Reaction of ketones with the organotitanium oxide [{TiCp*(μ-O)}$_3$(μ$_3$-CMe)] *via* the hydride–vinylidene [{TiCp*(μ-O)}$_3$(μ-C=CH$_2$)(H)] intermediate‡

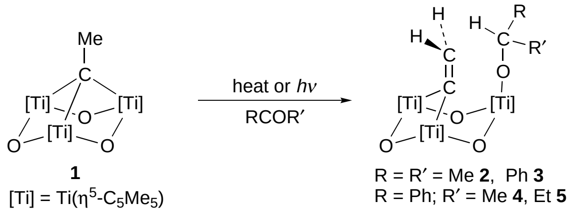
Mikhail Galakhov, Miguel Mena*† and Cristina Santamaría

Departamento de Química Inorgánica de la Universidad de Alcalá, E-22871 Alcalá de Henares, Madrid, Spain

Thermal and/or photochemical treatment of [{TiCp*(μ-O)}$_3$(μ$_3$-CMe)] 1 (Cp* ≡ η^5-C$_5$Me$_5$) with organic ketones affords the new oxo derivatives [{TiCp*(μ-O)}$_3$(μ-C=CH$_2$)(OCHRR′)] (R = R′ = Me 2, Ph 3; R = Ph, R′ = Me 4, Et 5); these reactions take place by insertion of the ketones CO group into the Ti–H bond of the *in situ* formed [{TiCp*(μ-O)}$_3$(μ-CCH$_2$)(H)] intermediate.

We have reported the unprecedented oxotitanium complexes, [{TiCp*(μ-O)}$_3$(μ$_3$-CR)] (R = H, Me),[1] possessing a μ$_3$-alkylidyne sp^3-carbon similar to that found for the early-transition-metal clusters [M$_3$(μ$_3$-CR′)(OR)$_9$] (M = Mo, W)[2] and in contrast with the sp-hybridized alkylidyne carbon of the species as [Co$_3$(μ$_3$-CR)(CO)$_9$].[3] The chemistry of these μ$_3$-alkylidynetrimetal clusters have been extensively explored.[3a,4] Meanwhile, to our knowledge, the [{CrCp(μ-Cl)}$_3$(μ$_3$-CH)],[5] [{TiCp*(μ-O)}$_3$(μ$_3$-CR)][1] and [{TiCp*}$_4$(μ$_3$-CH)$_4$][6] complexes are the only reported examples of μ$_3$-alkylidyne units supported on trinuclear cores without metal–metal bonds and their reactivity is, as yet, practically unknown.[7] This chemistry might be of great current interest, imitating the behaviour of the alkylidyne groups attached to metal or metal oxide surfaces and establishing a clear connection between organometallic and solid surface systems.[8] Here, we report the surprising reactivity of diverse ketones and the μ$_3$-ethylidyne group on an organotitanium oxide.

Treatment of [{TiCp*(μ-O)}$_3$(μ$_3$-CMe)] **1** with 1 equiv. of RCOR′ (R = R′ = Me, Ph; R = Ph, R′ = Me, Et) in toluene or hexane, heating at temperatures between 100 and 120 °C or irradiating with a sunlamp for several days, leads to the formation (46–77% yield) of blue–violet complexes characterised as [{TiCp*(μ-O)}$_3$(μ-CCH$_2$)(OCHRR′)] (R = R′ = Me **2**, Ph **3**; R = Ph, R′ = Me **4**, Et **5** (Scheme 1).§



Scheme 1

The IR spectra of these complexes show a weak band at 1580 (**2**) and 1598 cm^{-1} (**3**, **4**, **5**) assigned to the ν(C=C) of the μ-vinylidene moiety, as in the case of the bimetallic systems [Ru$_2$(CO)$_3$Cp$_2$(μ-C=CH$_2$)] (1586 cm^{-1})[9] and [ClNi(μ-dppm)$_2$(μ-C=CH$_2$)NiCl] (1580 cm^{-1}).[10] The NMR spectra (Table 1) are consistent with the proposed structure and reveal the presence of the characteristic signals for μ-vinylidene, alkoxide and Cp* ligands.

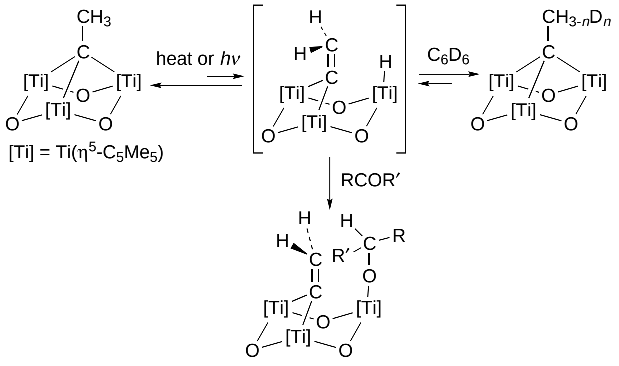
The ^{13}C NMR spectra of **2**–**5** reveal triplets at δ_{av} 317.5 (^2J 5 Hz) attributed to the C$_\alpha$ resonance of the bridging vinylidene fragment $>$C$_\alpha$=C$_\beta$H$_2$, which are very similar to those found for other known vinylidene complexes.[11] The terminal moiety (=C$_\beta$H$_2$) of this fragment appear, in both ^{1}H and ^{13}C NMR spectra, in the typical range for organic alkenes. The NMR spectra also display the clear presence of the OC*H*RR′ signals whose chemical shifts and multiplicity depend on the nature of the ketone substituents (Table 1) and the values of $^1J_{CH} \approx 142$ Hz are according to the proximity of the oxygen atom. Additionally, the NMR spectra of **4** and **5** show signals for three different Cp* ligands in 1 : 1 : 1 ratio and AB spin systems for the vinylidene protons due to the chiral carbon atoms of the alkoxy groups.

A plausible pathway for these reactions involves initial β-hydrogen elimination in the μ$_3$-ethylidyne ligand to generate the intermediate [{TiCp*(μ-O)}$_3$(μ-CCH$_2$)(H)]. Similar conversion of μ$_3$-alkylidyne complexes to vinylidenes has been found for many trinuclear clusters[11a] and may be responsible of the H/D exchange reactions in ethylidynes on metal surfaces.[8a,c] Interestingly, we have also observed that the complex **1** incorporate deuterium in the μ$_3$-ethylidyne group when a C$_6$D$_6$ solution of **1** is heated above 200 °C,¶ and this H/D exchange is easy to explain if we assume the participation of the above mentioned hydride intermediate.[12] Finally the insertion of the ketones into the Ti–H bond of [{TiCp*(μ-O)}$_3$(μ-CCH$_2$)(H)] takes place (Scheme 2).[13]

Table 1 Selected NMR data (δ, J/Hz) for complexes [{TiCp*(μ-O)}$_3$(μ-CCH$_2$)(OCHRR′)] (R = R′ = Me **2**, Ph **3**; R = Ph, R′ = Me **4**, Et **5**)[a]

	^{1}H				^{13}C			
Assignment	**2**	**3**	**4**	**5**	**2**	**3**	**4**	**5**
C$_5$*Me*$_5$	2.11 (s, 15 H) 1.99 (s, 30 H)	2.03 (s, 15 H) 1.97 (s, 30 H)	2.07 (s, 15 H), 2.03 (s, 15 H), 1.97 (s, 15 H)	2.05 (s, 15 H), 2.04 (s, 15 H), 1.97 (s, 15 H)	11.7, 11.4	11.9, 11.7	11.6, 11.7, 11.9	11.6, 11.7, 11.8
C$_5$Me$_5$					120.4, 122.3	120.7, 123.1	120.6, 122.6 125.7	120.5, 122.6, 126.0
μ-C=*CH*$_2$	6.04 (s, 2 H)	5.78 (s, 2 H)	5.93$_{av}$ (2 H, ^2J 4.5)	5.97$_{av}$ (2 H, ^2J 4.8)	120.9 (t, ^1J 154.9)	122.0 (t, ^1J 155.6)	121.6 (t, ^1J 155.4)	121.1 (t, ^1J 154.8)
μ-*C*=CH$_2$					317.3 (t, ^2J 5.2)	317.2 (t, ^2J 5.7)	317.5 (t, ^2J 4.8)	318.0 (t, ^2J 4.9)
–OC*H*RR′	4.80 (spt, 1 H, ^3J 6.0)	6.80 (s, 1 H)	5.78 (q, 1 H, ^3J 6.6)	5.46 (dd, 1 H, ^3J 4.5, 8.4)	74.9 (dm, ^1J 140.9)	85.3 (dm, ^1J 141.4)	79.5 (dm, ^1J 144.2)	85.5 (dm, ^1J 140.2)

[a] Recorded on Varian Unity 300 or 500 Plus in C$_6$D$_6$ at 20 °C.



Scheme 2

Thus the incorporation of the ketones onto the organometallic titanium oxide $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}CMe)]$ can be best interpreted in terms of an insertion process of the carbonyl groups into a Ti–H bond of the hydride–vinylidene species $[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}CCH_2)(H)]$. Further studies are required in order to determine the behaviour of other carbonyl derivatives and unsaturated molecules against these μ_3-alkylidyne complexes.

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Notes and References

† E-mail: mmena@inorg.alcala.es

‡ Dedicated to Professor Pascual Royo on the occasion of his 60th birthday.

§ *Preparations*: **2**: a solution of **1** (0.50 g, 0.80 mmol) and acetone (0.06 ml, 2.40 mmol) in toluene (50 ml) were transferred by cannula to a Carius tube (volume 100 ml), cooled to −78 °C, and flame-sealed. This tube was heated at 100 °C for 12 h to obtain a blue–violet lather (0.42 g, 77%). EI mass spectrum: *m*/*z* 624 ($M^+ - MeCOMe$, 9%), 613 ($M^+ - MeCHMe - C_2H_2$, 25%). **3**: this derivative was obtained analogously to **2** from 0.80 g (1.28 mmol) of **1** and 0.23 g (1.28 mmol) of benzophenone heating at 125 °C for 24 h to obtain a blue–violet crystalline solid (0.73 g, 71%). EI mass spectrum: *m*/*z* 624 ($M^+ - PhCOPh$, 6%), 613 ($M^+ - PhCHPh - C_2H_2$, 28%). **4**: acetophenone (0.16 ml, 1.33 mmol) diluted in 15 ml of hexane was added to a solution of **1** (0.80 g, 1.28 mmol) in hexane (100 ml). The reaction mixture was irradiated at room temp. for 45 h with a sunlamp. The solution was concentrated and a crystalline blue solid was obtained at room temp. (0.50 g, 52%). EI mass spectrum: *m*/*z* 624 ($M^+ - PhCOMe$, < 1%), 613 ($M^+ - PhCHMe - C_2H_2$, 3%). **5**: the preparation of this complex is similar to **4** from 0.80 g (1.28 mmol) of **1** and 0.17 ml (1.33 mmol) of ethyl phenyl ketone irradiating for 68 h with a sunlamp; 0.44 g (46%) of a blue solid was obtained. EI mass spectrum: *m*/*z* 624 ($M^+ - PhCOEt$, 5%), 613 ($M^+ - PhCHEt - C_2H_2$, < 1%).

Full NMR and analytical data for the new compounds **2**–**5** can be acquired as supplementary material upon request from the authors.

¶ In the ^1H NMR spectra we have detected the presence of μ_3-CCH_2D and μ_3-$CCHD_2$ isotopomers.

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