-}O)_3$ (7). The same procedure was used for the preparation of this compound from **5** (0.50 g, 0.68 mmol) and Ag_2CrO_4 (0.23 g, 0.68 mmol) or from **2** (0.50 g, 0.67 mmol) and $AgNO_3$ (0.11 g, 0.67 mmol); the product was isolated as a black crystalline solid in 85−95% yield. ^1H NMR (C_6D_6, 20 °C, δ): 1.95 (s, C_5Me_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C, δ): 127.9 (C_5Me_5); 11.4 (C_5Me_5). IR (KBr, cm^{-1}): 2913 s; 1555 vs; 1488 m; 1430 m; 1379 s; 1265 s; 1025 m; 975 vs; 948 vs; 836−730 vs, vb. Anal. Calcd for $C_{30}H_{45}Ti_3NCrO_{10}$: C, 46.47; H, 5.85; N, 1.81; Cr, 6.70. Found: C, 46.42; H, 5.78; N, 1.89; Cr, 6.51.

Preparation of $[Cp^*_3Ti_3(ReO_4)(\mu\text{-}CrO_4)](\mu\text{-}O)_3$ (8). A 0.45 g (0.60 mmol) sample of **2** was suspended in THF (150 mL), $AgReO_4$ (0.22 g, 0.60 mmol) was added, and the mixture was stirred at room temperature for 24 h. The solvent was removed in vacuo, the black residue extracted with hexane, and the filtered solution concentrated to 25 mL. Cooling to −40 °C for 24 h yielded black crystalline **8**. Yield: 60%. ^1H NMR (C_6D_6, 20 °C, δ): 1.95 (s, C_5Me_5). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, δ): 129.1 (C_5Me_5); 11.6 (C_5Me_5). IR (KBr, cm^{-1}): 2915 m; 1430 m; 1378 m; 976 s; 947 s; 888 s; 806 s; 744 vs; 429 s. Anal. Calcd for $C_{30}H_{45}Ti_3CrReO_{11}$: C, 37.40; H, 4.71; Cr, 5.40. Found: C, 37.49; H, 4.82; Cr, 5.50.

X-ray Structure Determination of $[Cp^*_3Ti_3Cl(\mu\text{-}O_2SO_2)](\mu\text{-}O)_3$ (3). Compound **3** was recrystallized from a toluene solution at −20 °C. Crystals were mounted on glass fiber with epoxy resin and transferred to a STOE four-circle diffractometer for characterization and data collection. Unit cell parameters were determined from the angular settings of 50 well-centered reflections: $20° < 2\theta < 25°$. Axial photographs and a limited search through an octant of reciprocal space revealed a lack of systematic absences and symmetry consistent with the triclinic space group $P\bar{1}$ for **3**. Details of the data collection are presented in Table 1 and in the Supporting Information. The data were corrected for Lorentz−polarization and absorption effects (semiempirical correction based on azimuthal reflections).

The structure was succesfully solved by direct methods and refined by full-matrix least-squares procedures. The non-hydrogen atoms were refined with anisotropic temperature parameters, hydrogen atoms were allowed to ride on their respective carbons [C−H = 0.96 Å, U(H) = 0.08 Å^2], and a weighting scheme based on $\sigma(F)$ was employed. Calculations were performed by using the SHELXTL PLUS package of programs.[22] Refinement converged to the R factors reported in Table 1. The largest and mean shift/esd in the final cycles for the structure refinement were 0.0019 and 0.001, respectively. The minimum and maximum excursions in the final difference Fourier map for compound **3** were −0.64 and +1.93 e Å^{-3}, situated in the Ti(3)−O(7)−S(1) zone and S(1)−O(6) bond, respectively. All the remaining residuals were less than 1 e Å^{-3}.

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Supporting Information Available: Listings of all positional parameters, anisotropic thermal parameters, complete bond distances and angles, and crystallographic data and data collection details (10 pages). Ordering information is given on any current masthead page.

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