# Reactivity of $\mu_3$-Alkylidyne Groups on an Organotitanium Oxide: Insertion of Isocyanides and Carbon Monoxide into the Complexes $[\{\mathrm{TiCp^*}(\mu\text{-O})\}_3(\mu_3\text{-CR})]$ (R = H, Me)

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

**Abstract:** *tert*-Butyl isocyanide reacts with the $\mu_3$-alkylidyne complex $[\{\mathrm{TiCp^*}(\mu\text{-O})\}_3(\mu_3\text{-CH})]$ (**1**, $\mathrm{Cp^*} = \eta^5\text{-C}_5\mathrm{Me}_5$) to give a single insertion into a $\mu_3$-carbon–titanium bond and the formation of the new derivative $[\{\mathrm{TiCp^*}(\mu\text{-O})\}_3(\mu_3\text{-}\eta^2\text{-HCCN}t\mathrm{Bu})]$ (**3**). Similar reactions of $2,6\text{-Me}_2\mathrm{C}_6\mathrm{H}_3\mathrm{NC}$ and $2,4,6\text{-Me}_3\mathrm{C}_6\mathrm{H}_2\mathrm{NC}$ with the complexes $[\{\mathrm{TiCp^*}(\mu\text{-O})\}_3(\mu_3\text{-CR})]$ (R = H (**1**), Me (**2**)) in a 1:2 molar ratio at room temperature lead to the double insertion compounds $[\{\mathrm{TiCp^*}(\mu\text{-O})\}_3\{\mu_3\text{-}\eta^4\text{-RC(CNAr)}_2\}]$ (R = H, Ar = $2,6\text{-Me}_2\mathrm{C}_6\mathrm{H}_3$ (**6**), $2,4,6\text{-Me}_3\mathrm{C}_6\mathrm{H}_2$ (**7**); R = Me, Ar = $2,6\text{-Me}_2\mathrm{C}_6\mathrm{H}_3$ (**8**), $2,4,6\text{-Me}_3\mathrm{C}_6\mathrm{H}_2$ (**9**)). Curiously, when the reactions with $2,6\text{-Me}_2\mathrm{C}_6\mathrm{H}_3\mathrm{NC}$ are carried out in a 1:1 molar ratio, diinsertion products **6** or **8**, and unchanged $\mu_3$-alkylidyne complex **1** or **2**, respectively, are detected. From the mixture of **6** and **1** the monoinsertion product $[\{\mathrm{TiCp^*}(\mu\text{-O})\}_3\{\mu_3\text{-}\eta^2\text{-HCCN}(2,6\text{-Me}_2\mathrm{C}_6\mathrm{H}_3)\}]$ (**10**) is formed slowly at room temperature. However, it is necessary to heat the mixture of **8** and **2** at 130 °C for five days to observe some evolution; this finally leads to the zwitterionic compound $[\{\mathrm{TiCp^*}(\mu\text{-O})\}_3\{\mu_3\text{-}\eta^2\text{-}\overset{-}{\mathrm{C}}\mathrm{C(Me)}\overset{+}{\mathrm{N}}(2,6\text{-Me}_2\mathrm{C}_6\mathrm{H}_3)\}]$ (**11**). Complex **1** also reacts with excess carbon monoxide at room temperature to produce only compound $[\{\mathrm{TiCp^*}(\mu\text{-O})\}_3]_2(\mu_6\text{-L})]$ ($\mathrm{L} = \mathrm{C}_6\mathrm{H}_2\mathrm{O}_4$) (**5**), in which the organic ligand L connects two $\mathrm{Ti}_3\mathrm{O}_3$ cores. The molecular structures of complexes **9** and **11** have been determined by X-ray diffraction analyses.

**Keywords:** alkylidyne complexes · cyclopentadienes · insertions · structure elucidation · titanium

## Introduction

A few years ago we reported a new class of oxotitanium complexes, $[\{\mathrm{TiCp^*}(\mu\text{-O})\}_3(\mu_3\text{-CR})]$ (R = H, Me), which contain a tetrahedral $\mathrm{Ti}_3\mathrm{CR}$ unit supported by oxygen atoms and pentamethylcyclopentadienyl (Cp*) ligands. The X-ray crystallographic studies of these complexes suggested that the apical carbon atom may be regarded as a saturated $\mathrm{sp}^3$ alkylidyne carbon.[1] This point of view is similar to that proposed by Chisholm et al.[2] for the early transition metal clusters $[\mathrm{M}_3(\mu_3\text{–CR}')(\mathrm{OR})_9]$ (M = Mo, W) as an alternative description of the sp-hybridized alkylidyne carbon of species such as the $[\mathrm{Co}_3(\mu_3\text{-CR})(\mathrm{CO})_9]$-type derivatives studied by Seyferth, Hoffmann, Hall, and co-workers.[3]

Interestingly, the $\mu_3$-alkylidyne, and in particular the $\mu_3$-ethylidyne groups, are not exclusive to polynuclear organometallic complexes; they have also been identified on numerous metal surfaces, thus providing evidence of a close relationship between organometallic and solid surface systems.[4, 5]

The chemistry of the $\mu_3$-alkylidynetrimetal clusters has been extensively explored.[3a, 6] Meanwhile, to our knowledge, the $[\{\mathrm{CrCp}(\mu\text{-Cl})\}_3(\mu_3\text{-CH})]$[7] ($\mathrm{Cp} = \eta^5\text{-C}_5\mathrm{H}_5$), $[\{\mathrm{TiCp^*}(\mu\text{-O})\}_3(\mu_3\text{-CR})]$[1] and $[\{\mathrm{TiCp^*}\}_4(\mu_3\text{-CH})_4]$[8] complexes are the only reported examples of $\mu_3$-alkylidyne units supported on trinuclear cores without metal–metal bonds, and their reactivity is as yet practically unknown.[9]

The facile and high-yield synthesis of these $[\{\mathrm{TiCp^*}(\mu\text{-O})\}_3(\mu_3\text{–CR})]$ complexes provide us with the opportunity to investigate the chemistry of these $\mathrm{d}^0$ $\mu_3$-alkylidyne compounds. This chemistry might be different to that of mononuclear hydrocarbyl complexes which contain metals in the highest oxidation state, as there may be cooperative effects between the metal centres and it may imitate the behaviour of the alkylidyne groups attached to metal or metal oxide surfaces. Here we report on the reactions of $[\{\mathrm{TiCp^*}(\mu\text{-O})\}_3(\mu_3\text{-CR})]$ (R = H, Me) with isocyanides and the isoelectronic carbon monoxide that give products derived from the insertion into titanium–carbon(alkylidyne) bonds.

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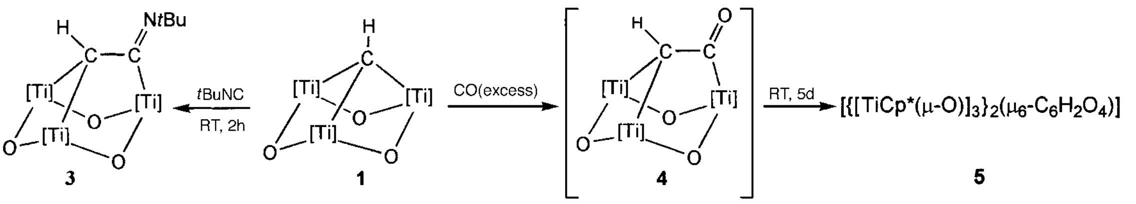


Scheme 1. Reactivity of complex **1** with *t*BuNC and CO. [Ti] = Ti($\eta^5$-$C_5Me_5$).

Table 1. Selected NMR data for complexes **3** and **4** in [D$_6$]benzene at 25 °C.[a]

| Assignment | 3 | | 4 | |
|---|---|---|---|---|
| | $\delta(^1H)$ | $\delta(^{13}C)$ | $\delta(^1H)$ | $\delta(^{13}C)$ |
| $C_5Me_5$ | 2.16, 1.94 | 12.1, 11.6 | 2.01, 2.12 | 12.4, 11.5 |
| $C_5$Me$_5$ | | 120.1, 120.2 | | 121.6,123.2 |
| *HC*–C=X | 8.40 | 176.5<br>$^1J_{C,H}$ = 160.5 Hz<br>$^1J_{C,C}$ = 25.7 Hz | 8.52 | 169.5<br>$^1J_{C,H}$ = 163.2 Hz<br>$^1J_{C,C}$ = 28.0 Hz |
| HC–*C*=X | | 201.7 | | 216.2 |
| $Me_3C$ | 1.17 | 62.4, 30.8 | | |

[a] Compounds labelled with $^{13}C$ (see the Experimental Section) were used.

## Results and Discussion

Reaction of a brownish orange solution of [{TiCp*($\mu$-O)}$_3$($\mu_3$-CH)] (**1**) in toluene with one equivalent of *t*BuNC at room temperature led to a dark brown complex characterized as the monoinserted product [{TiCp*($\mu$-O)}$_3$($\mu_3$-$\eta^2$-HCCN*t*Bu)] (**3**) (Scheme 1). Only monoinsertion takes place, even if two or three equivalents of *t*BuNC are used under the same experimental conditions, or the mixture is heated at 130 °C overnight.

$\mu_3$-Methylidyne **1** reacts slowly (two days in a NMR tube) with carbon monoxide to give, as the first product, the monoinsertion complex [{TiCp*($\mu$-O)}$_3$($\mu_3$-$\eta^2$-HCCO)] (**4**), analogous to **3** (see Scheme 1).

The NMR data for **3** and **4** (Table 1) are in agreement with the proposed structures for a single insertion of *t*BuNC or CO into one of the three Ti–CH(methylidyne) bonds of **1**. The $^{13}C$ NMR spectra show typical values for direct $^{13}C(sp^3)$–$^{13}C(sp^2)$[10] coupling constants, and shifts to higher field for the ≡*C*H carbon signals with respect to the starting $\mu_3$-methylidyne complex **1**: $\Delta\delta = \delta(\mathbf{1}) - \delta(\mathbf{3}) = 207.3$ ppm and $\Delta\delta = \delta(\mathbf{1}) - \delta(\mathbf{4}) = 214.3$ ppm. These strong displacements are essentially induced by the change in the coordination mode of the carbon atom from $\mu_3$ to $\mu_2$, similar to that reported for the reactions of **1** with [CpM(CO)$_3$H] (M = Mo, W) to give [Ti$_3$Cp*$_3$($\mu$-O)$_3$($\mu_2$-*C*H$_2$)][($\mu$-OC)M(CO)$_2$Cp] ($\Delta\delta$ = 185.1 ppm).[1b] We have also observed a doublet at $\delta$ = 201.7 (**3**) and 216.2 (**4**) corresponding to the iminoacyl and acyl carbons, respectively (C=X, X = N*t*Bu, O). The IR spectrum of **3** contains a band at $\tilde{\nu} = 1559\ cm^{-1}$ due to the C=N stretching of an iminoacyl moiety bonded to a d$^0$ early transition metal.[11]

The reaction of **4** with excess carbon monoxide at room temperature leads to the formation of [{[TiCp*($\mu$-O)]$_3$}$_2$($\mu_6$-$C_6H_2O_4$)] (**5**) in high yield, and is independent of the solvent used (benzene, hexane, toluene, THF). The NMR data for **5** (Table 2) are consistent with the presence of two organometallic units {TiCp*($\mu$-O)}$_3$, with six inequivalent Cp* ligands, connected through an organic fragment formed by a combination of four CO molecules and two CH groups. The proposed bonding in **5** is depicted in Figure 1. Unfortunately, all attempts to obtain crystals suitable for X-ray diffraction studies for the confirmation of this proposed structure have been unsuccessful.

Table 2. Selected NMR data for [{[TiCp*($\mu$–O)]$_3$}$_2$($\mu_6$–$C_6H_2O_4$)] (**5**) in [D$_6$]benzene at 25 °C.[a]

| $\delta(^1H)$ | $\delta(^{13}C)$ |
|---|---|
| 2.30, 2.25, 2.18, 2.14, 1.93, 1.81 (s, $C_5Me_5$) 6.37, 5.27 (AB spin system, $^3J$ = 4.5 Hz, C*H*) | 126.0, 123.9, 122.8, 122.1, 120.4, 120.3 (*C*$_5$Me$_5$), 13.6, 12.2, 12.1, 12.0, 11.8, 11.7 ($C_5Me_5$), 115.1 ($^1J$ = 172.9 Hz), 105.9 ($^1J$ = 176.6 Hz) (*C*H), 291.1 (C$_6$), 156.5 (C$_5$), 150.3 (C$_4$), 105.8 (C$_3$) |

spin-spin coupling constants (Hz)

| | | | |
|---|---|---|---|
| C$_1$–C$_2$ ($^1J$) | 48.3 | C$_3$–C$_5$ ($^2J$) | 18.4 |
| C$_1$–C$_5$ ($^1J$) | 52.7 | C$_3$–C$_6$ ($^1J$) | 35.0 |
| C$_2$–C$_3$ ($^1J$) | 45.2 | C$_4$–C$_5$ ($^1J$) | 69.4 |
| C$_3$–C$_4$ ($^1J$) | 52.8 | | |

[a] Compounds labelled with $^{13}C$ (see the Experimental Section) were used.

**Abstract in Spanish:** *El complejo metilidino* **1** *reacciona con tert-butil isocianuro para dar la inserción de una molécula de isocianuro en uno de los tres enlaces Ti–C del grupo metilidino y formación del complejo [{TiCp*(μ-O)}$_3$($\mu_3$-$\eta^2$-HCCNtBu)]* (**3**)*, mientras que el complejo etilidino* **2***, en las mismas condiciones experimentales, no conduce a reacción alguna. El tratamiento a temperatura ambiente de ambos complejos alquilidino con los isocianuros aromáticos 2,6-$Me_2C_6H_3NC$ y 2,4,6-$Me_3C_6H_2NC$, en proporción 1:2, permite preparar los complejos de diinserción, [{TiCp*(μ-O)}$_3${$\mu_3$-$\eta^4$-RC(CNAr)$_2$}] (R = H, Ar = 2,6-$Me_2C_6H_3$* (**6**)*, 2,4,6-$Me_3C_6H_2$* (**7**)*; R = Me, Ar = 2,6-$Me_2C_6H_3$* (**8**)*, 2,4,6-$Me_3C_6H_2$* (**9**)*), tanto en tubo de RMN como a escala preparativa. Cuando la reacción se realiza en proporción 1:1 a temperatura ambiente, se pueden detectar los alquilidinos de partida* **1** *ó* **2** *y los complejos de diinserción* **6** *u* **8** *respectivamente. En el caso de la mezcla de* **1** *y* **6***, el producto de monoinserción, [{TiCp* (μ-O)}$_3${$\mu_3$-$\eta^2$-HCCN(2,6-$Me_2C_6H_3$)}]* (**10**)*, se forma lenta y gradualmente a temperatura ambiente, mientras que con la mezcla de la especie etilidino y* **8** *es preciso calentar a 130 °C durante 5 días para obtener el producto zwitteriónico [{TiCp*(μ-O)}$_3${$\mu_3$-$\eta^2$-$\underset{-}{C}C(Me)\underset{+}{N}$(2,6-$Me_2C_6H_3$)}]* (**11**)*. El complejo metilidino* **1** *también reacciona con un exceso de CO para dar el compuesto [{TiCp*(μ-O)}$_3$]$_2$($\mu_6$-L)] (L = $C_6H_2O_4$)* (**5**) *en el que el ligando orgánico L conecta dos unidades $Ti_3O_3$. Las estructuras moleculares de* **9** *y* **11** *han sido determinadas por estudios de difracción de rayos-X.*

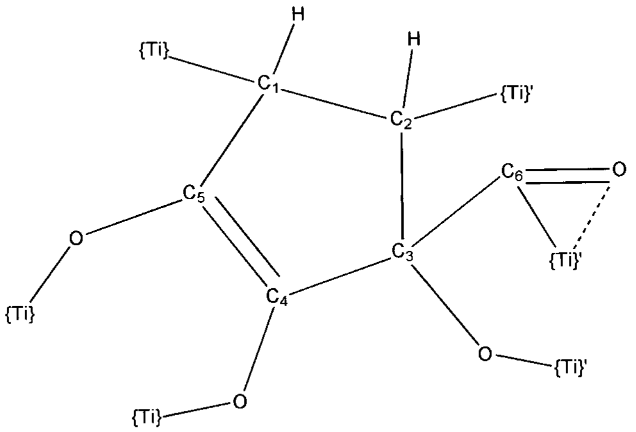


Figure 1. Structural proposal for compound **5**. {Ti} = TiCp*($\mu$-O).

In contrast with the behaviour found for **1**, *t*BuNC did not react with the $\mu_3$-ethylidyne complex [{TiCp*($\mu$-O)}$_3$($\mu_3$-CMe)] (**2**), and carbonylation led only to unidentified products.

Complexes **1** and **2** were then treated with aromatic isocyanides, ArNC (Ar = 2,6-Me$_2$C$_6$H$_3$, 2,4,6-Me$_3$C$_6$H$_2$), in 1:1, 1:2 and 1:3 molar ratios under various conditions (Scheme 2).

Treatment of **1** and **2** with both isocyanides in 1:2 molar ratio at room temperature gave orange solutions from which the products [{TiCp*($\mu$-O)}$_3${$\mu_3$-$\eta^4$-RC(CNAr)$_2$}] (**6**–**9**) were isolated in 75–90% yield as orange microcrystalline solids (see Scheme 2). They arise from the insertion of two isocyanide molecules into the titanium–alkylidyne group connectivity.

The analogous reaction with excess isocyanide did not lead to the triinsertion product, instead, only the diinsertion reaction occurred. Furthermore, we have observed that the addition of a different isocyanide to a [D$_6$]benzene solution of **6**–**9** gave rise to deinsertion and consequently a mixture of diinsertion products was detected by NMR spectroscopy.[12] It should be noted that deinsertion of CO from acyl complexes is a well-known reaction,[11a] while the analogous process in iminoacyl compounds is not so frequent.[13]

*Molecular structure of complex **9***: Complex **9** crystallised from a diluted hexane solution at 4 °C and was characterised in the solid state by an X-ray diffraction study. The molecular structure and atom-labelling scheme of **9** are shown in Figure 2 and the relevant geometrical parameters are summarised in Table 3.

Complex **9** has a crystallographic plane of symmetry which contains Ti1, O11, C2, C3 and which bisects a Cp* ring. The structure of this compound may be considered as an organic fragment, comprising N1, C1, C2, C3, C1a and N1a, supported on the organometallic oxide Cp$^*_3$Ti$_3$O$_3$. The C1–C2 distance of 1.390(12) Å is intermediate between a single (sp$^3$–sp$^2$, 1.50 Å) and a double bond (sp$^2$–sp$^2$, 1.34 Å).[14] The N1–C31 bond length of 1.465(13) Å is clearly longer than a C–N bond

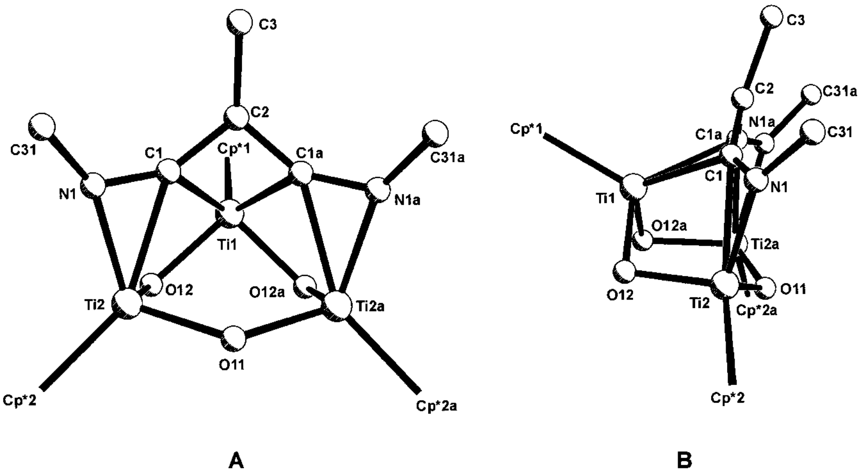
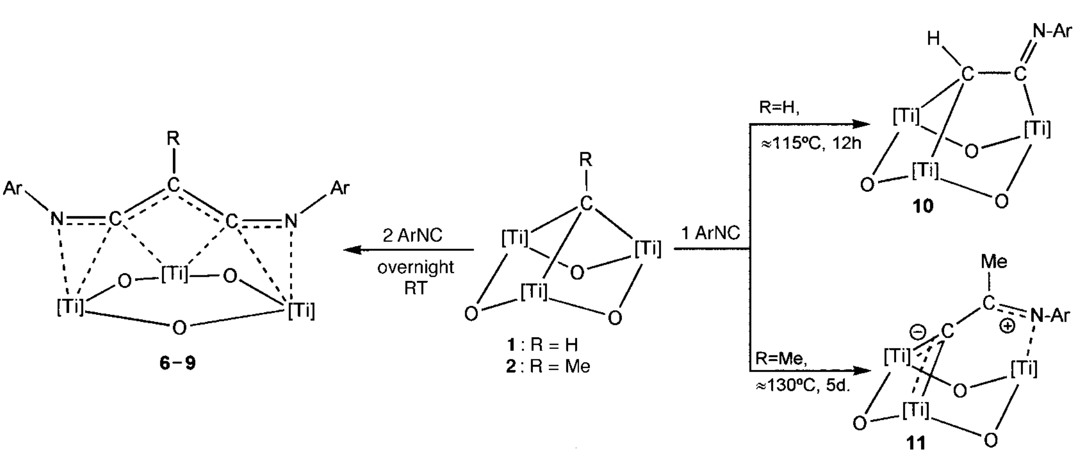


Figure 2. Front (A) and side (B) view of molecular structure of **9**. $\eta^5$–C$_5$Me$_5$ and 2,4,6-Me$_3$C$_6$H$_2$ groups are omitted for clarity. Cp* are the centroids of the corresponding C$_5$Me$_5$ rings. C31 and C31a are the *ipso*-carbon atoms of the 2,4,6-Me$_3$C$_6$H$_2$ groups.



Scheme 2. Reactivity of complexes **1** (R = H) and **2** (R = Me) with ArNC (Ar = 2,6-Me$_2$C$_6$H$_3$, 2,4,6-Me$_3$C$_6$H$_2$). [Ti] = Ti($\eta^5$-C$_5$Me$_5$). **6**: R = H, Ar = 2,6-Me$_2$C$_6$H$_3$; **7**: R = H, Ar = 2,4,6-Me$_3$C$_6$H$_2$; **8**: R = Me, Ar = 2,6-Me$_2$C$_6$H$_3$; **9**: R = Me, Ar = 2,4,6-Me$_3$C$_6$H$_2$; **10**, **11**: Ar = 2,6-Me$_2$C$_6$H$_3$.

Table 3. Selected bond lengths [Å] and angles [°] for **9**. Cp* are the centroids of the $C_5Me_5$ rings.

| | | | |
|---|---|---|---|
| Ti1–O12 | 1.851(6) | Ti1–C1 | 2.273(10) |
| Ti1–C2 | 2.577(14) | Ti1 ··· Ti2 | 2.834(2) |
| Ti2 ··· Ti2a | 3.428(3) | Ti2–O12 | 1.827(6) |
| Ti2–O11 | 1.889(4) | Ti2–N1 | 2.049(9) |
| Ti2–C1 | 2.221(9) | N1–C1 | 1.296(12) |
| N1–C31 | 1.465(13) | C1–C2 | 1.390(12) |
| C2–C3 | 1.53(2) | Ti1–Cp*1 | 2.101 |
| Ti2–Cp*2 | 2.127 | | |
| O12-Ti1-O12a | 94.6(4) | O12a-Ti1-C1 | 124.8(3) |
| O12-Ti1-C1 | 82.9(3) | C1-Ti1-C1a | 56.4(5) |
| Ti2-Ti1-Ti2a | 74.45(9) | O12-Ti2-O11 | 100.1(3) |
| O12-Ti2-N1 | 104.7(3) | O11-Ti2-N1 | 111.9(4) |
| O12-Ti2-C1 | 84.9(3) | O11-Ti2-C1 | 87.7(4) |
| N1-Ti2-C1 | 35.1(3) | C1-N1-C31 | 125.1(9) |
| C1-N1-Ti2 | 79.8(6) | C31-N1-Ti2 | 149.0(7) |
| Ti2-O11-Ti2a | 130.3(5) | Ti2-O12-Ti1 | 100.8(3) |
| N1-C1-C2 | 140.9(10) | N1-C1-Ti2 | 65.2(6) |
| C2-C1-Ti2 | 145.5(7) | N1-C1-Ti1 | 132.5(7) |
| C2-C1-Ti1 | 85.8(7) | Ti2-C1-Ti1 | 78.2(3) |
| C1a-C2-C1 | 101.3(11) | C1-C2-C3 | 128.6(6) |
| C1a-C2-Ti1 | 61.6(6) | C1-C2-Ti1 | 61.6(6) |
| C3-C2-Ti1 | 148.7(10) | C36-C31-C32 | 121.1(12) |
| C36-C31-N1 | 121.4(11) | C32-C31-N1 | 117.4(11) |
| Cp*1-Ti1-O12 | 109.6 | Cp*1-Ti1-C1 | 123.1 |
| Cp*2-Ti2-O12 | 106.8 | Cp*2-Ti2-O11 | 115.4 |
| Cp*2-Ti2-N1 | 116.0 | Cp*2-Ti2-C1 | 150.8 |

($sp^2$-N, 1.36 Å) and close to that reported for methylamine ($sp^3$-N, 1.47 Å),[14] while the N1–C1 bond length of 1.296(12) Å is in the range of a C=N bond (1.28 Å).[11a, 14] The aromatic ring linked to N1 is perpendicular to the plane formed by the atoms N1, C1 and Ti2 (dihedral angle = 92.4(4)°). All this data is consistent with a π electronic delocalisation along the organic fragment formed by N1, C1, C2, C1a and N1a with no contribution from the two aromatic rings joined to the nitrogen atoms.

In the organometallic oxide fragment, Ti2, Ti2a, O12 and O12a form a plane with O11 located 0.414 Å below and Ti1 1.253 Å above that plane. This arrangement represents a very constrained chair conformation, with a dihedral angle of 86.1(2)° between the [Ti2, Ti2a, O12, O12a] and [Ti1, O12, O12a] planes, due to the coordination of Ti1 to C1 and C1a from the organic fragment.

As regards the connection of both fragments, the Ti2–N1 distance of 2.048(8) Å compares well with the Ti–N bond lengths in titanium $\eta^2$-iminoacyl complexes[11a, 15] and is very similar to those of $[Ti^{III}Cp^*_2(NMePh)]$ (2.054(2) Å)[16] and $[(CO_5)W\{C(NMe_2)O\}TiCp^*(NMe_2)_2]$ (av 2.058 Å)[17] in which a Ti–N single bond with the absence of multiple bonding is suggested. Moreover, the Ti2–C1 and Ti1–C1 distances of 2.222(9) Å and 2.274(10) Å, respectively, are considerably longer than the titanium–iminoacyl carbon distances in $[TiCp_2\{\eta^2\text{-}(2,6\text{-}Me_2Ph)NCPh\}]$ (2.096(4) Å)[18] and in compounds of the general formula $[Ti(ArO)_2(\eta^2\text{-}RCNR')(R)]$ (2.086(6), 2.096(5) Å).[19] And finally, the Ti1 ··· C2 distance (2.577(14) Å) is far longer than the previous ones, indicating non-bonding interactions between both atoms.

On the basis of the structural features, we propose that the compounds **6–9** can be described by the contribution of the Lewis structures I and II (Figure 3), in which the iminoacyl carbon atoms are coordinated to two titanium atoms and the ethylidyne group is orientated away from the $Ti_3O_3$ core.

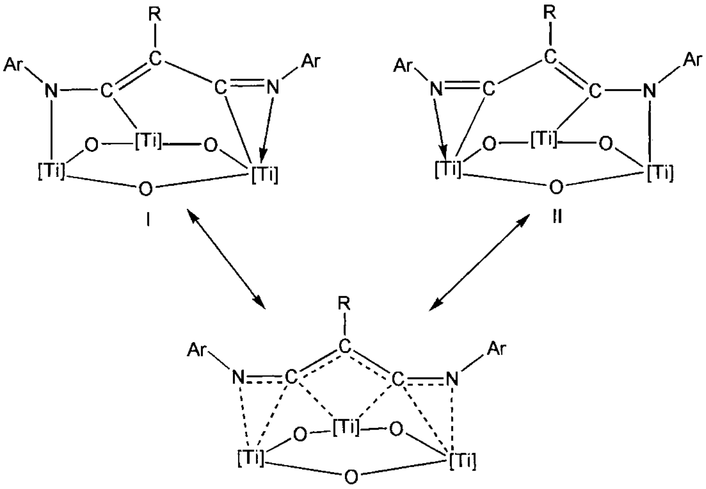


Figure 3. Bonding in the compounds **6–9**. [Ti] = Ti($\eta^5$-$C_5Me_5$).

The $^1H$ and $^{13}C$ NMR spectra of **6–9** (Table 4) are in agreement with a $C_s$ symmetry for these compounds, which is in contrast with the $C_{3v}$ symmetry of **1** and **2**. The NMR spectra clearly reveal a very impressive highfield displacement of the ≡*CH* [$\Delta\delta(^1H) = 7.52$ (**6**), 7.36 (**7**); $\Delta\delta(^{13}C) = 305.2$ (**6**), 305.3 (**7**)] and ≡*CCH*$_3$ [$\Delta\delta(^1H) = 1.64$ (**8**), 1.57 (**9**);

Table 4. Selected NMR data for compounds **1**, **2**, **6–9** in [D$_6$]benzene at 25 °C.[a]

| Compound | $\delta(^1H)$ | $\delta(^{13}C)$ |
|---|---|---|
| **1** | 1.96 ($C_5Me_5$); 12.59 (≡CH) | 119.8, 11.7 ($C_5Me_5$); 383.8 ($J = 138.2$, ≡CH) |
| **6**[b] | 1.96, 1.84 ($C_5Me_5$); 5.07 (HC-C=N) | 120.1, 119.5, 12.3, 11.7 ($C_5Me_5$); 78.6 (d, $J = 174.9$, HC-C=N); 218.3 (d, $J_{CC} = 44.0$, HC-C=N) |
| | 2.23, 1.69 (2,6-$Me_2C_6H_3$); 6.96, 6.87 (2,6-$Me_2C_6H_3$) | 20.0, 19.7 (2,6-$Me_2C_6H_3$); 146.9, 132.3, 131.1, 128.4, 125.4 (2,6-$Me_2C_6H_3$) |
| **7** | 1.99, 1.87 ($C_5Me_5$); 5.23 (HC-C=N) | 120.0, 119.5, 12.4, 11.8 ($C_5Me_5$); 78.5 (d, $J = 173.0$, HC-C=N); 218.4 (s, HC-C=N) |
| | 2.24, 2.16, 1.71 (2,4,6-$Me_3C_6H_2$); 6.81, 6.69 (2,4,6-$Me_3C_6H_2$) | 20.8, 20.0, 19.7 (2,4,6-$Me_3C_6H_2$); 144.2, 134.4, 132.0, 130.8, 129.2, 129.1 (2,4,6-$Me_3C_6H_2$) |
| **2** | 1.95 ($C_5Me_5$); 2.81 (≡CMe) | 119.5, 11.3 ($C_5Me_5$); 401.7 ($^2J = 6.4$, ≡CMe); 39.1 (≡CMe) |
| **8** | 1.97, 1.91 ($C_5Me_5$); 1.17 (MeC-C=N) | 120.0, 119.2, 12.1, 11.8 ($C_5Me_5$); 92.4 (d, $^2J = 5.4$, MeC-C=N); 215.5 (s, MeC-C=N) |
| | 2.26, 1.75 (2,6-$Me_2C_6H_3$); 6.92, 6.83 (2,6-$Me_2C_6H_3$) | 20.3, 19.8 (2,6-$Me_2C_6H_3$); 147.2, 132.1, 131.9, 127.3, 125.3, (2,6-$Me_2C_6H_3$) |
| **9** | 2.00, 1.93 ($C_5Me_5$); 1.24 (MeC-C=N) | 119.9, 119.1, 12.1, 11.8 ($C_5Me_5$); 92.2 (d, $^2J = 5.4$, MeC-C=N); 215.7 (s, MeC-C=N) |
| | 2.26, 2.14, 1.77 (2,4,6-$Me_3C_6H_2$); 6.76, 6.66 (2,4,6-$Me_3C_6H_2$) | 20.9, 20.3, 19.8 (2,4,6-$Me_3C_6H_2$); 144.5, 134.3, 131.5, 131.7, 128.8, 129.0 (2,4,6-$Me_3C_6H_2$) |

[a] Spin-spin coupling constants in Hz. [b] $^{13}C$-labelled derivative **6** was used.

$\Delta\delta(^{13}C) = 309.3$ (**8**), 309.5 (**9**)] resonances with respect to the starting complexes **1** and **2.** The $^{13}C$ chemical shifts for the alkylidyne carbons $\equiv CH$ [$\delta = 78.5$ (**6**, **7**)] and $\equiv CMe$ [$\delta = 92.3$ (**8**, **9**)] and the values of direct carbon–proton [$J = 174$ Hz (**6**, **7**)] and carbon–carbon [$J = 44$ Hz (**6**)] coupling constants are typical of organic olefin fragments. These data are in agreement with the insertion of isocyanide molecules into Ti–C(alkylidyne) bonds and the loss of coordination to any metal atom for the $\alpha$-carbon of the ethylidyne group as found in the X-ray study of **9**.

The $^{13}C$ NMR signals for the iminoacyl groups $RC(CNAr)_2$ lie in the range $\delta = 215–219$ and the IR spectra show absorption bands at $\tilde{\nu} = 1548$ (**6**), 1550 (**7**), 1563 (**8**) and 1570 (**9**) $cm^{-1}$ attributable to the C=N stretching, in agreement with the values found for other $\eta^2$-iminoacyl complexes.[11] The NMR spectra of **6**–**9** indicate the existence of two equivalent Ar rings without $C_{2v}$ symmetry; this is attributed to the slow rotation of the bulky Ar groups around the $N-C_{ipso}$(Ar) bonds.

All these complexes show peaks for the molecular ion in the EI-MS spectra (see the Experimental Section). In addition, the consecutive losses of two isocyanide molecules and formation of the alkylidyne fragments $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}CR)^+]$ [$m/z = 610$ (R = H), 624 (R = Me)] are observed as a fairly general fragmentation pathway.

Reactions of $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}CR)]$ (R = H (**1**), Me(**2**)) with $(2,6\text{-}Me_2C_6H_3)NC$ in a 1:1 ratio initially proceed in the same way and the product of diinsertion (**6** or **8**), together with unconverted starting $\mu_3$-alkylidyne complex (**1** or **2**), were observed by NMR spectroscopy at room temperature. From the mixture of **1** and **6**, the formation of the monoinsertion product $[\{TiCp^*(\mu\text{-}O)\}_3\{\mu_3\text{-}\eta^2\text{-}HCCN(2,6\text{-}Me_2C_6H_3)\}]$ (**10**) was slow and gradual at room temperature (see Scheme 2); it was necessary to heat the mixture at 115 °C for 12 hours to complete the reaction in good yield. The bonding in complex **10**, as proposed from the NMR data (see the Experimental Section), is analogous to that in complexes **3** and **4**.

Surprisingly, a mixture of **2** and **8** did not progress to the monoinsertion product at room temperature, and it was necessary to heat the mixture at 130 °C for five days to obtain only **11** in high yields (see Scheme 2). The molecular ion ($m/z = 755$) and the fragment [$M^+ - N(2,6\text{-}Me_2C_6H_3)$, $m/z = 636$] were observed in the EI–MS spectrum of **11**.

The NMR spectra of complex **11** are consistent with a $C_S$ symmetry: there are signals for two different Cp* ligands (1:2), one $2,6\text{-}Me_2C_6H_3$ aromatic ring with local $C_{2v}$ symmetry and one $\equiv CMe$ group (for more details see the Experimental Section).

The $^{13}C$ NMR spectrum displays two quartets at $\delta = 179.0$ ($^2J = 5.4$ Hz) and 18.9 ($J = 127.5$ Hz) that are assigned to the $C(sp^2)-Me$ moiety. The $^{13}C\{^1H\}$ NMR spectrum of the $^{13}C$-labelled complex **11** shows a doublet of doublets at $\delta = 284.1$ ($J = 18.3$ and $^2J = 19.1$ Hz) for the $\mu_2$-coordinated carbon atom through carbon–carbon direct and geminal spin coupling with the $^{13}C(sp^2)-{}^{13}Me$ group. As in the starting complex **2**, the direct carbon–carbon spin coupling between the ethylidyne carbon atoms is not observed.[20]

In order to clarify the detailed structure of compound **11** and to determine the ethylidyne/isocyanide rearrangement, we obtained crystals suitable for X-ray diffraction analysis.

*Solid-state structure of complex **11***: The molecular structure and atom-labelling scheme of **11** are shown in Figure 4 and relevant geometrical parameters are summarised in Table 5.

Complex **11** has a crystallographic plane of symmetry which contains Ti1, N1, C1, C2, C3, O2, C(41) and which bisects a $C_5Me_5$ ring. The structure of **11** shows a $\mu_3\text{-}\eta^2\text{-}CC(Me)N(2,6\text{-}Me_2C_6H_3)$ ligand supported on a trinuclear organometallic

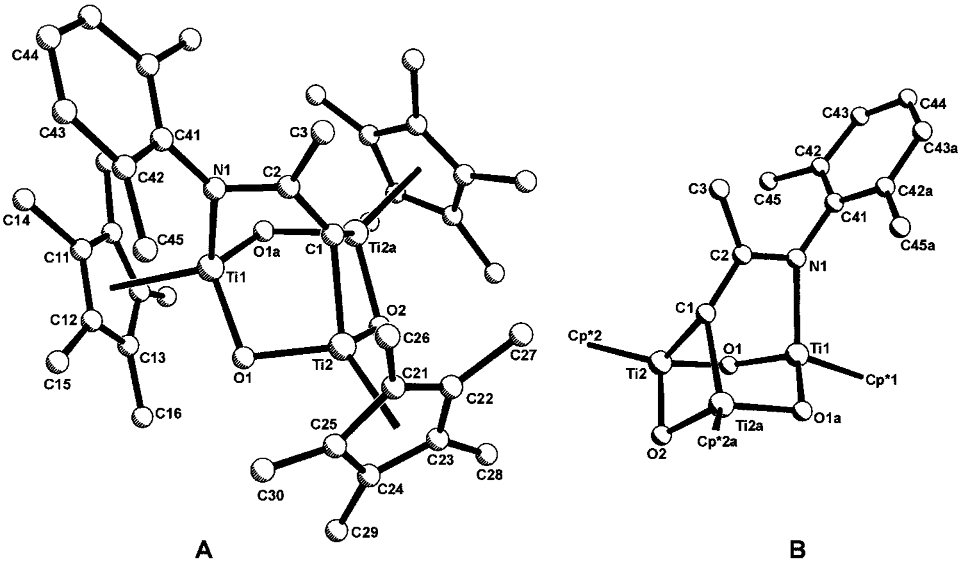
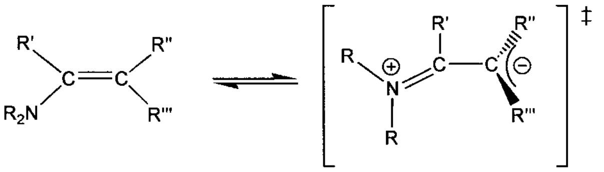


Figure 4. Molecular structure (A) and a simplified view (B) of **11**, as determined by single-crystal X-ray analysis.

Table 5. Selected bond lengths [Å] and angles [°] for **11**. (Cp* are the centroids of the $C_5Me_5$ rings.)

| | | | |
|---|---|---|---|
| Ti1–O1 | 1.853(3) | Ti1–N1 | 2.135(5) |
| Ti1–C1 | 2.559(7) | Ti1···Ti2 | 2.960(1) |
| Ti2···Ti2a | 2.757(2) | Ti2–O2 | 1.835(3) |
| Ti2–O1 | 1.841(4) | Ti2–C1 | 2.017(5) |
| N1–C2 | 1.334(8) | N1–C41 | 1.436(8) |
| C1–C2 | 1.409(9) | C2–C3 | 1.511(9) |
| Ti1–Cp*1 | 2.125 | Ti2–Cp*2 | 2.065 |
| O1a-Ti1-O1 | 113.7(2) | O1-Ti1-N1 | 107.5(2) |
| Ti2-Ti1-Ti2a | 55.5(1) | O2-Ti2-O1 | 106.9(2) |
| O2-Ti2-C1 | 86.9(2) | O1-Ti2-C1 | 92.2(2) |
| Ti2a-Ti2-Ti1 | 62.2(1) | Ti2-O1-Ti1 | 106.5(2) |
| Ti2-O2-Ti2a | 97.4(2) | C2-N1-C41 | 120.0(6) |
| C2-N1-Ti1 | 102.1(4) | C41-N1-Ti1 | 137.8(4) |
| C2-C1-Ti2 | 132.5(2) | Ti2a-C1-Ti2 | 86.3(3) |
| N1-C2-C1 | 116.9(6) | N1-C2-C3 | 121.2(6) |
| C1-C2-C3 | 121.9(6) | Cp*1-Ti1-N1 | 116.8 |
| Cp*1-Ti1-O1 | 105.8 | Cp*2-Ti2-O1 | 117.3 |
| Cp*2-Ti2-O2 | 118.0 | Cp*2-Ti2-C1 | 129.4 |

oxide. The C1–C2 (1.409(9) Å), C2–C3 (1.511(9) Å) and N1–C41 (1.436 (8) Å) bond lengths correspond to single bonds, while the C2–N1 (1.334(8) Å) bond length is longer than the double bond C=N in imines (1.28 Å).[14] C1 is located 0.277(7) Å above the plane formed by Ti2, Ti2a and C2 to adopt a slightly pyramidal geometry, while C2 and N1 have planar environments. As can be seen in Figure 4, the plane formed by N1, C1, C2, C3 and C41 is perpendicular to that formed by the atoms Ti2, C1, Ti2a and to the 2,6-$Me_2C_6H_3$ group. Hence, the organic fragment can be described as the ionic form proposed to explain the wide and useful reactivity of the enamines and shown in Scheme 3.[21] Furthermore, this ionic form may be regarded as the transition state of the rotation about the C=C bond in organic[22] and organometallic[23] enamines.



Scheme 3. Ground state and transition state (ionic form) for organic enamines.

The analysis of the supporting organometallic fragment reveals an isosceles triangle of titanium atoms with two distances Ti1–Ti2 (2.960(1) Å) longer than Ti2–Ti2a (2.757(2) Å), and angles Ti2-Ti1-Ti2a of 55.5(1)° and Ti1-Ti2-Ti2a of 62.2(1)°. The Ti-O-Ti angles (av 103.5(2)°) are clearly smaller than those in $[TiCp^*Me(\mu\text{-}O)]_3$ (av 132.9°),[24a] $[TiCp^*Cl(\mu\text{-}O)]_3$ (av 133.9°)[24b] and $[TiCp^*(\eta^1\text{-crotyl})(\mu\text{-}O)]_3$ (av 133.6°),[24c] but are comparable to those found for $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}CR)]$ (R = H, Me; av 100.8°).[1]

The connection of both fragments show Ti2–C1, Ti2a–C1 bond lengths (2.017(5) Å), which are much shorter than those found for other organotitanium oxides, such as $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}CR)]$ (R = H, 2.10 Å; R = Me, av 2.11 Å),[1] $[TiCp^*Me(\mu\text{-}O)]_3$ (av 2.09 Å),[24a] $[TiCp^*(\eta^1\text{-crotyl})(\mu\text{-}O)]_3$ (av 2.13 Å),[24c] $[(Ti_4Cp^*_4Me_2)(\mu\text{-}O)_5]$ (av 2.11(2) Å),[25] and are unprecedented for a titanium–carbon single bond.[26] This possibly denotes double-bond character. Moreover, it is noteworthy that the Ti1–N1 distance (2.135(5) Å) is very long compared with that involving the $\eta^2$-iminoacyl ligands in complex **9** (2.048(8) Å).

The structure of complex **11** in solution appears to be rigid on the NMR time scale since no changes are observed in its NMR spectra between −100 °C (11.7 T) and +80 °C (7.3 T). Hence, we propose that the $Ti_3O_3$ core fixes the geometry and stabilises the zwitterionic $\overset{-}{C}C(Me)\overset{+}{N}(2,6\text{-}Me_2C_6H_3)$ ligand by delocalising the negative and positive charges over the $Ti_2(\mu_2\text{-}C)$ and Ti···NC(Me) systems, respectively.

## Conclusions

The $\mu_3$-alkylidyne complexes described provide a very good system for the investigation of the rich chemistry of alkylidyne groups on a trinuclear support without metal–metal bonds. Unsaturated molecules, such as CO or isocyanides, are incorporated into the $Ti_3O_3$ core by insertion into the alkylidyne units in a quite specific manner and under mild reaction conditions. The $Ti_3O_3$ core in such complexes exhibits chemical and geometrical flexibility, stabilising unexpected bonding, as found in the complexes $[\{TiCp^*(\mu\text{-}O)\}_3\{\mu_3\text{-}\eta^4\text{-}RC(CNAr)_2\}]$ and especially in the zwitterionic derivative $[\{TiCp^*(\mu\text{-}O)\}_3\{\mu_3\text{-}\eta^2\text{-}CC(Me)\overset{+}{N}(2,6\text{-}Me_2C_6H_3)\}]$.

This preliminary study on the reactivity of the trinuclear organometallic oxide complexes $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}CR)]$ suggests that its behaviour towards other molecules should be worthy of further investigation.

## Experimental Section

**General Procedures**: All reactions were carried out under atmosphere of dry, $O_2$-free, Ar, with Schlenk techniques or in a MBraun glovebox.[27] Solvents were reagent grade, carefully dried from the appropriate drying agents (Na/K or Na) and distilled under argon prior to use.

$[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}CR)]$ (R = H (**1**), Me (**2**)) were synthesised according to the published procedures,[1] (2,4,6-$Me_3C_6H_2$)NC was prepared by the standard method[28] and (2,6-$Me_2C_6H_3$)NC and *t*BuNC were purchased from Aldrich. $^{13}CH_3I$, $CH_3{}^{13}CH_2I$, $^{13}CO$ (99 %, $^{13}C$) were purchased from Cambridge Isotope Laboratory and CO from SEO (Sociedad Española de Oxígeno, S.A.).

NMR spectra were recorded on Varian Unity 300 or 500-Plus spectrometers. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to TMS. IR spectra were recorded on a Perkin Elmer 883 spectrophotometer with KBr pellets. Electron Impact (EI) mass spectra were recorded at 70 eV on a Hewlett Packard 5988 spectrometer. C, H and N microanalyses were performed with a Heraeus CHN-O-RAPID and/or Perkin Elmer 240-C microanalyzers. Thermal reactions were carried out in a Roth autoclave model III (300 mL), with heater model 30S (20–300 °C) and temperature regulator model DR500.

**$[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}^{13}CH)]$** ([$^{13}$C]**1**): [($^{13}CH_3$)MgI] in diethyl ether (30 mL) was prepared by the standard method from $^{13}$C–methyl iodide (1.30 mL, 26.19 mmol, 99 % $^{13}$C) and magnesium turnings (3.00 g). The solution was filtered onto $[\{TiCp^*Cl(\mu\text{-}O)\}_3]$[1, 29] (8.30 g, 11.79 mmol) in THF (250 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature, stirred overnight and dried. The solid residue was extracted three times with toluene/hexane (50 mL, 1:1), and evaporated to dryness to give a partially methylated solid (6.20 g). LiMe (7.1 mL, 11.37 mmol, 1.6 M in $Et_2O$) was added to a cold solution (0 °C) of this solid in THF (150 mL). The mixture was stirred overnight at room temperature, evaporated to dryness and the solid extracted three times with toluene/hexane (50 mL, 1:1). The final solution was evaporated in vacuo to afford $[\{TiCp^*(^{13}Me)(\mu\text{-}O)\}_3]$. Yield: 5.6 g, 74 %.

A solution of $[\{TiCp^*(^{13}Me)(\mu\text{-}O)\}_3]$ (1.00 g, 1.55 mmol) in toluene (50 mL) was sealed in a Carious tube and heated at 205 °C for 10 days. The Carious tube was opened in a glovebox and the solvent removed in vacuo to yield a brownish orange solid, identified by $^1$H and $^{13}$C NMR spectroscopy as $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}^{13}CH)]$ ([$^{13}$C]**1**). Yield: 0.90 g, 95 %.

**$[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}^{13}C^{13}CH_3)]$** ([$^{13}$C]**2**): $[\{TiCp^*(^{13}CH_2CH_3)(\mu\text{-}O)\}_3]$ was prepared by an analogous method to that described for $[\{TiCp^*(^{13}Me)(\mu\text{-}O)\}_3]$ from $CH_3{}^{13}CH_2I$ (0.5 mL, 6.37 mmol, 99 % $^{13}$C), magnesium turnings (0.15 g, 6.37 mmol), $[\{TiCp^*Cl(\mu\text{-}O)\}_3]$ [1, 29] (1.43 g, 2.04 mmol) and EtMgCl (0.85 mL, 1.69 mmol, 2.0 M in THF). The final solution was filtered, concentrated and cooled to −40 °C, to give $[\{TiCp^*(^{13}CH_2CH_3)(\mu\text{-}O)\}_3]$ as an orange crystalline solid. Yield: 0.65 g, 47 %.

A solution of $[\{TiCp^*(^{13}CH_2CH_3)(\mu\text{-}O)\}_3]$ (30 mg, 0.04 mmol) in $C_6D_6$ (0.6 mL) in a NMR tube was sealed and heated at 200 °C for 12 hours to give the compound $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}^{13}C^{13}CH_3)]$ ([$^{13}$C]**2**) in practically quantitative yield.

**[{TiCp*(μ-O)}$_3$(μ$_3$-η$^2$-HCCN*t*Bu)] (3)**: *t*BuNC (81 μL, 8.19 mmol) diluted in toluene (10 mL) was slowly added to a solution of **1** (0.50 g, 8.19 mmol) in toluene (40 mL) at 0 °C. The reaction mixture was stirred for 2 hours at room temperature. The solvent was removed to afford **3** as a brown solid. Yield: 0.55 g, 96 %; IR (KBr): $\tilde{\nu} = 2910$ (m), 1559 (m), 1436 (s), 1374 (m), 1193 (m), 782 (vs), 715 (m), 680 (m), 606 (m), 418 (m) cm$^{-1}$; anal. calcd for $Ti_3O_3NC_{36}H_{55}$ ($M_T = 693.45$): C 62.35, H 7.99, N 2.02; found: C 61.49, H 8.03, N 1.32.

**Reaction of [$^{13}$C]1 with *t*BuNC**: A solution of [$^{13}$C]**1** (40 mg, 0.06 mmol) and *t*BuNC (6.4 μL, 0.06 mmol) in $C_6D_6$ (0.60 mL) was sealed in a NMR tube and kept at room temperature. After 30 min the product [{TiCp*(μ-O)}$_3$(μ$_3$-η$^2$-$^{13}$CHCN*t*Bu)] was identified by $^1$H and $^{13}$C NMR spectroscopy.

**[{[TiCp*(μ-O)]$_3$}$_2$(μ$_6$-$C_6H_2O_4$)] (5)**: A solution of **1** (0.50 g, 0.82 mmol) in toluene (50 mL) was placed in a 500-mL Schlenk flask. The solution was frozen with liquid $N_2$ and the argon atmosphere was replaced by CO. The mixture was allowed to warm to room temperature and stirred for five days. Then the CO atmosphere and the solvent were removed in vacuo to yield a crude product (1.00 g, 93 %). This was crystallised from THF/hexane to afford **5** as a brown solid. IR (KBr): $\tilde{\nu} = 2913$ (s), 2850 (m), 1603 (m), 1437 (m), 1374 (m), 1261 (m), 1192 (m), 1135 (m), 998 (m), 820 (s), 776 (vs), 707 (vs), 650 (s), 606 (s), 420 (m) cm$^{-1}$; anal. calcd for $Ti_6O_{10}C_{66}H_{92}$ ($M_T = 1332.68$): C 59.48, H 6.96; found: C 58.81, H 7.56.

**Reaction of [$^{13}$C]1 with CO and $^{13}$CO**: A solution of [$^{13}$C]**1** (50 mg, 0.08 mmol) in $C_6D_6$ (0.7 mL) was transferred into a NMR tube, placed under CO atmosphere at −78 °C and the tube sealed. The mixture was allowed to warm to room temperature. After two days the final product was identified by NMR spectroscopy. The reaction with $^{13}$CO was carried out in an analogous manner.

**[{TiCp*(μ-O)}$_3${μ$_3$-η$^4$-RC(CNAr)$_2$}] (R = H, Ar = 2,6-$Me_2C_6H_3$ (6), 2,4,6-$Me_3C_6H_2$ (7); R = Me, Ar = 2,6-$Me_2C_6H_3$ (8), 2,4,6-$Me_3C_6H_2$ (9))**: All these compounds were prepared in the same way by addition of a solution of the corresponding isocyanide in hexane to a solution of [{TiCp*(μ-O)}$_3$(μ$_3$-CR)] (R = H (**1**), Me (**2**)) in hexane at room temperature. The reaction mixture was stirred overnight, then concentrated and cooled to 4 °C. The products were obtained in good yield (75–90 %) and high purity (> 95 % by $^1$H NMR). The preparation of **6** is reported as an example.

**[{TiCp*(μ-O)}$_3${μ$_3$-η$^4$-HC(2,6-$Me_2C_6H_3$NC)$_2$}] (6)**: 2,6-$Me_2C_6H_3$NC (0.17 g, 1.29 mmol) in hexane (5 mL) was added to a solution of **1** (0.40 g, 0.65 mmol) in hexane (50 mL). The reaction was stirred at room temperature overnight. The orange solution was concentrated (30 mL) and cooled to 4 °C to afford microcrystalline **6**. Yield: 0.42 g, 74 %; IR (KBr): $\tilde{\nu} = 2909$ (m), 1548 (m), 1488 (s), 1440 (m), 1371 (s), 1024 (s) cm$^{-1}$; MS (EI): *m*/*z* (rel. int. %): 741 [$M^+$ − (2,6-$Me_2C_6H_3$NC)] (39), 610 [$M^+$ − 2(2,6-$Me_2C_6H_3$NC)] (21); anal. calcd for $Ti_3O_3N_2C_{49}H_{64}$ ($M = 872.66$): C 67.43, H 7.39, N 3.20; found: C 67.12, H 7.83, N 2.99.

**[{TiCp*(μ-O)}$_3${μ$_3$-η$^4$-HC(2,4,6-$Me_3C_6H_2$NC)$_2$}] (7)**: The reaction of **1** (0.40 g, 0.65 mmol) and 2,4,6-$Me_3C_6H_2$NC (0.19 g, 1.31 mmol) gave **7** as an orange microcrystalline solid. Yield: 0.46 g, 78 %; IR (KBr): $\tilde{\nu} = 2911$ (m), 1550 (m), 1494 (s), 1440 (m), 1371 (s), 1023 (s) cm$^{-1}$; MS (EI): *m*/*z* (rel. int. %): 755 [$M^+$ − (2,4,6-$Me_3C_6H_2$NC)] (32), 610 [$M^+$ − 2(2,4,6-$Me_3C_6H_2$NC)] (57); anal. calcd for $Ti_3O_3N_2C_{51}H_{68}$ ($M_T = 900.71$): C 68.00, H 7.61, N 3.10; found: C 68.58, H 8.19, N 2.91.

**[{TiCp*(μ-O)}$_3${μ$_3$-η$^4$-MeC(2,6-$Me_2C_6H_3$NC)$_2$}] (8)**: The reaction of **2** (0.40 g, 0.64 mmol) and 2,6-$Me_2C_6H_3$NC (0.18 g, 1.28 mmol) gave orange crystals of **8**. Yield: 0.50 g, 87 %; IR (KBr): $\tilde{\nu} = 2908$ (m), 1563 (m), 1460 (s), 1440 (m), 1370 (s), 1023 (s) cm$^{-1}$; MS (EI): *m*/*z* (rel. int. %): 755 [$M^+$ − (2,6-$Me_2C_6H_3$NC)] (13), 624 [$M^+$ − 2(2,6-$Me_2C_6H_3$NC)] (3); anal. calcd for $Ti_3O_3N_2C_{52}H_{70}$ ($M_T = 886.69$): C 67.72, H 7.50, N 3.16; found: C 68.09, H 8.20, N 3.23.

**[{TiCp*(μ-O)}$_3${μ$_3$-η$^4$-MeC(2,4,6-$Me_3C_6H_2$NC)$_2$}] (9)**: The reaction of [{TiCp*(μ-O)}$_3$(μ$_3$-CMe)] (**2**) (0.40 g, 0.64 mmol) and 2,4,6-$Me_3C_6H_2$NC (0.18 g, 1.28 mmol) gave **9** as an orange crystalline solid. Yield: 0.52 g, 89 %; IR (KBr): $\tilde{\nu} = 2910$ (m), 1570 (m), 1465 (s), 1372 (s), 1022 (s) cm$^{-1}$; MS (EI): *m*/*z* (rel. int. %): 769 [$M^+$ − (2,4,6-$Me_3C_6H_2$NC)] (1); anal. calcd for $Ti_3O_3N_2C_{52}H_{70}$ ($M_T = 914.74$): C 68.27, H 7.71, N 3.06; found: C 68.70, H 7.85, N 2.85.

**[{TiCp*(μ-O)}$_3${μ$_3$-η$^2$-HCCN(2,6-$Me_2C_6H_3$)}] (10)**: A solution of **1** (0.40 g, 0.65 mmol) and 2,6-$Me_2C_6H_3$NC (0.08 g, 0.65 mmol) in toluene (60 mL) was transferred by cannula into a 150-mL Carious tube and then sealed under vacuum by flame. This solution was heated in an autoclave at 115 °C for 12 h. The Carious tube was opened in a glovebox and the solution was concentrated and cooled to ≈ −40 °C to yield a dark brown solid. Yield: 0.30 g, 63 %; IR (KBr): $\tilde{\nu} = 2910$ (m), 1547 (m), 1436 (s), 1374 (m), 1025 (s) cm$^{-1}$; $^1$H NMR (300 MHz, $C_6D_6$, 20 °C): $\delta = 7.99$ (s, 1 H, *H*C-C=N), 6.94 (m, 3 H, 2,6-$Me_2C_6$*H*$_3$), 2.01 (s, 15 H, $C_5$*Me*$_5$), 1.95 (s, 30 H, $C_5$*Me*$_5$), 1.80 (s, 6 H, 2,6-*Me*$_2C_6H_3$); $^{13}$C NMR (75 MHz, $C_6D_6$, 20 °C): $\delta = 204.9$ (s, $^2J = 3.6$ Hz, HC-*C*=N), 172.5 (d, $J = 160.3$ Hz, H*C*-C=N), 147.2, 132.3, 128.3, 127.9, 125.2 ($J = 156.9$ Hz, 2,6-$Me_2$*C*$_6H_3$), 121.3, 120.1 (m, *C*$_5Me_5$), 19.3 (q, $J = 125.6$ Hz, 2,6-*Me*$_2C_6H_3$), 11.1, 11.9 (q, $J = 125.6$ Hz, $C_5$*Me*$_5$); anal. calcd for $Ti_3O_3NC_{40}H_{55}$ ($M_T = 741.49$): C 64.78, H 7.47, N 1.89; found: C 64.69, H 7.72, N 1.95.

**Reaction of [$^{13}$C]1 with 2,6-$Me_2C_6H_3$NC**: The compound [{TiCp*(μ-O)}$_3${μ$_3$-η$^2$-H$^{13}$CCN(2,6-$Me_2C_6H_3$)}] was prepared similarly to **10** from [$^{13}$C]**1** (40 mg, 0.06 mmol) and 2,6-$Me_2C_6H_3$NC (8.59 mg, 0.06 mmol) in $C_6D_6$ (0.7 mL). The NMR tube was sealed in a vacuum and heated at 115 °C for 12 hours. The product was identified by NMR spectroscopy.

**[{TiCp*(μ-O)}$_3${μ$_3$-η$^2$-$\overset{-}{C}$ C(Me)$\overset{+}{N}$(2,6-$Me_2C_6H_3$)}] (11)**: Compound **11** was prepared in 92 % yield in an analogous manner to **10**: The solution was heated in an autoclave at 130 °C for five days. IR (KBr): $\tilde{\nu} = 2909$ (s), 1426 (s), 1390 (s), 1373 (s), 1255 (m), 1161 (m), 1089 (m), 1023 w, 1190 (m), 844 (s), 773 (s), 685 (vs), 659 (s), 621(m), 602 (m), 402 (s), 328 (m) cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$, 20 °C): $\delta = 6.93$ (m, 3 H, 2,6-$Me_2C_6$*H*$_3$), 2.12 (s, 30 H, $C_5$*Me*$_5$), 1.89 (s, 6 H, 2,6-*Me*$_2C_6H_3$), 1.82 (s, 15 H, $C_5$*Me*$_5$), 0.97 (s, 3 H, CC(*Me*)=N); $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C): $\delta = 284.1$ (s, *C*C(Me)=N), 179.0 (q, $^2J = 5.4$ Hz, C*C*(Me)=N) 144.8, 132.3, 128.0, 125.4 ($J = 156.6$ Hz, 2,6-$Me_2C_6H_3$), 122.6, 119.2 (m, *C*$_5Me_5$), 22.2 (q, $J = 127.5$ Hz, 2,6-*Me*$_2C_6H_3$), 18.9 (q, $J = 127.5$ Hz, CC(*Me*)=N), 11.6, 10.9 (q, $J = 125.6$ Hz, $C_5$*Me*$_5$); MS (EI): *m*/*z* (rel. int. %): 755 [$M^+$] (15), 636 [$M^+$ − N(2,6-$Me_2C_6H_3$)] (11); anal. calcd for $Ti_3O_3NC_{41}H_{57}$ ($M_T = 755.52$): C 64.80, H 7.43, N 1.72; found: C 65.17, H 7.60, N 1.85.

**Reaction of [$^{13}$C]2 with 2,6-$Me_2C_6H_3$NC**: 2,6-$Me_2C_6H_3$NC (8.40 mg, 0.06 mmol) was added to a solution of [$^{13}$C]**2** (40 mg, 0.06 mmol) in $C_6D_6$ (0.7 mL). The NMR tube was sealed and heated at 130 °C for five days. The compound [{TiCp*(μ-O)}$_3${μ$_3$-η$^2$-$\bar{C}$$^{13}$C($^{13}$Me)$\overset{+}{N}$(2,6-$Me_2C_6H_3$)}] was identified by $^1$H and $^{13}$C NMR spectroscopy.

**X-ray structure determination of 9 and 11**: Table 6 provides a summary of the crystal data, data collection and refinement parameters for complexes **9** and **11**. Both sets of data were collected on an Enraf Nonius CAD 4 diffractometer at room temperature. Intensity measurements were performed by ω scans in the range $2° < 2\theta < 50°$ for **9** ($2° < 2\theta < 54°$ for **11**). Of the 6230 measured reflections for **9**, 5700 were independent; *R1* = 0.120 and *wR2* = 0.336 (for 2249 reflections with $F > 4\sigma(F)$). Of the 8811 measured reflections for **11**, 4472 were independent; *R1* = 0.089 and *wR2* = 0.261 (for 3213 reflections with $F > 4\sigma(F)$). The values of *R1* and *wR2* are defined $R1 = \Sigma||F_0| - |F_c||/[\Sigma|F_0|]$; $wR2 = \{[\Sigma w(F_0^2 - F_c^2)^2]/[\Sigma w(F_0^2)^2]\}^{1/2}$. The structures were solved by direct methods (SHELXS-90)[30] and refined by least-squares against $F^2$ (SHELXL-93).[31]

The molecule of **9** showed severe disorder in one of the two located pentamethylcyclopentadienyl ligands (linked to Ti2) which prevented a precise solution, presenting two sites (50 % occupancy) for each carbon atom, except for C23. However, this disorder did not affect the location of the core of the molecule. All non-hydrogen atoms, except those disordered, were anisotropically refined and the hydrogen atoms positioned geometrically and refined by use of a riding model in the last cycles of refinement when possible.

The poor quality of the crystal prevented a precise solution for the molecule of **11**. All non-hydrogen atoms except C14, C15, C16, C26 and C30, were anisotropically refined and the hydrogen atoms positioned geometrically and refined by use of a riding model in the last cycles of refinement.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100746. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax.: (+ 44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 6. Crystal data and structure refinement for **9** and **11**.

| | **9** | **11** |
|---|---|---|
| empirical formula | $C_{52}H_{70}N_2O_3Ti_3$ | $C_{41}H_{57}NO_3Ti_3$ |
| formula weight | 914.80 | 755.58 |
| temperature [K] | 293(2) | 293(2) |
| wavelength ($Mo_{K\alpha}$) | 0.71073 Å (graphite monochromator) | |
| crystal system; space group | orthorhombic; *Pnma* | orthorhombic; *Pnma* |
| *a* [Å] | 11.438(1) | 17.345(3) |
| *b* [Å] | 18.324(1) | 18.119(4) |
| *c* [Å] | 29.871(1) | 12.620(3) |
| volume [Å$^3$]; *Z* | 6260.7(7); 4 | 3966(2); 4 |
| $\rho_{calcd}$ [g cm$^{-3}$] | 0.971 | 1.265 |
| absorption coefficient [ mm$^{-1}$] | 0.406 | 0.626 |
| *F*(000) | 1944 | 1600 |
| crystal size [mm] | $0.35 \times 0.32 \times 0.25$ | $0.45 \times 0.35 \times 0.33$ |
| diffractometer | Enraf Nonius CAD4 | |
| scan mode; $\theta$ range | $\omega$; 2.21 to 25.01° | $\omega$; 2.25 to 27.03° |
| index ranges | $0 < h < 13$, $0 < k < 21$, $0 < l < 35$ | $0 < h < 22$, $-23 < k < 23$, $0 < l < 16$ |
| collected reflections | 6230 | 8811 |
| Independent reflections | 5700 ($R_{int} = 0.0001$) | 4472 ($R_{int} = 0.0288$) |
| observed reflections [$F > 4\sigma(F)$] | 2249 | 3213 |
| goodness-of-fit on $F^2$ | 1.170 | 1.059 |
| final *R* indices [$F > 4\sigma(F)$] | $R1 = 0.1205$, $wR2 = 0.3365$ | $R1 = 0.0889$, $wR2 = 0.2609$ |
| *R* indices (all data) | $R1 = 0.2991$, $wR2 = 0.4233$ | $R1 = 0.1542$, $wR2 = 0.3440$ |
| weighting scheme (calcd) | $w = 1/[\sigma^2(F_o^2) + (0.2086P)^2 + 0.0000P]$<br>where $P = (F_o^2 + 2F_c^2)/3$ | $w = 1/[\sigma^2(F_o^2) + (0.1788P)^2 + 9.2043P]$ |
| Largest diff. peak and hole [e Å$^{-3}$] | 0.795 and $-0.433$ | 1.059 and $-0.821$ |

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