Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information for:

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

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[Li(μ-O)$_3${(TiCp*)$_3$(μ$_3$-CCH$_2$)}] (**2**): 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 ≈60ºC overnight and the red solid formed was filtered, washed with hexane and dried at vacuum 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); 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.

Table 1 NMR data for complexes [M(μ-O)$_3${(TiCp*)$_3$(μ$_3$-CCH$_2$)}] (M = Li **2**, Na **3**, K **4**, Rb **5**, Cs **6**)[a].

Assignment	**2**	**3**	**4**	**5**	**6**
	^{1}H				
$C_5\mathit{Me}_5$	1.88 (s, 45 H)	1.88 (s, 45 H)	1.87 (s, 45 H)	1.87 (s, 45 H)	1.87 (s, 45 H)
μ_3-$\mathrm{C}C\mathit{H}_2$	2.20 (s, 2 H)	2.33 (s, 2 H)	2.21 (s, 2 H)	2.25 (s, 2 H)	2.17 (s, 2 H)
	^{13}C{^{1}H}				
$\mathit{C}_5\mathrm{Me}_5$	114.7	119.3	114.5	119.3	114.4
$\mathrm{C}_5\mathit{Me}_5$	11.5	11.4	11.3	11.4	11.4
μ_3-$\mathrm{C}\mathit{C}\mathrm{H}_2$	76.3[b]	76.8[b]	76.3[b]	76.2[b]	76.1[b]
μ_3-$\mathit{C}\mathrm{CH}_2$	373.1	373.0	370.3	369.8	369.3

[a] Recorded on varian Unity 300 in [D$_8$]THF at 20ºC. [b] Triplet with $J_{C\text{-}H}$ ≈ 148 Hz in ^{13}C NMR.

[Na(μ-O)$_3${(TiCp*)$_3$(μ$_3$-CCH$_2$)}] (**3**): The preparation is analogous to **2** from 0.30 g (0.48 mmol) of **1**, [NaN(SiMe$_3$)$_2$] (88 mg, 0.48 mmol) and hexane (40 mL) to give 0.22 g of **3** (yield: 70%). IR (KBr, cm^{-1}): $\bar{\nu}$ = 2908(vs), 2856(s), 1436(m), 1378(s), 1024(w), 769(vs), 654(vs), 628(s), 573(s); elemental analysis calcd. (%) for $C_{32}H_{47}NaO_3Ti_3$ (646.31): C 59.46, H 7.33; found C 58.87, H 7.61.

[K(μ-O)$_3${(TiCp*)$_3$(μ$_3$-CCH$_2$)}] (**4**): The preparation is similar to that for **2** from 0.30 g (0.48 mmol) of **1** with 96 mg (0.48 mmol) of [KN(SiMe$_3$)$_2$] in hexane (40 mL). (Yield: 0.28 g, 88%). IR (KBr, cm^{-1}): $\bar{\nu}$ = 2909(vs), 2855(s), 1437(m), 1375(m), 1096(m), 1023(s), 791(vs), 767(vs), 714(m), 657(s), 629(s), 384(m); elemental analysis calcd. (%) for $C_{32}H_{47}KO_3Ti_3$ (662.41): C 58.02, H 7.15; found C 57.83, H 7.36.

[Rb(μ-O)$_3${(TiCp*)$_3$(μ$_3$-CCH$_2$)}] (**5**): In a 100 mL Carius tube with valve, 0.50 g (0.80 mmol) of [{TiCp*(μ-O)}$_3$(μ$_3$-CMe)] (**1**), 0.20 g (0.80 mmol) of [RbN(SiMe$_3$)$_2$] and 40 ml of THF were added. The reaction mixture was stirred overnight at room temperature. After that, the red solution was filtered, and the solvent was removed under vacuum to afford 0.48 g of **5** (yield: 84%). IR (KBr, cm^{-1}): $\bar{\nu}$ = 2906(vs), 2855(s), 1432(m), 1375(s), 1023(w), 774(w), 658(vs), 630(s), 585(m), 436(m), 383(m); elemental analysis calcd. (%) for $C_{32}H_{47}RbO_3Ti_3$ (708.776): C 54.22, H 6.68; found C 53.08, H 6.69.

[Cs(μ-O)$_3${(TiCp*)$_3$(μ_3-CCH$_2$)}] (**6**): It was prepared in a similar way to the preparation of **5** from 0.50 g (0.80 mmol) of **1**, 0.24 g (0.80 mmol) of [CsN(SiMe$_3$)$_2$] and 40 ml of THF. (Yield: 0.47 g, 78%). IR (KBr, cm^{-1}): $\bar{\nu}$ = 2908(s), 2856(s), 1435(m), 1374(m), 1024(w), 789(vs), 711(s), 658(s), 625(m), 402(m); elemental analysis calcd. (%) for $C_{32}H_{47}CsO_3Ti_3$ (756.21): C 50.82, H 6.26; found C 50.83, H 6.47.

[{TiCp*(μ-O)}$_3$(μ-CHMe)(OCMe$_3$)] (**7**): *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, [D$_6$]benzene, 20ºC, TMS): δ = 1.28 (s, 9H, OC*Me*$_3$), 1.94 (d, 3H, $^3J_{HH}$ = 7.8 Hz, μ-CH*Me*), 1.98 (s, 30H, C$_5$*Me*$_5$), 2.13 (s, 15H, C$_5$*Me*$_5$), 6.08 (q, 1H, $^3J_{HH}$ = 7.8 Hz, μ-C*H*Me); ^{13}C NMR (75 MHz, [D$_6$]benzene, 20ºC, TMS): δ = 11.4, 12.2 (q, C$_5$*Me*$_5$), 29.5 (qd, J_{CH} = 124.6 Hz, μ-CH*Me*), 32.8 (qm, J_{CH} = 124.6 Hz, OC*Me*$_3$), 119.5, 121.8 (m, *C*$_5$Me$_5$), 207.0 (dq, J_{CH} = 116.5 Hz, μ-*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.

[{TiCp*(μ-O)}$_3$(μ-CHMe)(OCPh$_3$)] (**8**): The preparation is similar to that of **7** from 0.10 g (0.16 mmol) of **1**, 42 mg (0.16 mmol) of Ph$_3$COH and 50 mL of hexane. (Yield: 88 mg, 62%). IR (KBr, cm^{-1}): $\bar{\nu}$ = 2904(s), 1489(m), 1445(s), 1374(m), 1227(m), 1156(m), 1088(m), 1058(vs), 1028(s) 812(vs), 743(vs), 656(vs); ^{1}H NMR (300 MHz, [D$_6$]benzene, 20ºC, TMS): δ= 1.91 (s, 15H, C$_5$*Me*$_5$), 1.92 (s, 30H, C$_5$*Me*$_5$), 1.97 (d, 3H, $^3J_{HH}$ = 7.8 Hz, μ-CH*Me*), 5.96 (q, 1H, $^3J_{HH}$ = 7.8 Hz, μ-C*H*Me), 6.9-7.7 (m, 15H, OC*Ph*$_3$); ^{13}C NMR (75 MHz, [D$_6$]benzene, 20ºC, TMS): δ= 11.4, 12.4 (q, J_{CH} = 124.9 Hz, C$_5$*Me*$_5$), 28.9 (qd, J_{CH} = 123.5 Hz, μ-CH*Me*), 93.6 (s, O*C*Ph$_3$), 119.9, 123.1 (m, *C*$_5$Me$_5$), 126.6, 127.3, 129.2, 147.7 (OC*Ph*$_3$), 203.7 (dq, J_{CH} = 112.7 Hz, μ-*C*HMe); EI mass spectrum: *m/z* (%) 721 (1) [M$^+$- Cp*-C$_2$H$_4$], 641 (1) [M$^+$-CPh$_3$], 613 (8) [M$^+$-CPh$_3$-C$_2$H$_4$]; elemental analysis calcd. (%) for $C_{51}H_{64}O_4Ti_3$ (884.66): C 69.24, H 7.29; found C 67.90, H 7.13. Several attempts to improve the elemental analysis were failed.

X-Ray structure determination of 6. Single crystals of **6** were obtained from a tetrahydrofurane/toluene solution. The crystals were removed from the Schlenk 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 200K on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit. The same treatment was also applied to crystals of **7** once they were obtained.

Crystallographic data for all the complexes are presented in Table 2. The structures were solved, using the WINGX package,[1] by direct methods (SIR-97)[2] and refined by least-squares against F^2 (SHELXL-97).[3]

All non-hydrogen atoms of **6** were refined anisotropically. All the hydrogen atoms were positioned geometrically and refined by using a riding model except those attached to C(2) which were located in the difference Fourier map and refined isotropically.

X-Ray structure determination of 7. Crystals of **7** were grown by slow evaporation at room temperature of a n-hexane solution. Several attempts were made to get single crystals of complex **7**. The high solubility in hexane made very hard the task and once obtained they showed poor quality. During the first diffraction experiments all of them showed contribution of two different unit cells; the interest of the compound and the impossibility of getting better crystals prompted us to perform the data collection. The COLLECT[4] program was used to establish the strategy and the EvalCCD[5] program to carry out the data reduction removing the contribution of the secondary unit cell. Certainly, this process led to work with a very limited number of reflections. Further, two independent molecules of complex **7** crystallized in the orthorhombic space group P*bca*. All the non-hydrogen atoms of **7** were anisotropically refined. All the hydrogen atoms of **7** were positioned geometrically and refined by using a riding model.

Table 2.- Crystallographic data for complexes **6** and **7**.

Compound	**6**	**7**
Empirical formula	$C_{40}H_{63}CsO_5Ti_3$	$C_{36}H_{58}O_4Ti_3$
Formula weight	900.51	698.5
Temperature	200(2) K	
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	*Pbca*
a(Å)	13.396(5)	17.575(3)
b(Å)	15.694(5)	22.434(3)
c(Å)	20.544(5)	38.629(8)
Volume (Å^3)	4319(2)	15231(5)
Z	4	16
Density (calculated) (Mg m^{-3})	1.385	1.219
Absorption coefficient (mm^{-1})	1.410	0.647
F(000)	1856	5952
Crystal size	0.499 × 0.234 × 0.197 mm^3	0.15 × 0.13 × 0.12 mm^3
Theta range for data collection	3.04 to 27.50°	5.01 to 22.01°
Index ranges	$-17<=h<=16$, $-20<=k<=20$, $-25<=l<=18$	$-18<=h<=17$, $-23<=k<=16$, $-40<=l<=40$
Reflections collected	22667	32094
Independent reflections	9605 [*R*(int) = 0.083]	8704 [*R*(int) = 0.336]
Completeness to theta	98.4%	93.1%
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9605 / 0 / 451	8704 / 0 / 775
Goodness-of-fit on F^2	1.070	0.750
Final *R* indices [$I>2\sigma(I)$]	$R_1 = 0.060$, $wR_2 = 0.099$	$R_1 = 0.081$, $wR_2 = 0.169$
R indices (all data)	$R_1 = 0.145$, $wR_2 = 0.129$	$R_1 = 0.268$, $wR_2 = 0.246$
Largest diff. peak and hole (e.Å^{-3})	0.689 and -0.721 e.Å^{-3}	0.441 and -0.395 e.Å^{-3}
Absolute structure parameter	0.20(3)	--

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