Transfer Hydrogenation Processes to μ_3-Alkylidyne Groups on the Organotitanium Oxide $[Ti_3Cp^*_3O_3]$

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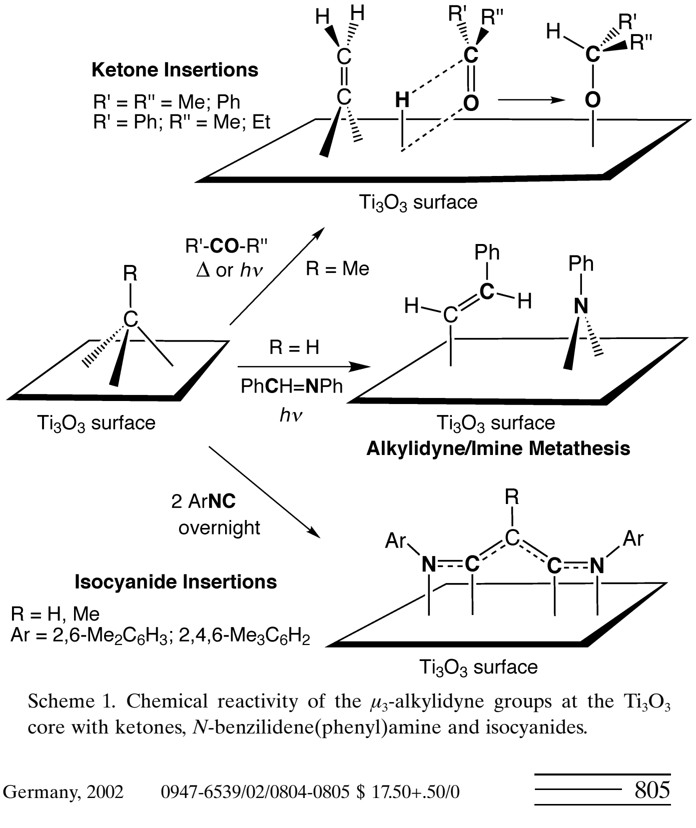
Abstract: The photochemical treatment of μ_3-alkylidyne complexes $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}CR)]$ (R = H (**1**), Me (**2**), Cp* = η^5-C_5Me_5) with the amines $(2,6\text{-}Me_2C_6H_3)NH_2$, Et_2NH, and Ph_2NH and the imine $Ph_2C{=}NH$ leads to the partial hydrogenation of the alkylidyne moiety that is supported on the organometallic oxide, $[Ti_3Cp^*_3O_3]$, and the formation of new oxoderivatives $[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}CHR)(R'NR'')]$ ($R'' = 2,6\text{-}Me_2C_6H_3$, R′ = H, R = H (**3**), Me (**4**); R′ = R″ = Et, R = H (**5**), Me (**6**); R′ = R″ = Ph, R = H (**7**), Me (**8**)) and $[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}CHR)(N{=}CPh_2)]$ (R = H (**9**), R = Me (**10**)), respectively. A sequential transfer hydrogenation process occurs when complex **1** is treated with $tBuNH_2$, which initially gives the μ-methylene $[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}CH_2)(HNtBu)]$ (**11**) complex and finally, the alkyl derivative $[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}NtBu)Me]$ (**12**). Furthermore, irradiation of solutions of the μ_3-alkylidyne complexes **1** or **2** in the presence of diamines $o\text{-}C_6H_4(NH_2)_2$ and $H_2NCH_2CH_2NH_2$ (en) affords $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}\eta^2\text{-}NC_6H_4NH)]$ (**13**) and $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}\eta^2\text{-}NC_2H_4NH)]$ (**14**) by either methane or ethane elimination, respectively. In the reaction of **1** with en, an intermediate complex $[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}CH_2)(NHCH_2CH_2NH_2)]$ (**15**) is detected by ^1H NMR spectroscopy. Thermal treatment of the complexes **4**–**10** quantitatively regenerates the starting μ_3-alkylidyne compounds and the amine R'_2NH or the imine $Ph_2C{=}NH$; however, heating of solutions of **3** or **4** in [D$_6$]benzene or a equimolecular mixture of both at 170 °C produces methane, ethane, or both, and the complex $[\{TiCp^*(\mu\text{-}O)\}_3\{\mu_3\text{-}\eta^2\text{-}NC_6H_3(Me)CH_2\}]$ (**16**). The molecular structure of **8** has been established by single-crystal X-ray analysis.

Keywords: hydrogenation · N ligands · oxo ligands · titanium

Introduction

Anchoring of alkylidyne groups on the organometallic oxide $[Ti_3Cp^*_3O_3]$ in the complexes $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}CR)]$ (R = H (**1**), Me (**2**))[1] constitutes a molecular approach to hydrocarbon–metal(oxo) surface interactions.[2, 3] μ_3-Alkylidyne groups, which are supported on the Ti_3O_3 core, show surprising chemical reactivity with organic substrates (see Scheme 1) similar to that proposed for metal–oxide surfaces.



Scheme 1. Chemical reactivity of the μ_3-alkylidyne groups at the Ti_3O_3 core with ketones, *N*-benzilidene(phenyl)amine and isocyanides.

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Supporting information for this article (a complete table of all the NMR data) is available on the WWW under http://wiley-vch.de/home/chemistry/ or from the author.

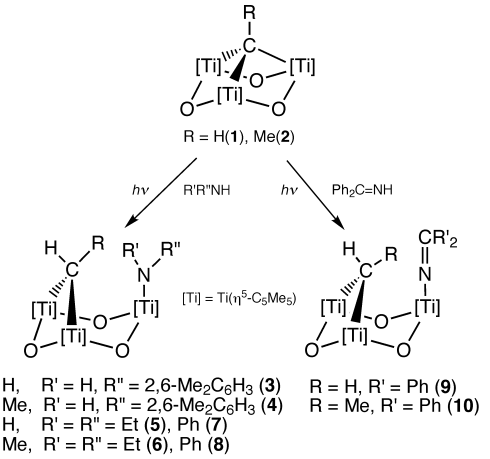
The reactions with unsaturated molecules such as carbon monoxide and isocyanides proceed by their insertion into the μ_3-alkylidyne unit.[4] However, the reactivity with ketones follows a different pathway that involves the insertion of the $R_2C{=}O$ carbonyl group into the Ti−H bond of the intermediate $[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}C{=}CH_2)(H)]$, which is formed in situ, to form the alkoxide-vinylidine derivatives $[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}C{=}CH_2)(OCHR_2)]$.[5] The behavior toward the *N*-benzylidine(phenyl)amine can be described as an alkylidyne/imine metathesis-like process.[6] All these results reveal the important role of the oxygen atoms in these systems, which bridge the titanium atoms and enhance the cooperative effect between them.[7]

Here we report the reactions of the μ_3-alkylidyne complexes **1** and **2** with different organic amines, diamines, and the imine $Ph_2C{=}NH$ as hydrogen–donor reagents. These processes provide insight into transfer hydrogenation reactions on surfaces.[2]

Results and Discussion

The photochemical treatment at room temperature of solutions of the μ_3-alkylidyne oxo complexes $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}CR)]$ (R = H (**1**), Me (**2**)) in hexane with the amines $(2,6\text{-}Me_2C_6H_3)NH_2$, Et_2NH, Ph_2NH, and the imine $Ph_2C{=}NH$ affords the μ-alkylidene amido complexes **3**–**10** (Scheme 2).

Abstract in Spanish: *El tratamiento fotoquímico de los complejos alquilidino $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}CR)]$ (R = H (**1**), Me (**2**)) en presencia de aminas $[(2,6\text{-}Me_2C_6H_3)NH_2$, Et_2NH y $Ph_2NH]$ y de la imina $Ph_2C{=}NH$ conduce a la hidrogenación parcial de la especie alquilidino soportada sobre el óxido organometálico $[Ti_3Cp^*_3O_3]$ y la formación de los oxocomplejos $[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}CHR)(R'NR'')]$ ($R'' = 2,6\text{-}Me_2C_6H_3$, R′ = H, R = H (**3**), Me (**4**); R′ = R″ = Et, R = H (**5**), Me (**6**); R′ = R″ = Ph, R = H (**7**), Me (**8**)) y $[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}CHR)(N{=}CPh_2)]$ (R = H (**9**), R = Me (**10**)), respectivamente. La reacción análoga con tercbutil amina y el derivado metilidino **1** transcurre inicialmente mediante la formación de la especie μ-metileno $[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}CH_2)(HNtBu)]$ (**11**), y evoluciona para dar el alquil derivado $[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}NtBu)Me]$ (**12**). Cuando la irradiación de **1** o **2** se lleva a cabo en presencia de las diaminas $o\text{-}C_6H_4(NH_2)_2$ y $H_2NCH_2CH_2NH_2$ (en) se obtienen $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}\eta^2\text{-}NC_6H_4NH)]$ (**13**) y $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}\eta^2\text{-}NC_2H_4NH)]$ (**14**), junto con metano o etano. En el caso de la reacción de **1** con en se ha detectado mediante RMN-^1H el intermedio $[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}CH_2)(NHCH_2CH_2NH_2)]$ (**15**). Por otra parte, el tratamiento térmico de los complejos **4**–**10** conduce a la regeneración prácticamente cuantitativa de los alquilidinos de partida y de la amina R'_2NHO imina $Ph_2C = NH$. Sin embargo, cuando se calienta por encima de 170°C los complejos **3** y **4** o una mezcla equimolecular de los dos en benceno-d_6, tiene lugar la aparición de metano, etano o una mezcla de ambos, y el nuevo oxocomplejo $[\{TiCp^*(\mu\text{-}O)\}_3\{\mu_3\text{-}\eta^2\text{-}NC_6H_3(Me)CH_2\}]$ (**16**). La estructura molecular de **8** ha sido determinada por difracción de rayos-X.*



Scheme 2. Reactivity of μ_3-alkylidyne complexes **1** and **2** with amines and the imine $Ph_2C{=}NH$.

The NMR spectra of these complexes display two types of Cp* ligand in a 2:1 ratio, which are consistent with C_s symmetry and contrast with the C_{3v} symmetry of the starting materials **1** and **2**. In their ^1H NMR spectra, the compounds **3**, **5**, **7**, and **9** exhibit an AB spin system, which is assigned to a μ-methylene moiety between two titanium atoms, and those of the complexes **4**, **6**, **8**, and **10** show a doublet and a quartet, which correspond to an μ-ethylidene bridge between two metal centers (Table 1). Also, narrow signals at $\delta = 6.58$ and 6.69, which are attributed to the amido fragment Ti−*H*N$(2,6\text{-}Me_2C_6H_3)$, are observed in the spectra of the complexes **3** and **4**, respectively.

The ^{13}C NMR spectra reveal a very strong shielding ($\Delta\delta = 190$ ppm) for the resonances of the μ-alkylidene carbons atoms (μ-CH_2 and μ-CHMe) with respect to those of the starting μ_3-alkylidyne groups. The chemical shift of the signal due to the μ-alkylidene carbon atom in these species (**3**–**10**) follows a similar trend to that observed for homo-[1b, 8] and heterodinuclear[9] μ-methylidene titanium systems reported in the literature.

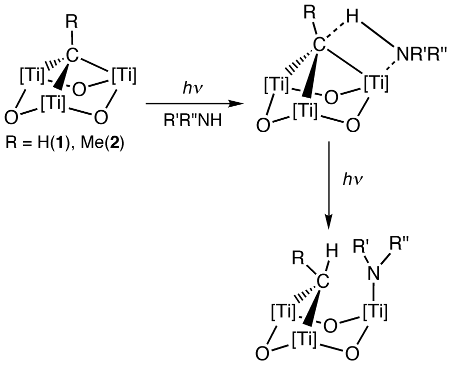
If we consider the mechanism of formation of these species, we would expect the coordination of the nitrogen atom (Scheme 3) to establish a four-centered transition state. This first step is decisive for the stereoselectivity of the reaction and forces the hydrogen atom to occupy an *endo* position. Therefore the $R = CH_3$ substituent in complexes **4**, **6**, and **8** should occupy the *exo* position.

To corroborate this proposal, we have attempted to establish a relationship between the chemical shifts of the ethylidene groups from complexes **4**, **6**, and **8** and the different amido fragments. Thus, it is observed that the electronic properties of the NR′R″ groups have a significant influence on both chemical shifts (^{13}C and ^1H) of the μ-CH fragment (δ (**8**) = 215.4 (6.21) > δ (**4**) = 212.3 (6.09) > δ (**6**) = 208.7 (6.05)). These results correlate with a lower chemical shift for a higher donor capacity of the amido groups. However, if the methyl group is considered there is little difference between the ^{13}C NMR data (μ-CH*Me*, $\delta = 28.8 \pm 0.3$) but a significant variation in the proton chemical shifts (μ-CH*Me*, $\delta = 1.63$ (**4**), 1.96 (**6**), 1.74 (**8**)) when the amido group is changed. The

Table 1. Selected NMR data for complexes **3**–**16** in [D$_6$]benzene at 25 °C.[a]

Compound	$\delta(^1\mathrm{H})$	$\delta(^{13}\mathrm{C})$
3	2.06, 1.94 ($\mathrm{C_5}\mathit{Me}_5$); 6.37, 4.96 ($^2J = 9.4$, μ-CH_2); 6.58 ($\mathrm{2,6\text{-}Me_2C_6H_3N}\mathit{H}$-)	122.1, 120.0, 12.0, 11.8 ($\mathit{C}_5\mathit{Me}_5$); 197.8 ($J = 127.4$, μ-$\mathit{C}\mathrm{H}_2$)
4	1.97, 1.94 ($\mathrm{C_5}\mathit{Me}_5$); 6.09, 1.63 ($^3J = 7.9$, μ-CHMe); 6.69 ($\mathrm{2,6\text{-}Me_2C_6H_3N}\mathit{H}$-)	122.5, 119.8, 12.1, 11.5 ($\mathit{C}_5\mathit{Me}_5$); 212.8 ($J = 116.5$, $^2J = 7.3$), 28.5 (μ-$\mathrm{CH}\mathit{Me}$)
5	2.08, 2.03 ($\mathrm{C_5}\mathit{Me}_5$); 6.42, 5.97 ($^2J = 8.5$, μ-CH_2)	119.5, 118.9, 11.2, 11.1 ($\mathit{C}_5\mathit{Me}_5$); 192.6 ($J = 125.6$, μ-$\mathit{C}\mathrm{H}_2$)
6	2.03, 2.00 ($\mathrm{C_5}\mathit{Me}_5$); 6.05, 1.96 ($^3J = 9.5$, μ-CHMe)	120.2, 119.3, 11.5, 12.0 ($\mathit{C}_5\mathit{Me}_5$); 208.7 ($J = 116.5$), 28.8 ($\mu$-$\mathit{CHMe}$)
7	2.02, 1.93 ($\mathrm{C_5}\mathit{Me}_5$); 6.54, 6.16 ($^2J = 9.0$, μ-CH_2)	123.4, 120.8, 12.0, 11.8 ($\mathit{C}_5\mathit{Me}_5$); 197.6 ($J = 126.6$, 129.7, μ-$\mathit{C}\mathrm{H}_2$)
8	1.95, 1.92 ($\mathrm{C_5}\mathit{Me}_5$); 6.21, 1.74 ($^3J = 7.5$, μ-CHMe)	123.2, 120.4, 12.1, 11.5 ($\mathit{C}_5\mathit{Me}_5$); 215.4 ($J = 117.4$), 29.2 ($\mu$-$\mathrm{CH}\mathit{Me}$)
9	1.98, 2.07 ($\mathrm{C_5}\mathit{Me}_5$); 6.20, 5.68 ($^2J = 9$, μ-CH_2)	119.5, 122.5, 11.7, 12.0 ($\mathit{C}_5\mathit{Me}_5$); 186.4 ($J = 126.1$, μ-$\mathit{C}\mathrm{H}_2$); 170.9 (-$\mathit{C}{\equiv}\mathit{N}$)
10	1.99, 2.03 ($\mathrm{C_5}\mathit{Me}_5$); 6.20, 1.75 ($^3J = 7.8$, μ-CHMe)	119.0, 122.3, 11.5, 12.1 ($\mathit{C}_5\mathit{Me}_5$); 208.2 ($J = 117.2$), 30.6 ($\mu$-$\mathrm{CH}\mathit{Me}$); 171.1 (-$\mathit{C}{\equiv}\mathit{N}$)
11	2.04, 2.01 ($\mathrm{C_5}\mathit{Me}_5$); 6.53, 6.02 ($^2J = 9.2$, μ-CH_2); 6.10 ($\mathrm{CMe_3N}\mathit{H}$-)	121.1, 119.7, 12.2, 11.8 ($\mathit{C}_5\mathit{Me}_5$); 192.0 ($J = 125.6$, μ-$\mathit{C}\mathrm{H}_2$)
12	2.05, 2.03 ($\mathrm{C_5}\mathit{Me}_5$); 0.56 (Ti-$\mathit{Me}$)	121.7, 119.7, 12.0, 11.7 ($\mathit{C}_5\mathit{Me}_5$); 42.9 ($J = 121.7$, Ti-$\mathit{Me}$)
13	2.00, 1.90 ($\mathrm{C_5}\mathit{Me}_5$); 7.04 ($>\mathrm{NC_6H_4N}\mathit{H}$-)	121.8, 121.0, 11.6, 11.3 ($\mathit{C}_5\mathit{Me}_5$)
14	2.04, 1.99 ($\mathrm{C_5}\mathit{Me}_5$); 5.22, 3.62, 2.97 ($>\mathrm{NC}\mathit{H}_\mathrm{A}\mathrm{C}\mathit{H}_{\mathrm{A'}}\mathrm{C}\mathit{H}_\mathrm{B}\mathit{H}_{\mathrm{B'}}\mathrm{N}\mathit{H}_\mathrm{K}$)	120.4, 11.5 ($\mathit{C}_5\mathit{Me}_5$); 65.0 ($J = 132.9$), 59.1 ($J = 131.2$) ($>\mathrm{N}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2NH}$-)
15	2.01, 2.03 ($\mathrm{C_5Me_5}$); 6.52, 5.99 ($^2J = 9.3$, μ-CH_2), 6.08 ($\mathit{H}\mathrm{NCH_2CH_2NH_2}$); 3.70, 2.55 (-$\mathit{CH}_2\mathit{CH}_2\mathrm{NH_2}$)	
16	2.02, 1.89 ($\mathrm{C_5}\mathit{Me}_5$); 2.48, 1.83 ($>\mathrm{NC_6H_3}(\mathit{Me})\mathit{CH}_2$-)	122.4, 120.6, 11.7, 11.3 ($\mathit{C}_5\mathit{Me}_5$); 65.7 ($>\mathrm{NC_6H_3(Me)}\mathit{C}\mathrm{H_2}$-); 21.7 ($>\mathrm{NC_6H_3}(\mathit{Me})\mathrm{CH_2}$-)

[a] Spin-spin coupling constants in Hz



Scheme 3. Proposal for a concerted mechanism. [Ti] = Ti(η^5-C$_5$Me$_5$).

magnetic anisotropy of the amido-nitrogen lone pair, which affects nearby atoms, must be taken into account to explain these results. This places the methyl group in the *endo* position and does not support the proposed mechanism.

In complexes **3**, **5**, **7**, and **9**, the more shielded protons of the μ-CH$_2$ ligands exhibit a $\Delta\delta = 1.2$ ppm, while the less shielded show a $\Delta\delta = 0.34$ ppm. This difference allows us to assign the resonances between $\delta = 6.20$–6.54 to the *exo* protons.

Furthermore, single crystals of [{TiCp*(μ-O)}$_3$(μ-CHMe)-NPh$_2$] (**8**) obtained from a dilute hexane solution at 4 °C allowed us confirm the position of the methyl group in the μ-CHR fragment by X-ray structure analysis.

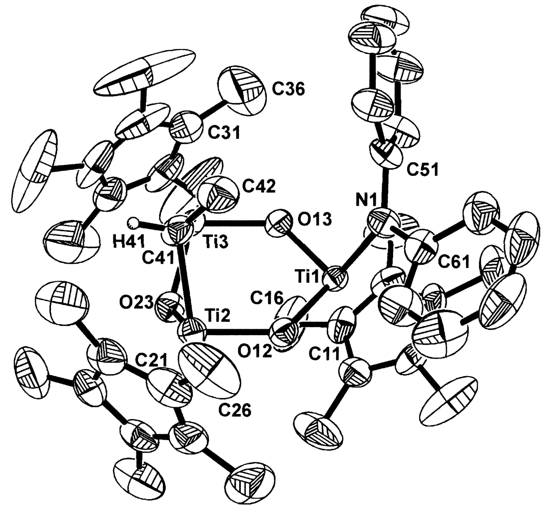


Figure 1. View of molecular structure of **8**.

Molecular structure of complex 8: The molecular structure and atom-labeling scheme of **8** are shown in Figure 1 and the most relevant geometrical parameters are summarized in Table 2. The structure of **8** reveals a trinuclear species, in which an ethylidene group bridges two titanium atoms and a diphenylamido ligand is located on the third metal center. The atom O23 is located 1.11 Å below the plane formed by Ti3, O13, Ti1, O12, and Ti2.[10] Also, a bridging ethylidene group, an amido ligand, and two Cp* groups are situated above this plane, while the third Cp* ligand lies below it.

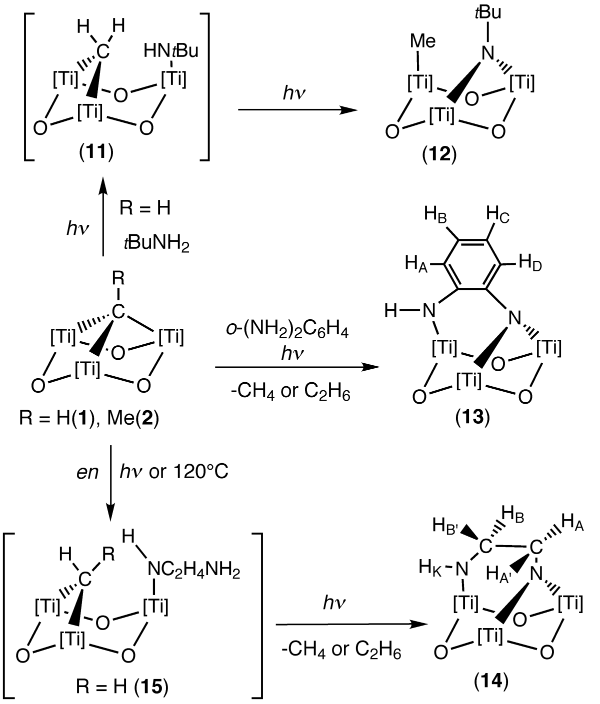
The environment of each titanium atom can be considered as pseudotetrahedral. The average Ti–Cp* (2.07 Å) and Ti–O (1.84 Å) bond lengths are very similar to those found in **2**[1a] and other trinuclear oxo complexes.[11, 12, 7a] The Ti2 ··· Ti3 bond length is approximately 0.5 Å smaller than the distances Ti1 ··· Ti3 and Ti1 ··· Ti2 in the same molecule, and this difference can be attributed to the bridging ethylidene group as was the difference of 0.2 Å in the analogous bond lengths in [{TiCp*(μ-O)}$_3$(μ-SO$_4$)Cl][12] and [{TiCp*(μ-O)}$_3${μ_3-η^2-CC-(Me)N(2,6-Me$_2$C$_6$H$_3$)}];[4] these were also assigned to the bridging ligands. The Ti3-O23-Ti2 angle (99.4(1)°) is smaller than the other Ti-O-Ti angles (128.0(19), 126.7(1)), which are comparable to those reported for other trinuclear titanium species, in which the metal centers are not bridged by chelating ligands.[11]

The bridging ethylidene group shows that the C41 atom is in a tetrahedral environment and almost equidistant between the two titanium centers. The Ti–C41 (av 2.11(4) Å) bond length is in the expected range observed for Ti$^{\mathrm{IV}}$–C(sp^3) bond lengths, not only in trinuclear species[1a, 11a,d] but also in mononuclear [TiCp*Me$_3$] (2.11 Å),[13] dinuclear [{TiCp*-Me(η^2-MeNNCPh$_2$)}(μ-O)(TiCp*Me$_2$)] (2.11 Å),[14] and tetranuclear [Ti$_4$Cp*$_4$O$_5$Me$_2$] (2.11 Å)[15] systems. The C41–C42

Table 2. Selected distances [Å] and angles [°] for complex **8**.[a]

Ti1−O13	1.812(2)	Ti3−O23	1.842(3)
Ti1−O12	1.835(2)	Ti3−O13	1.848(3)
Ti1−N1	2.008(3)	Ti3−C41	2.123(4)
Ti1 ··· Ti3	3.271(1)	N1−C61	1.410(5)
Ti1 ··· Ti2	3.305(1)	N1−C51	1.420(5)
Ti2−O23	1.836(3)	C41−C42	1.504(6)
Ti2−O12	1.842(3)	Ti1−Cp*1	2.094
Ti2−C41	2.114(4)	Ti2−Cp*2	2.068
Ti2 ··· Ti3	2.803(1)	Ti3−Cp*3	2.063
C41−H41	0.89(5)		
O13-Ti1-O12	103.4(1)	Ti2-O23-Ti3	99.3(1)
O13-Ti1-N1	102.1(1)	Ti2-C41-Ti3	82.8(1)
O12-Ti1-N1	104.0(1)	N1-C61-C66	121.3(4)
O23-Ti2-O12	104.1(1)	Cp*1-Ti1-N1	119.1
O12-Ti2-C41	98.5(1)	Cp*1-Ti1-O12	112.4
O23-Ti3-O13	104.4(1)	Cp*1-Ti1-O13	114.2
O23-Ti3-C41	84.2(1)	Cp*2-Ti2-O12	120.8
Ti2-Ti3-Ti1	65.4(1)	Cp*2-Ti2-O23	124.7
C61-N1-C51	116.1(3)	Cp*2-Ti2-C41	116.0
C51-N1-Ti1	119.6(2)	Cp*3-Ti3-O13	120.7
C61-N1-Ti1	124.3(3)	Cp*3-Ti3-O23	123.4
Ti1-O12-Ti2	128.0(1)	Cp*3-Ti3-C41	115.7
C42-C41-Ti3	126.4(3)	C42-C41-Ti2	120.8(3)
H41-C41-Ti2	108.9(30)	C52-C51-N1	122.0(4)
Ti1-O13-Ti3	126.7(1)	H41-C41-Ti3	105.3(30)
Cp*3-Ti3-C41	115.6	H41-C41-C42	109.4(32)

[a] Cp* are the centroids of the C_5Me_5 rings.



Scheme 4. Reactivity of **1** and **2** with tertbutylamine and diamines.

bond length of 1.520(7) Å is comparable to a single C−C (1.54 Å) bond.[16]

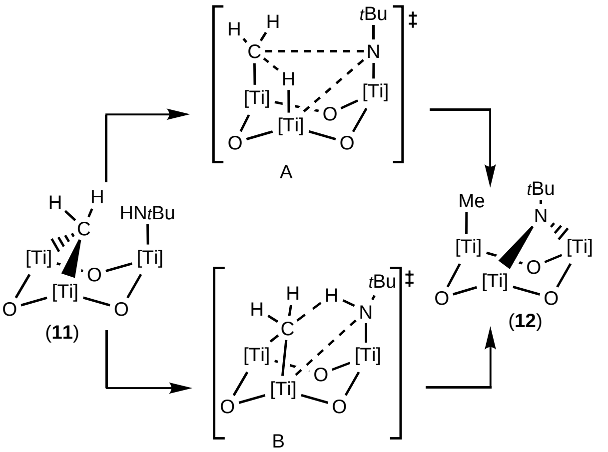
The diphenylamido ligand, which is located in the other extreme of the molecule, exhibits a Ti1−N1 bond length of 2.007(4) Å, which is similar to those found in other titanium complexes in which a single bond Ti−N is proposed, $[\mathrm{Ti^{III}Cp^*_2(NMePh)}]$ (2.054(2) Å)[17] and $[\mathrm{(CO)_5W\{C(NMe_2)O\}TiCp^*(NMe_2)_2}]$ (av 2.056 Å).[18]. This nitrogen atom (N1) has a planar environment (sum of angles 360°) with bond lengths (N1−C51 1.417(6), N1−C61 1.407(6) Å) that are slightly longer than that for $C(sp^2)-N(sp^2)$ bonds (1.36 Å).[16] The two rings of the amido ligand form an angle of 113.1(2)°.

Complex **8**, which is obtained by a transfer hydrogenation reaction in a 1,2-addition of the amine unit onto one of the three Ti-μ_3-C bonds, constitutes the first d^0 organometallic oxide supporting an alkylidene fragment to be characterized by X-ray diffraction studies.

The reaction of the μ_3-methylidyne complex **1** with *tert*-butylamine (Scheme 4) was monitored by ^1H NMR spectroscopy. Signals attributed to $[\{\mathrm{TiCp^*}(\mu\text{-O})\}_3(\mu\text{-CH}_2)(\mathrm{HN}t\mathrm{Bu})]$ (**11**) were observed after 30 min of irradiation with an ultraviolet lamp. The spectrum contained an AB spin system at $\delta = 6.53$ and 6.02 ($^2J = 9.3$ Hz), attributed to a methylene group bridging two titanium atoms, and a narrow signal at $\delta = 6.10$, which arises from the *H*N*t*Bu amido group.

After one hour, a resonance at $\delta = 0.56$, which was assigned to a methyl group bound to a titanium atom, was detected. After several hours, complete transformation of complex **11** into $[\{\mathrm{TiCp^*}(\mu\text{-O})\}_3(\mu\text{-N}t\mathrm{Bu})\mathrm{Me}]$ (**12**) had occurred. The IR spectrum of compound **12** contains a band at 1186 cm^{-1} that, in agreement with the literature, can be assigned to the stretching mode of $C-N_{imido}$: $[\{\mathrm{TiCpCl}\}_2(\mu\text{-N}t\mathrm{Bu})_2]$ (1160 cm^{-1}, nujol),[19] $[\{\mathrm{TiCp'F}(\mu\text{-N}t\mathrm{Bu})\}_2]$ (1180 cm^{-1}, CsI),[20] $[\mathrm{Ti_2\{MeC(NC_6H_{11})_2\}_2(\mu\text{-N}\mathit{t}Bu)_2Cl_2}]$ (1195, 1185 cm^{-1}, nujol).[21]

The transformation of **11** into **12**, which may be considered as the second step of a sequential transfer hydrogenation process, suggests that the migration of a hydrogen atom from the amido ligand to the μ-methylidene group occurs by a hydride (A) or a concerted (B) transition state mechanism (Scheme 5).



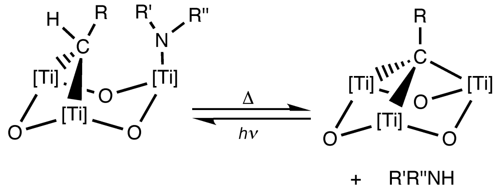
Scheme 5. Possible ways of transformation of **11** into **12**. [Ti] = Ti(η^5-C_5Me_5).

With the results of the reactions of **1** or **2** with simple amines in hand, we decided to study their reaction with diamines. Solutions of complexes **1** and **2** with o-$C_6H_4(NH_2)_2$ and $H_2NCH_2CH_2NH_2$ (en) in hexane were exposed to light from a solar lamp or, as in the case of **1** with en, heated at 120 °C. The reactions were monitored by ^1H NMR spectroscopy. Both μ_3-alkylidyne complexes are driven to the final products, [{TiCp*(μ-O)}$_3$(μ-η^2-NC$_6$H$_4$NH)] (**13**) and [{TiCp*(μ-O)}$_3$(μ-η^2-NC$_2$H$_4$NH)] (**14**), by methane or ethane elimination, respectively (see Scheme 4). These reactions, in which the μ_3-alkylidyne group is completely hydrogenated, can be considered as the ***final step*** in the sequential transfer hydrogenation processes mentioned above.

The IR spectra of these compounds confirm the presence of an amido group ($\tilde{\nu}_{st}$ N–H: 3380 (**13**), 3394 (**14**) cm^{-1}), and the EI-MS (70 eV) the corresponding molecular ions (*m*/*z* 702 (**13**), 654 (**14**)). The ^{1}H NMR spectra reveal two signals for Cp* in a 1:2 ratio, an ABCD spin system from the aromatic protons in **13**, and an AA′BB′K spin system attributable to the -NCH$_A$H$_{A'}$CH$_B$H$_{B'}$NH$_K$- moiety in **14** in accordance with C_s symmetry (see Table 1).

No intermediates were detected in the syntheses of complex **13**. However in the reaction of **1** with en, the intermediate complex [{TiCp*(μ-O)}$_3$(μ-CH$_2$)(HNC$_2$H$_4$NH$_2$)] (**15**) was detected (Scheme 4). Its ^{1}H NMR spectrum shows the presence of an AB spin system for the μ-CH$_2$ fragment, which is analogous to those found in the complexes **3**, **5**, **7**, **9**, and **11**; a broad signal at $\delta = 6.08$ which is assigned to the proton of the amido-nitrogen in Ti*H*N(CH$_2$CH$_2$NH$_2$); and two multiplets at $\delta = 3.70$ and 2.55 which are assigned to the methylene groups of the amido ligand. The terminal NH$_2$ was not detected in the spectrum.

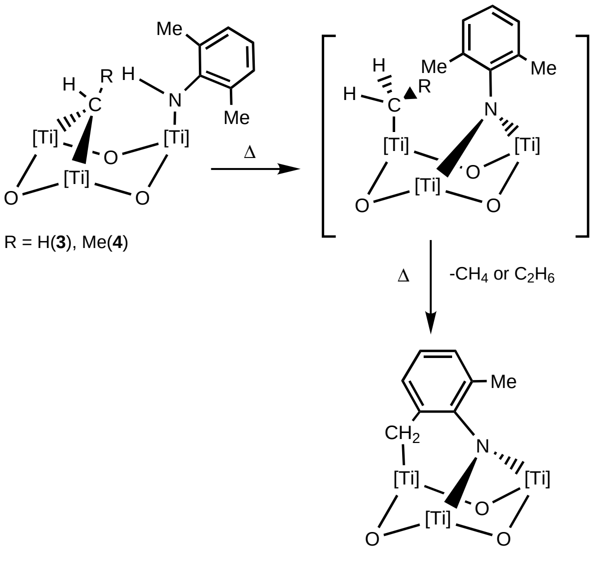
The thermal behavior between 170 and 220 °C of the compounds **3**–**11** and **14** in [D$_6$]benzene was inspected by NMR spectroscopy. The thermolysis of complexes **5**–**10** gives rise to the quantitative regeneration of the starting μ_3-alkylidyne compounds **1** and **2** and the corresponding amine (Scheme 6) or imine. This establishes the thermal reversibility of the transfer hydrogenation process for these compounds. Under similar condition reactions, the oxo derivatives **11**–**14** decompose to give a mixture of products from which only the tetranuclear species [{TiCp*}$_4$(μ-O)$_6$][1a] could be identified.



Scheme 6. Thermal treatment of complexes **5**–**8**. [Ti] = Ti(η^5-C$_5$Me$_5$).

Solutions of **3** and **4** in [D$_6$]benzene, or an equimolecular mixture of both, which are heated to over 170 °C, produce the oxo complex [{TiCp*(μ-O)}$_3${μ_3-η^2-NC$_6$H$_3$(Me)CH$_2$}] (**16**) by either methane or ethane elimination (Scheme 7). The pathway is similar in the first step to that described for the transformation of **11** into **12**. This is followed by the activation of a C–H bond from an aryl-imido methyl group and the elimination of the corresponding alkane.

The new derivative displays a triplet at $\delta = 65.7$ ($J = 118.3$ Hz) in the ^{13}C NMR spectrum that lies in a region typical for Ti–CH$_2$ resonances as those found for the trinuclear complex [{TiCp*(μ-O)(CH$_2$Ph)}$_3$] have been observed.[1a] The molecular ion was observed in the EI mass spectrum at *m*/*z* 715. The IR spectrum of the isolated complex **16** contains an absorption at 1222 cm^{-1} which is consistent with a C–N imido bond; a similar value has been reported for [(TiCpX)$_2$(μ-NPh)$_2$] (1230–1250 cm^{-1}, nujol).[19]



(**16**)

Scheme 7. Thermolysis of compounds **3** and **4**. [Ti] = Ti(η^5-C$_5$Me$_5$).

In summary, the photochemical reactions of μ_3-alkylidyne titanium(IV) complexes with amines, diamines, and the imine Ph$_2$C=NH can be considered as sequential transfer hydrogenation processes that occur under mild conditions on an organometallic oxide. The different steps of this process (alkylidene, alkyl, and alkane) have been identified. Also, thermal dehydrogenation of the μ-alkylidene groups to give the starting μ_3-alkilidyne compounds has been observed in some cases.

Experimental Section

General procedures: All syntheses and subsequent manipulation were carried out under argon by conventional Schlenk techniques or using a MBraun glovebox filled with argon.[22] All solvents were dried by usual methods and distilled under argon before use.[23] Compounds **1** and **2** were prepared according to previously reported procedures.[1] (2,6-Me$_2$C$_6$H$_3$)NH$_2$, Et$_2$NH, Ph$_2$NH, *t*BuNH$_2$, Ph$_2$CNH, *o*-C$_6$H$_4$(NH$_2$)$_2$, and H$_2$NCH$_2$CH$_2$NH$_2$ (en) were purchased from Aldrich and used after distillation or freshly sublimed.

Elemental analyses (C, H, N) were performed with a Heraeus CHN-O-RAPID and/or Perkin Elmer 240–C. Mass spectrometric analyses (Electron Impact, EI) were conducted at 70 eV on a Hewlett Packard 5988 spectrometer. IR spectra were obtained in KBr pellets by using a Perkin Elmer 883 and/or FT-IR Perkin Elmer SPECTRUM 2000 spectrophotometer. NMR spectra were recorded on Unity 300 or Unity Plus 500 spectrometers. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to TMS. Thermal reactions were carried out in a Roth autoclave model III (300 mL), with heater model 30 S (20 – 300 °C) and temperature regulator model DR 500.

[{TiCp*(μ-O)}$_3$(μ-CHR)(R′NR″)] (R″ = 2,6-Me$_2$C$_6$H$_3$, R′ = H, R = H (3), Me (4); R′ = R″ = Et, R = H (5), Me (6); R′ = R″ = Ph, R = H (7), Me (8)) and [{TiCp*(μ-O)}$_3$(μ-CHR)(N=CPh$_2$)] (R = H (9), R = Me (10)): These derivatives were prepared by the addition of the corresponding amine or imine 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 irradiated with an ultraviolet lamp for 4 h (**3**), 3 h (**4**, **5**), or 7 h (**6**), concentrated and cooled to 4°C. The products were obtained in high purity (> 95% by ^1H NMR spectroscopy). The preparation of **3** is reported as an example.

$[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}CH_2)\{HN(2,6\text{-}Me_2C_6H_3)\}]$ (3): A solution of **1** (0.60 g, 0.98 mmol) and $(2,6\text{-}Me_2C_6H_3)NH_2$ (0.12 mL, 1.05 mmol) in hexane (70 mL) was placed in a 100 mL Carious tube. The pressure of argon was reduced slightly and the reaction mixture irradiated with an ultraviolet lamp for 4 h. The red solution was concentrated (40 mL) and cooled to 4°C. This gave **3** as a reddish orange microcrystalline solid. Yield: 0.26 g, 36%; IR (KBr): $\tilde{\nu} = 3335$ (w), 2909 (s), 1431 (m), 1374 (s), 1029 (m), 753 (vs) cm^{-1}; MS (70 eV, EI): m/z (%): 612 (15) $[M - (2,6\text{-}Me_2C_6H_3)N]^+$, 598 (5) $[M - (2,6\text{-}Me_2C_6H_3) - (CH)]^+$, 611 (17) $[M - (2,6\text{-}Me_2C_6H_3)]^+$; elemental analysis calcd (%) for $Ti_3O_3NC_{39}H_{57}$ ($M_T = 731.49$): C 64.03, H 7.85, N 1.91; found: C 64.36, H 8.22, N 1.91.

$[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}CHMe)\{HN(2,6\text{-}Me_2C_6H_3)\}]$ (4): The reaction of **2** (0.60 g, 0.96 mmol) and $(2,6\text{-}Me_2C_6H_3)NH_2$ (0.12 mL, 1.00 mmol) in hexane gave **4** as a reddish orange microcrystalline solid. Yield: 0.34 g (46%). IR (KBr): $\tilde{\nu} = 3342$ (w), 2910 (s), 1436 (s), 1376 (s), 1024 (m), 748 (vs) cm^{-1}; MS (70 eV, EI): m/z (%): 624 (1) $[M - (2,6\text{-}Me_2C_6H_3)NH_2]^+$, 597 (1) $[M - (2,6\text{-}Me_2C_6H_3) - (C_2H_4)]^+$; elemental analysis calcd (%) for $Ti_3O_3NC_{40}H_{59}$ ($M_T = 745.51$): C 64.43, H 7.97, N 1.87; found: C 63.99, H 7.85, N 1.62.

$[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}CH_2)(NEt_2)]$ (5): The reaction of **1** (0.60 g, 0.98 mmol) with Et_2NH (0.10 mL, 0.98 mmol) in hexane gave **5** as a dark orange microcrystalline solid. Yield: 0.47 g (70%). IR (KBr): $\tilde{\nu} = 2911$ (s), 1480 (w), 1440 (w), 1373 (s), 1023 (m), 746 (vs) cm^{-1}; MS (70 eV, EI): m/z (%): 613 (5) $[M - C_3H_5]^+$, 612 (14) $[M - (EtN) - (C_2H_4)]^+$, 597 (1) $[M - (Et_2N) - (CH_2)]^+$; elemental analysis calcd (%) for $Ti_3O_3NC_{35}H_{57}$ ($M_T = 683.45$): C 61.50, H 8.41, N 2.05; found: C 61.85, H 8.42, N 1.51.

$[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}CHMe)(NEt_2)]$ (6): The reaction of $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}CMe)]$ (**2**) (0.80 g, 1.28 mmol) and Et_2NH (0.20 mL, 1.93 mmol) in hexane gave **6** as a dark red microcrystalline solid. Yield: 0.72 g (80%). IR (KBr): $\tilde{\nu} = 2923$ (s), 1497 (w), 1440 (s), 1370 (s), 740 (vs) cm^{-1}; MS (70 eV, EI): m/z (%): 613 (77) $[M - (2Et) - (C_2H_2)]^+$, 612 (30) $[M - (Et_2N) - (CH)]^+$, 611 (26) $[M - (2Et) - (C_2H_4)]^+$; elemental analysis calcd (%) for $Ti_3O_3NC_{36}H_{59}$ ($M_T = 697.47$): C 61.98, H 8.52, N 2.01; found: C 61.57, H 8.34, N 1.67.

$[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}CH_2)(NPh_2)]$ (7): A solution of **1** (0.80 g, 1.31 mmol) and Ph_2NH (0.25 g, 1.49 mmol) in hexane (100 mL) was placed in a 150 mL Carious tube. The argon pressure was reduced and the reaction mixture irradiated with a sun lamp for 72 h. The solution was concentrated and cooled to 4°C to give **7** as a red microcrystalline solid. Yield 0.78 g (76%). IR (KBr): $\tilde{\nu} = 2909$ (s), 1432 (m), 1374 (s), 1027 (m), 756 (vs) cm^{-1}; MS (70 eV, EI): m/z (%): 779 (2) $[M]^+$, 611 (100) $[M - (Ph_2N)]^+$, 610 (45) $[M - (Ph_2NH)]^+$; elemental analysis calcd (%) for $Ti_3O_3NC_{43}H_{57}$ ($M_T = 779.53$): C 66.25, H 7.37, N 1.79; found: C 66.18, H 7.48, N 1.96.

$[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}CHMe)(NPh_2)]$ (8): The compound **8** was prepared similarly to **7** from 0.40 g (0.64 mmol) of $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}CMe)]$ (**2**) and Ph_2NH (0.12 g, 0.71 mmol) in hexane (60 mL) irradiating with a sun lamp during four days to give red crystals suitable for X-ray diffraction analysis. Yield: 0.42 g (83%). IR (KBr): $\tilde{\nu} = 2905$ (s), 1482 (s), 1432 (m), 1375 (m), 1028 (m), 755 (vs) cm^{-1}; MS (70 eV, EI): m/z (%): 793 (1) $[M]^+$, 625 (35) $[M - (Ph_2N)]^+$, 624 (17) $[M - (Ph_2NH)]^+$, 613 (13) $[M - (2Ph) - (C_2H_2)]^+$, 597 (46) $[M - (Ph_2N) - (C_2H_4)]^+$; elemental analysis calcd (%) for $Ti_3O_3NC_{44}H_{59}$ ($M_T = 793.55$): C 66.59, H 7.49, N 1.76; found: C 65.95, H 7.58, N 2.02.

$[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}CH_2)(N{=}CPh_2)]$ (9): Compound **1** (0.6 g, 0.98 mmol) was dissolved in hexane in a Carious tube, and the imine $Ph_2C{=}NH$ (165 µL, 0.98 mmol) was added. The pressure of argon was reduced and the solution was stirred and irradiated with an ultraviolet lamp for 8 h. The resulting reddish solution was filtered, concentrated and cooled to 4°C. After 72 h, red crystals were obtained and identified as complex **9**. Yield: 0.50 g (60%). IR (KBr): $\tilde{\nu} = 2907$ (s), 1639 (vs), 1374 (m), 1027 (m), 759 (vs), 674 (s), 627 (s) cm^{-1}; MS (70 eV, EI): m/z (%); 792 (17) $[M]^+$, 612 (35) $[M - Ph_2C{=}N]^+$; elemental analysis calcd (%) for $Ti_3O_3NC_{44}H_{57}$ ($M_T = 791.54$): C 66.76, H 7.26, N 1.77; found: C 66.59, H 7.29, N 1.77.

$[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}CHMe)(N{=}CPh_2)]$ (10): $Ph_2C{=}NH$ (161 µL, 0.96 mmol) was added to a red solution of **2** in hexane (60 mL) in a Carious tube. The solution was stirred under irradiation by a sun lamp for 96 h. The resulting solution was filtered, concentrated, and cooled to 4°C. The solvent was removed to leave **10** as a red solid. Yield: 0.65 g (73%). IR (KBr): $\tilde{\nu} = 2908$ (s), 1374 (m), 1027 (w), 753 (vs), 666 (s), 625 (s) cm^{-1}; MS (70 eV, EI): m/z (%); 806 (6) $[M]^+$, 624 (38) $[M - Ph_2C{=}N]^+$; attempts to obtain a satisfactory elemental analysis were unsuccessful.

$[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}CH_2)(HN\mathit{t}Bu)]$ (11): $\mathit{t}BuNH_2$ (6 µL, 0.06 mmol) was added to a solution of **1** (30 mg, 0.05 mmol) in $[D_6]$benzene (0.6 mL). The NMR tube was flame-sealed and irradiated with an ultraviolet lamp for 30 mins. The solution was studied by ^1H and ^{13}C NMR spectroscopy to detect and characterize the red compound **11** (See Table 1).

$[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}N\mathit{t}Bu)Me]$ (12): $\mathit{t}BuNH_2$ (0.12 mL, 1.18 mmol) was added to a solution of **1** (0.60 g, 0.98 mmol) in hexane (70 mL) in a Carious tube. The pressure of the argon was reduced and the green reaction mixture was irradiated with a sun lamp for 20 h. The color of solution became reddish, due to the formation of compound **11**, before it finally became dark green. Solvent was removed to give complex **12**. Yield: 0.57 g (85%). IR (KBr): $\tilde{\nu} = 2912$ (m), 1492 (w), 1438 (s), 1374 (s), 1186 (s), 1024 (m) cm^{-1}; MS (70 eV, EI): m/z (%): 477 (7) $[M - (\mathit{t}BuN) - (Cp^*)]^+$, 475 (7) $[M - (\mathit{t}BuNH_2) - (Cp^*)]^+$; attempts to obtain a satisfactory elemental analysis were unsuccessful.

$[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}\eta^2\text{-}NC_6H_4NH)]$ (13): In a Carious tube, $o\text{-}C_6H_4(NH_2)_2$ (0.18 g, 1.66 mmol) was added to a solution of **1** (1.00 g, 1.64 mmol) in hexane (150 mL). The argon pressure was reduced and the reaction mixture irradiated with a sun lamp for 12 h. The solution was concentrated and cooled to 4°C to give a reddish brown solid, **13**. Yield: 0.68 g, 59%; IR (KBr): $\tilde{\nu} = 3380$ (w), 2910 (s), 1490 (m), 1438 (s), 1374 (s), 1035 (w), 685 (vs) cm^{-1}; MS (70 eV, EI): m/z (%): 702 (6) $[M]^+$; elemental analysis calcd (%) for $Ti_3O_3N_2C_{36}H_{50}$ ($M_T = 702.40$): C 61.55, H 7.17, N 3.99; found: C 61.00, H 7.22, N 3.35.

$[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}\eta^2\text{-}NC_2H_4NH)]$ (14): $H_2NCH_2CH_2NH_2$ (en) (0.11 mL, 1.64 mmol) in hexane (5 mL) was added to a solution of **2** (1.00 g, 1.60 mmol) in hexane (100 mL) in a 150 mL Carious tube. The argon pressure was reduced and the reaction mixture heated overnight at 120°C in a silicon oil bath. The solution was concentrated and cooled to 4°C to give a reddish brown microcrystalline solid, **14**. Yield: 0.95 g (90%). IR (KBr): $\tilde{\nu} = 3394$ (w), 2910 (s), 1493 (m), 1436 (s), 1375 (s), 1024 (w), 707 (vs) cm^{-1}; MS (70 eV, EI): m/z (%): 654 (1) $[M]^+$; elemental analysis calcd (%) for $Ti_3O_3N_2C_{32}H_{50}$ ($M_T = 654.36$): C 58.73, H 7.70, N 4.28; found: C 58.94, H 7.94, N 3.67.

$[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}CH_2)(HNCH_2CH_2NH_2)]$ (15): $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}CH)]$ (**1**) (30 mg, 0.05 mmol) and $H_2NCH_2CH_2NH_2$ (en) (6 µL, 0.06 mmol) in $[D_6]$benzene (0.60 mL) were transferred to a NMR tube (5 mm). The tube was sealed in vacuum and irradiated with an ultraviolet lamp for several minutes. Compound **15** was detected by NMR spectroscopy.

Thermal treatment of complexes 3 and 4: Thermal treatment of complexes **3** and **4** led to the formation of the compound $[\{TiCp^*(\mu\text{-}O)\}_3\{(\mu_3\text{-}\eta^2\text{-}NC_6H_3(Me)CH_2\}]$ (**16**) in both cases. A solution of $[\{TiCp^*(\mu\text{-}O)\}_3(\mu\text{-}CH_2)\{HN(2,6\text{-}Me_2C_6H_3)\}]$ (**3**) in hexane (50 mL) was transferred by cannula into a 100 mL Carious tube and then flame-sealed under vacuum. The solution was heated in an autoclave at 195°C for 12 h. The Carious tube was opened in a glovebox and the solution inside concentrated and cooled to 4°C to yield a dark red microcrystalline solid, **16**. Yield: 0.59 g (86%). IR (KBr): $\tilde{\nu} = 2911$ (s), 1490 (w), 1434 (m), 1374 (s), 1222 (s), 1025 (m), 716 (vs) cm^{-1}; MS (70 eV, EI): m/z (%): 715 (1) $[M]^+$, 701 (2) $[M - (CH_2)]^+$, 700 (1) $[M - (CH_3)]^+$, 612 (1) $[M - (NC_6H_3CH_2)]^+$, 611 (1) $[M - (MeC_6H_3CH_2)]^+$, 610 (1) $[M - (HNC_6H_3)]^+$; elemental analysis calcd (%) for $Ti_3O_3NC_{38}H_{53}$ ($M_T = 715.44$): C 63.79, H 7.47, N 1.96; found: C 63.54, H 7.70, N 1.62.

X-ray structure determination of 8: The single crystals used, red cubes, were obtained from a diluted hexane solution at 4°C. Table 3 provides a summary of the crystal data, data collection, and refinement parameters for complex **8**. Data were collected on an Enraf Nonius CAD 4 diffractometer at room temperature. Intensity measurements were performed by $\omega - 2\theta$ scans in the range $6° < 2\theta < 50°$ for **8**. Of the 7694 measured reflections for **8**, 7341 were independent; $R1 = 0.053$ and $wR2 = 0.148$ (for 5023 reflections with $F > 4\sigma(F)$). The values of $R1$ and $wR2$ are defined as $R1 = \Sigma||F_0| - |F_c||/[\Sigma|F_0|]$; $wR2 = \{[\Sigma w(F_0^2 - F_c^2)^2]/[\Sigma w(F_0^2)^2]\}^{1/2}$. The structure was solved, using the WINGX package,[24] by direct methods (SHELXS-97) and refined by least-squares against F^2 (SHELXL-97).[25] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned geometrically and refined by a riding model in the last cycles of refinement (except for H41 which was directly located and refined isotropically).

Table 3. Crystal data and structure refinement for complex **8**.

empirical formula	$C_{44}H_{59}NO_3Ti_3$
formula weight	793.62
temperature [K]	293(2)
wavelength ($Mo_{K\alpha}$)	0.71073 Å (graphite monochromator)
crystal system; space group	monoclinic; $P2_1/n$
a [Å]	12.585(4)
b [Å]; β[°]	19.829(3); 92.29(2)°
c [Å]	16.813(4)
V [Å^3]; Z	4192(2); 4
ρ_{calcd} [gcm^{-3}]	1.257
absorption coefficient [mm^{-1}]	0.595
F(000)	1680
crystal size [mm]	0.30 × 0.28 × 0.25 mm
diffractometer	Enraf Nonius CAD-4
scan mode; θ range	$\omega-2\theta$; 3–25°
index ranges	$0 \leq h \leq 14$, $0 \leq k \leq 23$, $-19 \leq l \leq 19$
collected reflections	7694
independent reflections	7341
observed reflections [$F > 4\sigma(F)$]	5023
goodness-of-fit on F^2	0.919
final R indices [$F > 4\sigma(F)$]	$R1 = 0.053$; $wR2 = 0.148$
R indices (all data)	$R1 = 0.097$; wR2 = 0.179
weighting scheme (calcd)	$w = 1/[\sigma^2(F_o^2) + (0.119P)^2 + 3.808P]$, where $P = (F_o^2 + 2F_c^2)/3$
largest diff. peak and hole [eÅ^{-3}]	0.694 and −0.475

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-164854. 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; deposit@ccdc.cam.ac.uk).

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