Hydrocarbon species μ_3-CCH_2^-, μ_3-CCH_3 and μ-$CHCH_3$ supported on Ti_3O_3†

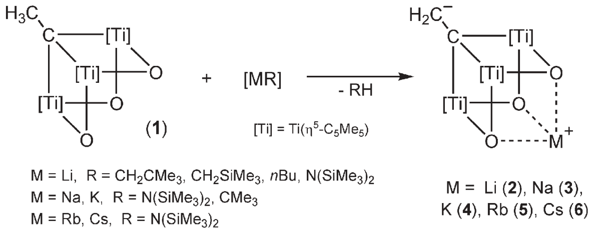
Octavio González-del Moral, Avelino Martín, Miguel Mena,* María del Carmen Morales-Varela and Cristina Santamaría

Received (in Cambridge, UK) 31st March 2005, Accepted 16th May 2005
First published as an Advance Article on the web 16th June 2005
DOI: 10.1039/b504467g

Treatment of the μ_3-ethylidyne complex [{TiCp*(μ-O)}$_3$(μ_3-CMe)] (1), (Cp* = η^5-C_5Me_5) with alkali metal amides leads to the oxoheterometallocubane derivatives [M(μ_3-O)$_3${(TiCp*)$_3$(μ_3-CCH_2)}] [M = Li (2), Na (3), K (4), Rb (5), Cs (6)] containing the naked carbanion μ_3-CCH_2^-; the addition of triphenylmethanol and *tert*-butanol to the compounds 2–6 gives rise to the oxoderivatives [{TiCp*(μ-O)}$_3$(μ-CHMe)(OCR_3)] [R = Me (7), Ph (8)] which show a μ-ethylidene bridge on the surface model Ti_3O_3.

The chemical behaviour of the μ_3-alkylidyne groups in the complexes [{TiCp*(μ-O)}$_3$(μ_3-CR)] (R = H, Me) has revealed a surprising and unprecedented reactivity,[1] which establishes bridges of understanding between molecular and surface chemistry. In particular, the ethylidyne is a well-known surface hydrocarbon fragment and its transformations to the C_2H_2 or C_2H_4 species have been studied.[2] Herein, we would like to show that these transformations are also possible on our molecular system [Ti_3O_3] by reactions of the trinuclear titanium derivative [{TiCp*(μ-O)}$_3$(μ_3-CMe)] (**1**) with alkali metal alkyls and amides, and subsequent treatment with alcohols.

Reaction of the complex [{TiCp*(μ-O)}$_3$(μ_3-CMe)] (**1**) with the alkyl derivatives [MR] (M = Li, R = CH_2CMe_3, CH_2SiMe_3, *n*Bu; M = Na, K, R = CMe_3) or the amides [MN($SiMe_3$)$_2$] (M = Li, Na, K, Rb, Cs) in a 1:1 ratio, at room temperature or heating smoothly at ≈60 °C, led us to isolate the compounds [M(μ_3-O)$_3${(TiCp*)$_3$(μ_3-CCH_2)}] [M = Li (**2**), Na (**3**), K (**4**), Rb (**5**), Cs (**6**)] as dark red solids in high yields (see Scheme 1). Complexes **2–6** proved to be stable under argon at room temperature and practically insoluble in most of the common solvents (toluene, hexane, dichloromethane…) with the exception of tetrahydrofuran, which allowed their NMR spectroscopic characterization.



Scheme 1

NMR spectra in tetrahydrofuran-d_8 of these species are consistent with the proposed oxoheterometallocubane structures and reveal the equivalence of the η^5-C_5Me_5 ligands, with only one signal in the ^1H NMR spectra (δ = 1.88–1.87) and two in the $^{13}C\{^1H\}$ NMR spectra (δ = 11.5–11.3, C_5Me_5; 114–119 C_5Me_5). Also, the NMR spectra display a singlet between 2.15–2.35 ppm in the ^1H and a triplet at δ = 76.1–76.8 (J_{CH} = 148 Hz) in the ^{13}C, attributed to the carbanion –CH_2^-. Otherwise, the apical carbon, μ_3-C, shows a singlet in the range 373–369 ppm, shifted to higher field with respect to **1** [δ(μ_3-*C*Me) = 401.7].[3]

The solid-state structure of **6** determined by X-ray diffraction[4] exhibits an organometallic polymeric chain (see Fig. 1) made up of oxoheterometallocubane [(thf)$_2$Cs(μ_3-O)$_3${(TiCp*)$_3$(μ_3-CCH_2)}] units with the caesium atom anchored on the deprotonated precursor **1** and linked to the contiguous molecule through a Cp* ligand. (see Fig. 2)

Bond lengths and angles of the [$Ti_3O_3C_2$] system of **1** remain unaltered in **6**, being the Ti–C(1) 2.099(8) Å (av.), Ti–C(2) 3.301(8) Å (av.) and the single bond C(1)–C(2) 1.528(11) Å. The value of the angle formed by the C(1)–C(2) bond and the Ti(1)–Ti(2)–Ti(3) plane is 89.7(5)°. Each alkali metal atom shows a trigonal prismatic environment constituted by the three oxygen atoms of the anionic tridentate ligand [(μ_3-O)$_3${(TiCp*)$_3$(μ_3-CCH_2)}]$^-$, two molecules of tetrahydrofuran and a Cp* ligand [C(11)–C(20)] of the closest molecule. Distances from caesium to the oxygen atoms of the tetrahydrofuran are in the usual range.[5] The incorporation of the pentamethylcyclopentadienyl ligand to the caesium atom distorts its coordination sphere, and distances

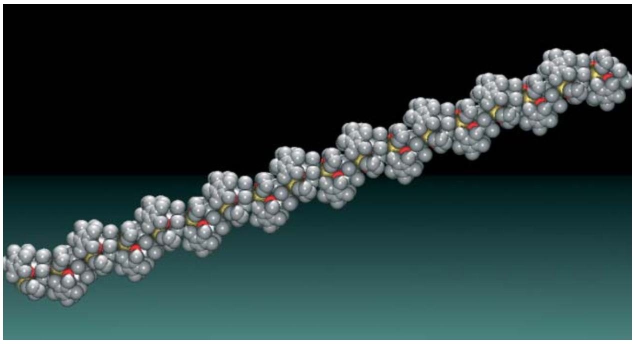


Fig. 1

Departamento de Química Inorgánica, Universidad de Alcalá. Campus Universitario, 28871 Alcalá de Henares-Madrid, Spain.
E-mail: miguel.mena@uah.es; Fax: +34 91 8854683; Tel: +34 91 8854684

† Electronic supplementary information (ESI) available: full experimental details of the synthesis and characterization of **2–8** and crystallographic data for **6** and **7**. See http://www.rsc.org/suppdata/cc/b5/b504467g/index.sht

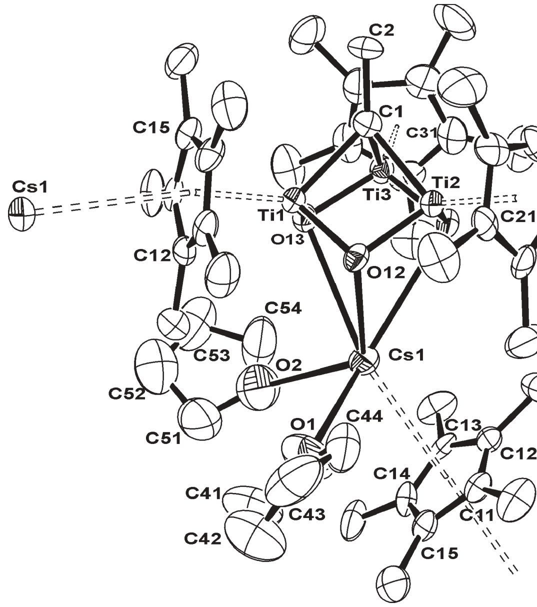
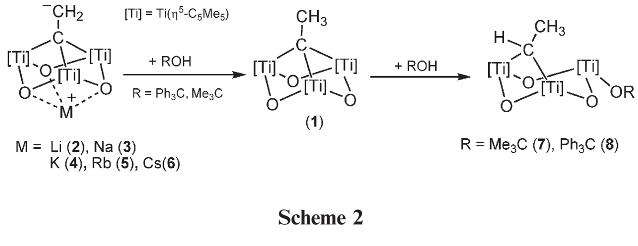


Fig. 2 Molecular structure of $[Cs(\mu_3\text{-}O)_3\{(TiCp^*)_3(\mu_3\text{-}CCH_2)\}]$ (**6**). Selected lengths (Å) and angles (°): Ti–O 1.865(6) (av.); Ti···Ti 2.754(2) (av.); O(1)–Cs(1) 3.034(8); O(2)–Cs(1) 3.065(10); Cs(1)–O(13) 3.168(6); Cs(1)–O(12) 3.175(5); Cs(1)–O(23) 3.275(5); Ti(1)–Cs(1) 3.835(1); Ti(2)–Cs(1) 3.952(1); Ti(3)–Cs(1) 3.953(1); Cs(1)–C(11) 3.495(8); Cs(1)–C(12) 3.355(6); Cs(1)–C(13) 3.453(9); Cs(1)–C(14) 3.700(9); Cs(1)–C(15) 3.714(8); O–Ti–C(1) 90.2(3) (av.); Ti–C(1)–Ti 81.9(3) (av.); Ti–O–Cs(1) 95.4(2)–100.2(2); Ti–O–Ti 95.2(2) (av.); O–Ti–O 105.1(2) (av.); O_{cube}–Cs(1)–O_{cube} 55.0(1) (av.); O_{THF}–Cs(1)–O_{THF} 94.5(3); O_{THF}–Cs(1)–O_{cube} 79.5(2)–129.5(2). Hydrogen atoms have been omitted for clarity.

from the metal to the oxygen atoms of the cube vary in the range 3.168(6)–3.275(5) Å, the longer distance corresponding to that closer to the sterically demanding ring. Distances from caesium to the C(11)–C(13) of the bridging Cp* are slightly longer than those found for other compounds with two caesium atoms bridged by a Cp or Cp* group,[6] while interactions with C(14) and C(15) are approximately 0.30 Å longer and could be indicative of a η^3 coordinative mode to the metal centre.

Reactions of **2**–**6** at room temperature with Me_3COH and Ph_3COH in benzene-d_6 caused the protonation of the carbanion moiety, and recovery of the complex $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}CMe)]$ (**1**) in a quantitative way. Moreover, in the presence of an excess of alcohol, the process evolves with transfer hydrogenation to the μ_3-CMe fragment giving the trinuclear complexes $[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}CHMe)(OCR_3)]$ [R = Me (**7**) Ph (**8**)] (Scheme 2). Complexes **7** and **8** were also successfully prepared by the one-pot reaction of **1** with the corresponding alcohol in hexane at room temperature. Both compounds are soluble in the usual solvents (toluene, hexane…) and can be stored under argon for long periods of time.



Scheme 2

The spectroscopic and analytical data are in agreement with the formulation given in Scheme 2 (see ESI†).

The NMR spectra of these species display two types of Cp* ligand in a 2:1 ratio, which is consistent with a C_s symmetry. The ^1H NMR spectra show as a remarkable feature a doublet at 1.94 (**7**), 1.97 (**8**) ppm and a quartet at 6.08 (**7**), 5.96 (**8**) ppm which correspond to the ethylidene bridge between the two metal centres. The ^{13}C NMR spectra reveal resonances at 29.5 (**7**), 28.9 (**8**) ppm (μ-CH*Me*) and 207.0 (**7**), 203.7 (**8**) ppm (μ-*C*HMe), this latter showing a very strong shielding with respect to the μ_3-apical carbon atom in **1**. The mass spectra show the expected molecular peak (m/z = 698) for **7** and other fragments consistent with the proposed stoichiometries for **7** and **8**.

The crystalline structure of **7** reveals a trinuclear species in which a Ti_3O_3 moiety supports one μ_3-ethylidene group and a *tert*-butoxide ligand (see Fig. 3).[4] The ethylidene group is bridging two of the three titanium atoms, and its methyl group is oriented towards the less crowded space existing among the three pentamethylcyclopentadienyl rings. The third titanium atom is linked to the *tert*-butoxide ligand which is located on the opposite side of the Ti_3O_3 unit with respect to the μ-ethylidene ligand in a similar way to that showed by other titanium trinuclear oxoderivatives.[7]

In conclusion, the results here reported show the use of the molecular oxide model $[Ti_3O_3]$ in the study of the transformation of the μ_3-ethylidyne unit into the hydrocarbon fragments $\mu_3\text{-}CCH_2^-$ and $\mu\text{-}CHCH_3$. Further experimental and theoretical work is necessary in order to understand the stabilization of these species and their reactivity.‡

The authors thank the Ministerio de Ciencia y Tecnología (BQU2001-1499) and the Comunidad de Madrid (07N/0091/2002) for financial support.

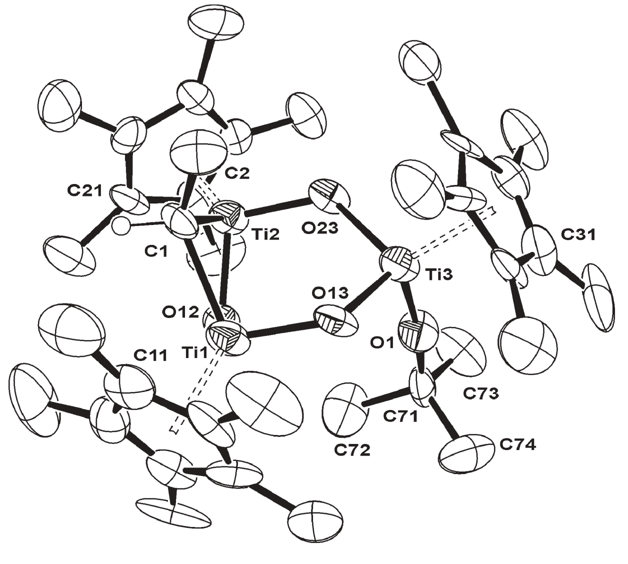


Fig. 3 Molecular structure of $[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}CHMe)(OCMe_3)]$ (**7**). Selected averaged lengths (Å) and angles (°) for the two independent molecules: C(1)–C(2) 1.533(14), C(1)–Ti 2.113(11), Ti(3)–O(1) 1.797(9), C(71)–O(1) 1.408(14), Ti–O_{bridge} 1.842(7), Ti–C(1)–C(2) 123.1(8), Ti–C(1)–Ti 83.4(4), O(12)–Ti–C(1) 83.5(4), Ti–O(13/23)–Ti 124.3(4), Ti(1)–O(12)–Ti(2) 99.4(3), O_{bridge}–Ti–O_{bridge} 103.9(3), O(1)–Ti(3)–O_{bridge} 104.9(3), Ti(3)–O(1)–C(71) 171.4(8) and 157.0(9). Hydrogen atoms except that of the ethylidene ligand have been omitted for clarity.

Notes and references

‡ Preparation of **2** from the reaction of **1** with [LiN(SiMe$_3$)$_2$] is reported as an example for complexes **2–6**. A solution of 80 mg (0.48 mmol) of [LiN(SiMe$_3$)$_2$] and 0.30 g (0.48 mmol) of **1** in hexane (40 mL) was placed in a 100 mL Carius tube with Young's valve. The reaction mixture was heated at ≈60 °C overnight and the red solid formed was filtered, washed with hexane and dried *in vacuo* to give 0.22 g of **2** (yield: 73%). IR (KBr, cm^{-1}): $\bar{\nu} = 2908$ (vs), 2851 (s), 1496 (w), 1439 (m), 1375 (m), 1024 (w), 802 (w), 647 (s), 585 (vs), 529 (s), 418 (s); ^{1}H NMR (300 MHz, THF-d_8, 20 °C, TMS): $\delta = 1.88$ (s, 45H, $C_5\mathit{Me}_5$), 2.20 (s, 2H, μ_3-$CC\mathit{H}_2$); ^{13}C{^{1}H} NMR (75 MHz, THF-d_8, 20 °C, TMS): $\delta = 11.5$ ($C_5\mathit{Me}_5$), 76.3 (μ_3-$C\mathit{C}H_2$), 114.7 (C_5Me_5), 373.1 (μ_3-$\mathit{C}CH_2$); elemental analysis calcd. (%) for $C_{32}H_{47}LiO_3Ti_3$ (630.25): C 60.98, H 7.52; found C 60.59, H 7.80. The syntheses of **7** and **8** are very similar, so only the preparation of **7** is included here: *tert*-butanol (12 mg, 0.16 mmol) was added to a solution of **1** (0.10 g, 0.16 mmol) in 50 mL of hexane in a 100 mL Carius tube with Young's valve. The reaction mixture was left stirring overnight at room temperature. The final solution was concentrated and cooled to obtain **7** as a violet solid (yield: 0.11 g, 99%). IR (KBr, cm^{-1}): $\bar{\nu} = 2965$ (s), 2908 (vs), 2856 (s), 1491 (w), 1438 (m), 1227 (m), 1183 (s), 1021 (vs), 740 (vs), 654 (vs), 621 (s), 566 (s); ^{1}H NMR (300 MHz, benzene-d_6, 20 °C, TMS): $\delta = 1.28$ (s, 9H, $OC\mathit{Me}_3$), 1.94 (d, 3H, $^{3}J_{HH} = 7.8$ Hz, μ-$CH\mathit{Me}$), 1.98 (s, 30H, $C_5\mathit{Me}_5$), 2.13 (s, 15H, $C_5\mathit{Me}_5$), 6.08 (q, 1H, $^{3}J_{HH} = 7.8$ Hz, μ-$C\mathit{H}Me$); ^{13}C NMR (75 MHz, benzene-d_6, 20 °C, TMS): $\delta = 11.4$, 12.2 (q, $C_5\mathit{Me}_5$), 29.5 (qd, $J_{CH} = 124.6$ Hz, μ-$CH\mathit{Me}$), 32.8 (qm, $J_{CH} = 124.6$ Hz, $OC\mathit{Me}_3$), 119.5, 121.8 (m, C_5Me_5), 207.0 (dq, $J_{CH} = 116.5$ Hz, μ-$\mathit{C}HMe$); EI mass spectrum: *m*/*z* (%) 698 (1) [M$^+$], 641 (6) [M$^+$ − CMe$_3$], 613 (30) [M$^+$ − CMe$_3$ − C$_2$H$_4$]; elemental analysis calcd. (%) for $C_{36}H_{58}O_4Ti_3$ (698.46): C 61.90, H 8.37; found C 61.40, H 7.79.

1 (*a*) R. Andrés, M. Galakhov, M. P. Gómez-Sal, A. Martín, M. Mena and C. Santamaría, *Chem. Eur. J.*, 1998, **4**, 1206–1213; (*b*) R. Andrés, M. V. Galakhov, M. P. Gómez-Sal, A. Martín, M. Mena, M. C. Morales-Varela and C. Santamaría, *Chem. Eur. J.*, 2002, **8**, 805–811.

2 (*a*) G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis*, John Wiley and Sons, New York, 1994, p. 400; (*b*) F. Zaera, *Chem. Rev.*, 1995, **95**, 2651–2693; (*c*) B. E. Bent, *Chem. Rev.*, 1996, **26**, 1361–1390.

3 R. Andrés, M. Galakhov, A. Martín, M. Mena and C. Santamaría, *Organometallics*, 1994, **13**, 2159–2163.

4 Crystal data for **6**: $C_{40}H_{63}CsO_5Ti_3$, $M = 900.51$, orthorhombic, $a = 13.396(5)$, $b = 15.694(5)$, $c = 20.544(5)$ Å, $U = 4319(2)$ Å^3, $T = 200(2)$ K, space group $P2_12_12_1$, $Z = 4$, μ(Mo-Kα) = 1.410 mm^{-1}, 22667 reflections measured, 9605 unique ($R_{\mathrm{int}} = 0.083$) which were used in all calculations. $R_1(F^2) = 0.060$ [for 5699 reflections with $F_o > 4\sigma(F_o)$] and w$R_2 = 0.129$ for all data. Crystal data for **7**: $C_{36}H_{58}O_4Ti_3$, $M = 698.5$, orthorhombic, $a = 17.575(3)$, $b = 22.434(3)$, $c = 38.629(8)$ Å, $U = 15231(5)$ Å^3, $T = 200(2)$ K, space group *Pbca*, $Z = 16$, μ(Mo-Kα) = 0.647 mm^{-1}, 32094 reflections measured, 8704 unique ($R_{\mathrm{int}} = 0.336$) which were used in all calculations. $R_1(F^2) = 0.081$ [for 2653 reflections with $F_o > 4\sigma(F_o)$] and w$R_2 = 0.246$ for all data. CCDC 268264–268265. See http://www.rsc.org/suppdata/cc/b5/b504467g/index.sht for crystallographic data in CIF or other electronic format.

5 U. Englich, K. Hassler, K. Ruhlandt-Senge and F. Uhlig, *Inorg. Chem.*, 1998, **37**, 3532–3537.

6 (*a*) R. E. Dinnebier, F. Olbrich and G. M. Bendele, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1997, **53**, 699–701; (*b*) J. Paap and F. Olbrich, *Private Communication*, CCDC 130236. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

7 (*a*) S. García Blanco, M. P. Gómez-Sal, S. Martínez Carreras, M. Mena, P. Royo and R. Serrano, *J. Chem. Soc., Chem. Commun.*, 1986, 1572–1573; (*b*) A. Abarca, A. Martín, M. Mena and P. R. Raithby, *Inorg. Chem.*, 1995, **34**, 5437–5440; (*c*) R. Andrés, M. Galakhov, M. P. Gómez-Sal, A. Martín, M. Mena and C. Santamaría, *J. Organomet. Chem.*, 1996, **526**, 135–143.