Organotitanium Oxides as Lewis Acidic Supports of Metal Carbonyl Species: $[\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}O)_3Me\}\{(\mu\text{-}OC)M(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ (M = Mo, W)

Román Andrés, Mijail Galakhov, Avelino Martín, Miguel Mena* and Cristina Santamaría

Departamento de Química Inorgánica de la Universidad de Alcalá de Henares, E-28871 Alcalá de Henares, Madrid, Spain

Reaction of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CH)]$ **1** with $[M(\eta^5\text{-}C_5H_5)(CO)_3H]$ (M = Mo, W) leads to the formation of Lewis acid carbonyl adducts $[\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}O)_3Me\}\{(\mu\text{-}OC)M(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ **4**, **5** showing the transformation of the μ_3-methylidyne group into a Me group through the μ-methylene intermediates $[\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}O)_3(\mu\text{-}CH_2)\}(\mu\text{-}OC)M(CO)_2(\eta^5\text{-}C_5H_5)]$ **2**, **3**.

Early–middle/late transition metal heterobimetallic complexes are very interesting substrates to study the cooperative activation of small molecules such as carbon monoxide in homogeneous catalytic processes. To date, Group 4 complexes of this type incorporate mono- or di-nuclear units, with electron-deficient metal(s), linked by bridging ligands or metal–metal bonds to other moieties, which contain one or more low-valent metals; however, there are no examples containing trinuclear oxophilic metal fragments.[1] We report here the preparation of heterobimetallic complexes by generation of a trinuclear organometallic oxide Lewis acid, with a TiO_2-like arrangement, in the reaction of a μ_3-alkylidyne of titanium(IV) with carbonyl metal hydrides.

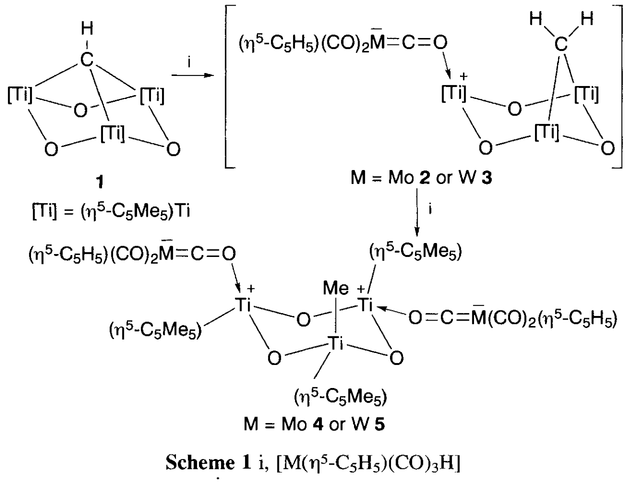
The reaction of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CH)]$ **1**[†] with 2 equiv. of $[M(\eta^5\text{-}C_5H_5)(CO)_3H]$ (M = Mo, W) in toluene, at 70 °C, leads to the formation (85–90% yield) of dark red complexes characterised as $[\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}O)_3Me\}(\mu\text{-}OC)M(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$[‡] (M = Mo **4**, W **5**, Scheme 1). The starting complex **1** was easily obtained in high yield by thermolysis of $[\{Ti(\eta^5\text{-}C_5Me_5)Me(\mu\text{-}O)\}_3]$, under analogous conditions to those used for the preparation of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CMe)]$.[2]

The spectroscopic and analytical data for complexes **4** and **5** are in agreement with the formulations given in Scheme 1. The IR spectra reveals a strong band at 1552 [Ti(μ-OC)Mo], and at 1554 cm^{-1} [Ti(μ-OC)W], assigned to the bridging carbonyl ligands. The ^1H and ^{13}C NMR spectra of these complexes show the clear presence of two inequivalent types of $\eta^5\text{-}C_5H_5$ groups in a 1 : 1 ratio and three different $\eta^5\text{-}C_5Me_5$ ligands (1 : 1 : 1) in accord with the structure suggested. Moreover, the ^{13}C NMR spectra at −50 °C show six signals for the CO ligands, two of them [δ 244.8, 244.0 (**4**); 239.6, 238.8 (**5**)] assigned to the CO bridges and the other four peaks [δ 232.6, 232.3, 232.2, 232.1 (**4**); 222.4, 221.9, 221.8, 221.7 (**5**)] to inequivalent terminal carbonyls. All these data suggest that the bonding in these complexes is similar to that described for the Lewis-acid adducts $[Ti(\eta^5\text{-}C_5Me_5)_2Me(\mu\text{-}OC)Mo(CO)_2(\eta^5\text{-}C_5H_5)]$[3] and $[Zr(\eta^5\text{-}C_5H_5)_2Me(\mu\text{-}OC)M(CO)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo, W).[4]

When the reactions are monitored conveniently by NMR, transformation of μ_3-CH into a terminal Me group is observed, presumably through the formation of $(Ti\text{–}O\text{–}Ti)(\mu\text{-}CH_2)$ complexes **2**, **3**[§] as outlined in Scheme 1. In the ^1H NMR spectra, the μ-methylene intermediates are characterized by AB spin systems at δ 6.63, 6.07, $^2J_{HH}$ 9.6 Hz, **2** and δ 6.62, 6.06, $^2J_{HH}$ 10.0 Hz, (**3**). On the other hand, if the ^{13}C labelled (55% ^{13}C) derivative $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}^{13}CH)]$ $[^{13}C_1]$ **1** and $[Mo(\eta^5\text{-}C_5H_5)(CO)_3H]$ are used, the ^{13}C NMR spectrum of the reaction (Fig. 1), in line with the above data, show the corresponding resonances of the $Ti_3(\mu_3\text{-}^{13}CH)$ (δ 383.2, d, $^1J_{CH}$ 139.2 Hz), $Ti_2(\mu\text{-}^{13}CH_2)$ (δ 198.1, t, $^1J_{CH}$ 126.9 Hz) and $Ti\text{–}^{13}CH_3$ (δ 51.0, q, $^1J_{CH}$ 124.5 Hz) groups of $[^{13}C_1]$ **1**, $[^{13}C_1]$ **2** and $[^{13}C_1]$ **4**, respectively.

A series of μ-methylene heterodinuclear titanium complexes have been reported by Tebbe *et al.*,[5] $\{[Ti(\eta^5\text{-}C_5H_5)_2\text{-}CH_2AlClMe_2]\}$ and by Grubbs and coworkers,[6] $\{Ti(\eta^5\text{-}C_5H_5)_2\text{-}ML_n(\mu\text{-}CH_2)(\mu\text{-}X)]$ (ML_n = late transition-metal chloride/methoxide complex}, but species analogous to **2** or **3**, containing the system $(Ti\text{–}O\text{–}Ti)(\mu\text{-}CH_2)$, had not been previously characterized.

Attempts to trap our proposed methylidene intermediates, and to obtain suitable single crystals for X-ray diffraction of the complexes $[\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}O)_3Me\}\{(\mu\text{-}OC)M(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$, under a variety of experimental conditions, were unsuccessful, but are continuing. Further studies to extend the scope of these reactions to other transition-metal hydrides and μ_3-alkylidynes, as well as studies on the reactivity of the products obtained, are under way.



Scheme 1 i, $[M(\eta^5\text{-}C_5H_5)(CO)_3H]$

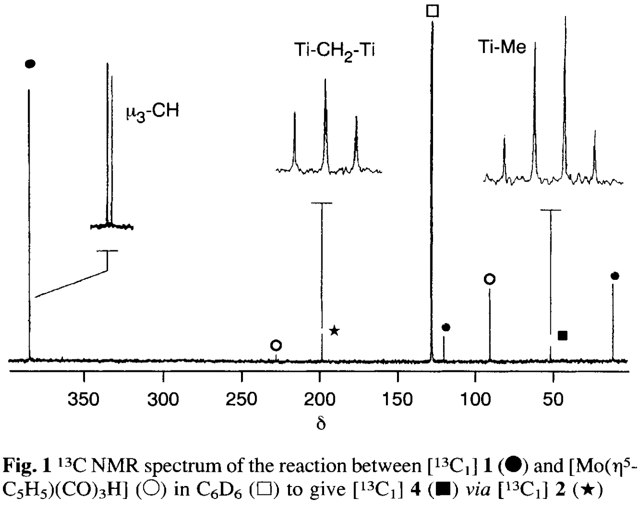


Fig. 1 ^{13}C NMR spectrum of the reaction between $[^{13}C_1]$ **1** (●) and $[Mo(\eta^5\text{-}C_5H_5)(CO)_3H]$ (○) in C_6D_6 (□) to give $[^{13}C_1]$ **4** (■) *via* $[^{13}C_1]$ **2** (★)

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Footnotes

† $[\{\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5Me_5})(\mu\text{-}\mathrm{O})\}_3(\mu_3\text{-}\mathrm{CH})]$ **1**: ^{1}H NMR (300 MHz, C_6D_6, 20 °C) δ 1.96 (s, 45H, C_5Me_5), 12.59 (s, 1H, CH). ^{13}C NMR (75 MHz, C_6D_6, 20 °C) δ 383.8 (d, $^1J_{CH}$ 138.2 Hz, CH), 119.8 (m, $\mathit{C}_5\mathrm{Me}_5$), 11.7 (q, $^1J_{CH}$ 125.6 Hz, $\mathrm{C}_5\mathit{Me}_5$). EI-MS, *m/z* (assignment, rel. inten.): 610 (M^+, 100%, correct isotope distribution). Satisfactory analytical data were obtained.

‡ $[\{\mathrm{Ti_3}(\eta^5\text{-}\mathrm{C_5Me_5})_3(\mu\text{-}\mathrm{O})_3\mathrm{Me}\}\{(\mu\text{-}\mathrm{OC})\mathrm{Mo(CO)_2}(\eta^5\text{-}\mathrm{C_5H_5})\}_2]$ **4**: ^{1}H NMR (500 MHz, C_7D_8, 25 °C) δ 5.28 (s, 5H, C_5H_5), 5.25 (s, 5H, C_5H_5), 2.09 (s, 15H, C_5Me_5), 2.08 (s, 15H, C_5Me_5), 1.87 (s, 15H, C_5Me_5), 0.71 (s, 3H, TiMe). ^{13}C{^{1}H} NMR (125 MHz, C_7D_8, −50 °C) δ 244.9, 244.1 (TiOCMo); 232.8, 232.41, 232.37, 232.31 [$\mathrm{Mo(CO)_2}$]; 129.4, 129.3, 124.4 ($\mathit{C}_5\mathrm{Me}_5$); 91.4, 91.1 ($C_5H_5$); 51.1 (TiMe); 12.8, 12.73, 12.66 ($\mathrm{C}_5\mathit{Me}_5$). IR (KBr) ν/cm^{-1} 1862s, 1552s br. Satisfactory analytical data were obtained.

$[\{\mathrm{Ti_3}(\eta^5\text{-}\mathrm{C_5Me_5})_3(\mu\text{-}\mathrm{O})_3\mathrm{Me}\}\{(\mu\text{-}\mathrm{OC})\mathrm{W(CO)_2}(\eta^5\text{-}\mathrm{C_5H_5})\}_2]$ **5**: ^{1}H NMR (500 MHz, C_7D_8, 25 °C) δ 5.21 (s, 5H, C_5H_5), 5.18 (s, 5H, C_5H_5), 2.10 (s, 15H, C_5Me_5), 2.08 (s, 15H, C_5Me_5), 1.86 (s, 15H, C_5Me_5), 0.67 (s, 3H, TiMe). ^{13}C{^{1}H} NMR (125 MHz, C_7D_8, −50 °C) δ 239.7, 238.9 (TiOCW); 222.4, 221.9, 221.8, 221.7 [$\mathrm{W(CO)_2}$]; 126.5, 121.6, 121.1 ($\mathit{C}_5\mathrm{Me}_5$); 88.7, 88.5 ($C_5H_5$); 49.2 (TiMe); 11.8, 11.7, 11.6 ($\mathrm{C}_5\mathit{Me}_5$). IR (KBr) ν/cm^{-1} 1862s; 1552s br. Satisfactory analytical data were obtained.

§ $[\{\mathrm{Ti_3}(\eta^5\text{-}\mathrm{C_5Me_5})_3(\mu\text{-}\mathrm{O})_3(\mu\text{-}\mathrm{CH_2})\}\{(\mu\text{-}\mathrm{OC})\mathrm{Mo(CO)_2}(\eta^5\text{-}\mathrm{C_5H_5})\}]$ **2**: ^{1}H NMR (300 MHz, C_6D_6, 25 °C) δ 6.63 (d, 9.6 Hz, 1H, $\mathrm{TiCH_2Ti}$), 6.07 (d, 9.6 Hz, 1H, $\mathrm{TiCH_2Ti}$), 5.37 (s, C_5H_5), 2.10 (s, 15H, C_5Me_5), 1.91 (s, 30H, C_5Me_5). $[\{\mathrm{Ti_3}(\eta^5\text{-}\mathrm{C_5Me_5})_3(\mu\text{-}\mathrm{O})_3(\mu\text{-}\mathrm{CH_2})\}\{(\mu\text{-}\mathrm{OC})\mathrm{W(CO)_2}(\eta^5\text{-}\mathrm{C_5H_5})]$ **3**: ^{1}H NMR (300 MHz, C_6D_6, 25 °C) δ 6.62 (d, 10.0 Hz, 1H, $\mathrm{TiCH_2Ti}$), 6.06 (d, 10.0 Hz, 1H, $\mathrm{TiCH_2Ti}$), 5.27 (s, C_5H_5), 2.13 (s, 15H, $\mathrm{C}_5\mathit{Me}_5$), 1.92 (s, 30H, $\mathrm{C}_5\mathit{Me}_5$).

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