

# Organometallic oxides: preparation of the heterometallic (cyclopentadienyl) titanium–molybdenum oxide cluster [( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Ti]<sub>2</sub>[( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)MoCl]( $\mu$ <sub>2</sub>-O)<sub>3</sub>( $\mu$ <sub>3</sub>-O)

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## Abstract

The reaction between ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti(CO)<sub>2</sub> and ( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)MoCl(O)<sub>2</sub> gave the heterometallic cluster [( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Ti]<sub>2</sub>[( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)MoCl]( $\mu$ <sub>2</sub>-O)<sub>3</sub>( $\mu$ <sub>3</sub>-O) (**1**). The formula and structure of **1** were proven by microanalysis, high resolution mass spectrometry, <sup>1</sup>H NMR and infrared spectroscopies. The two cluster electrons of diamagnetic **1** are localised in an orbital which is anti-bonding between the two titanium atoms.

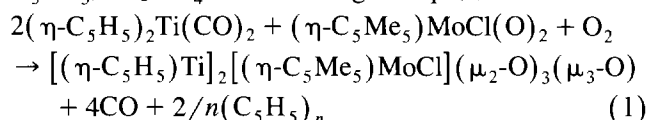
**Keywords:** Titanium; Molybdenum; Oxide clusters; Cyclopentadienyls

## 1. Introduction

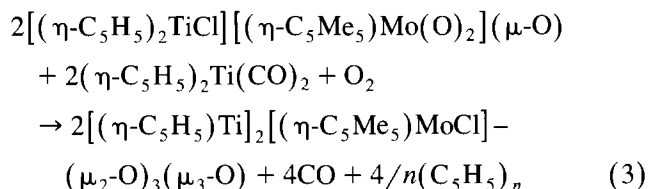
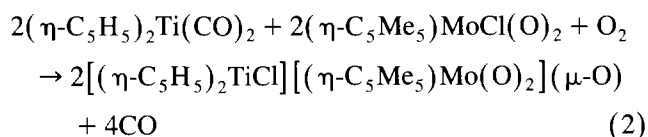
Organo-heterometallic oxides are of current interest as models for, and precursors to, heterometallic oxide catalysts [1–4]. Of particular relevance to work presented here is the preparation of several Group 4–Group 6 hetero-bimetallic oxo complexes, for example [( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>TiCl][( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)Mo(O)<sub>2</sub>]( $\mu$ -O), by Geoffroy and coworkers [4]. In these compounds the metal atoms are in their highest possible formal oxidation states (Ti<sup>IV</sup>, Mo<sup>VI</sup>), and therefore they contain no d-electrons. We have been searching for (cyclopentadienyl)heterometallic oxide clusters having cluster d-electrons. We report here the preparation of [( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Ti]<sub>2</sub>[( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)MoCl]( $\mu$ <sub>2</sub>-O)<sub>3</sub>( $\mu$ <sub>3</sub>-O), which contains two cluster electrons.

## 2. Results and discussion

The reaction between ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti(CO)<sub>2</sub> and ( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)MoCl(O)<sub>2</sub> gave green [( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Ti]<sub>2</sub>[( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)Mo]ClO<sub>4</sub> (**1**) according to Eq. (1).



A minor product was the orange-red [( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>TiCl][( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)Mo(O)<sub>2</sub>]( $\mu$ -O) (**2**) previously described by Geoffroy and coworkers [4] (Eq. (2)). It is possible that **2** is an intermediate in the formation of **1** via reaction 3.

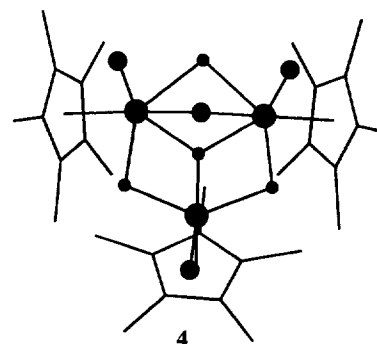
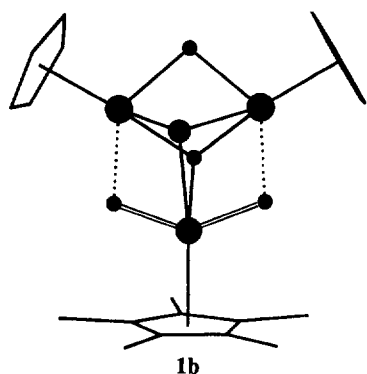
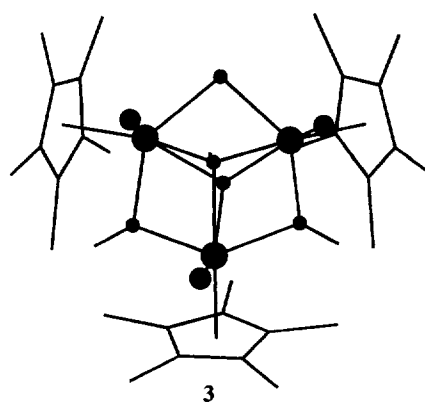
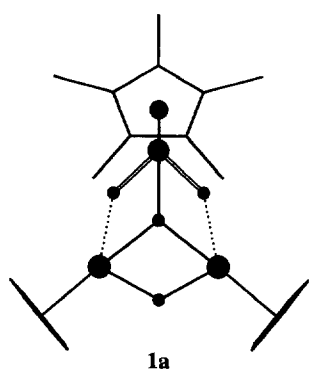
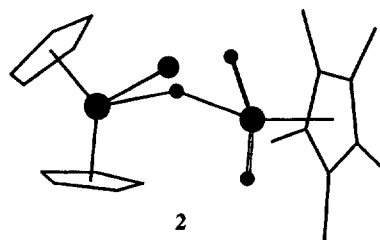


The empirical formula (C<sub>20</sub>H<sub>25</sub>ClMoO<sub>4</sub>Ti<sub>2</sub>) of **1** was proven by microanalysis and high- and low-resolution mass spectrometry. The structure was proven by <sup>1</sup>H NMR and infrared spectroscopies, and by the diamagnetism of **1**. The <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub> solution) showed two sharp singlets, at 6.01 ppm, assigned to the protons of  $\eta$ -C<sub>5</sub>H<sub>5</sub>, and at 1.88 ppm assigned to the protons of  $\eta$ -C<sub>5</sub>Me<sub>5</sub>. The relative integration of the two signals was 1:1.58, showing that there are two equivalent  $\eta$ -C<sub>5</sub>H<sub>5</sub> ligands for each  $\eta$ -C<sub>5</sub>Me<sub>5</sub>. The infrared spectrum showed four moderately intense absorptions between 900 and 700 cm<sup>-1</sup> (889, 852, 814 and

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772  $\text{cm}^{-1}$ ). There were no absorption bands in the  $\nu(\text{OH})$  or  $\nu(\text{CO})$  regions of the spectrum. The band at 814  $\text{cm}^{-1}$  was assigned to  $\pi(\text{C}-\text{H})$  of  $\eta\text{-C}_5\text{H}_5$ . The two bands at higher frequency (889 and 852  $\text{cm}^{-1}$ ) were assigned to the symmetric and anti-symmetric vibrations of an  $[\text{M}(\text{O})_2]$  unit, and the band at 772  $\text{cm}^{-1}$  was assigned to a  $\text{Ti}_2\text{OMo}$  vibration, following the assignments of Geoffroy and coworkers [4]. The spectra show that the structure of  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ti}]_2[(\eta\text{-C}_5\text{Me}_5)\text{MoCl}](\mu_2\text{-O})_3(\mu_2\text{-O})$  is **1a**. The notation  $\text{Mo}=\text{O} \cdots \text{Ti}$  is used to indicate a very asymmetric interaction, as found in  $[(\eta\text{-C}_5\text{H}_5)_2\text{Zr}][(\eta\text{-C}_5\text{Me}_5)\text{W}(\text{O})_2(\mu\text{-O})_2]$ , in which the  $\text{W}=\text{O}$  distances were 1.72 Å, the  $\text{W}-\text{O}$  distance was 1.86 Å and the  $\text{Zr}-\text{O}$  distance was 2.00 Å [4].

$\text{Ti}_2\text{Mo}$  and  $(\mu_2\text{-O})_3$  planes are separated by 0.85 Å. In either case the plane of symmetry through the  $(\eta\text{-C}_5\text{Me}_5)\text{MoCl}$  unit which bisects the  $(\eta\text{-C}_5\text{H}_5)\text{Ti}$  units must be maintained.



There are several zirconium, niobium and tantalum oxides with structures related to **1a** [5–10], for example  $\{[(\eta\text{-C}_5\text{Me}_5)\text{TaCl}]_3(\mu_2\text{-OH})(\mu_2\text{-O})_2(\mu_3\text{-OH})(\mu_3\text{-O})\}^+$  (**3**) [5]. These compounds show subtle differences in the mode of bonding of the chloride (terminal, doubly-, or triply-bridging) and oxide (doubly-, or triply-bridging ligands). Examples are **3** and  $[(\eta\text{-C}_5\text{Me}_5)\text{NbCl}]_3(\mu_2\text{-O})_3(\mu_2\text{-Cl})(\mu_3\text{-O})$  (**4**) [8]. Assuming that such subtleties are shown by  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ti}]_2[(\eta\text{-C}_5\text{Me}_5)\text{MoCl}](\mu_2\text{-O})_3(\mu_3\text{-O})$ , structures such as **1b** may be present. In **1a** the  $[\text{Ti}_2\text{Mo}(\mu_2\text{-O})_3]$  unit is planar, whereas in **1b** the

Extended Hückel molecular orbital calculations were performed on  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ti}]_2[(\eta\text{-C}_5\text{H}_5)\text{MoCl}](\mu_2\text{-O})_3(\mu_3\text{-O})$  with structures **1a** and **1b**. In both cases the  $\text{Mo}-\text{O}$  distance was 1.70 Å, the  $\text{Ti}-\text{O}$  distance 2.10 Å. The calculations showed that the HOMO of the cluster was largely localised on the titanium atoms, and represented an anti-bonding interaction between these atoms (Fig. 1(a) Fig. 1(b)). Thus **1** can be described as formally containing  $\text{Ti}^{\text{III}}\text{Mo}^{\text{VI}}$ , which is in accord with its green color. The HOMO–LUMO energy difference was

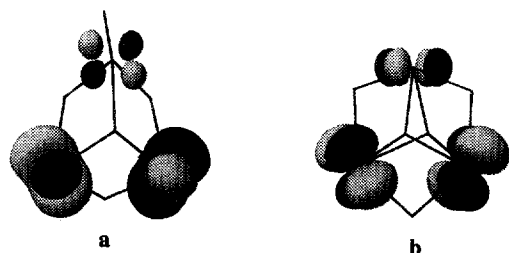


Fig. 1. The HOMO orbital of (a)  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ti}][(\eta\text{-C}_5\text{H}_5)\text{MoCl}](\mu_2\text{-O})_3(\mu_3\text{-O})$  and (b)  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ti}][(\eta\text{-C}_5\text{H}_5)\text{Mo}](\mu_2\text{-O})(\mu_3\text{-Cl})(\mu_3\text{-O})$ .

0.189 eV for **1a** and 0.028 eV for **1b**. Since **1** is diamagnetic, the large HOMO–LUMO gap suggests that **1a** is the correct structure. The fact that the most intense ion in the mass spectrum is  $[\text{M–Cl}]^+$  is also in accord with the presence of the terminal chloride ligand in **1a**.

### 3. Experimental

The starting materials  $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$  and  $(\eta\text{-C}_5\text{Me}_5)\text{MoCl}(\text{O})_2$  were prepared by literature methods [11,12]. Microanalyses were performed by Beller Laboratory, Göttingen, Germany. NMR spectra were obtained on a Varian XL200 instrument, infrared spectra on a Perkin–Elmer 683, and mass spectra on a Kratos MS50 at 70 eV. Extended Hückel calculations used the CAChe suite of programs.

#### 3.1. Synthesis of $[(\eta\text{-C}_5\text{H}_5)_2\text{Ti}][(\eta\text{-C}_5\text{Me}_5)\text{MoCl}](\mu_2\text{-O})_3(\mu_3\text{-O})$ (**1**)

A solution of  $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$  (0.98 g, 4.2 mmol) in toluene ( $100\text{ cm}^3$ ) was added to solid  $(\eta\text{-C}_5\text{Me}_5)\text{MoCl}(\text{O})_2$  (0.88 g, 2.99 mmol). The mixture was stirred at room temperature under argon for 18 h. Evolution of CO was observed. The mixture was filtered, giving a dark green residue and a dark red filtrate. The precipitate was dried under vacuum, then extracted with thf ( $100\text{ cm}^3$ ) for 12 h at room temperature. The resultant moss green precipitate of **1** was dried under vacuum. Yield 0.51 g, 43% based on titanium. Anal. Found: C, 42.7; H, 4.4; Cl, 6.6.  $\text{C}_{20}\text{H}_{25}\text{ClMoO}_4\text{Ti}_2$  Calc.: C, 43.1; H, 4.5; Cl, 6.4%.  $^1\text{H}$  NMR (200 MHz,  $\text{C}_6\text{D}_6$  solution): 6.011 ppm ( $\text{C}_5\text{H}_5$ ); 1.880 ppm ( $\text{C}_5(\text{CH}_3)_5$ ). The relative intensities were 11.0:17.4 (1:1.58). IR

(Nujol mull, KBr plate):  $3100\text{ cm}^{-1}$ , vw ( $\nu(\text{C–H})$ ,  $\text{C}_5\text{H}_5$ );  $1018\text{ cm}^{-1}$ , vw ( $\vartheta(\text{C}_5\text{H}_5\text{ ring})$ );  $889\text{ cm}^{-1}$ , m and  $852\text{ cm}^{-1}$ , m ( $\vartheta_{\text{symm}}$  and  $\vartheta_{\text{asymm}}$  ( $\text{Mo}(\text{=O})_2$ );  $814\text{ cm}^{-1}$ , m ( $\pi(\text{C–H})$ ,  $\text{C}_5\text{H}_5$ );  $772\text{ cm}^{-1}$ , m ( $\text{Ti}_2\text{OMO}$  vibration);  $395\text{ cm}^{-1}$ , w ( $\nu(\text{C}_5\text{Me}_5\text{ ring})$  or  $\nu(\text{Mo–Cl})$ ). Mass spectrum (EI, low resolution): envelope of ions centered at  $m/e$  523,  $(\text{C}_{20}\text{H}_{25}\text{Ti}_2\text{MOO}_4)^+$ ,  $((\text{C}_5\text{H}_5)_2(\text{C}_5\text{Me}_5)\text{Ti}_2\text{MoO}_4)^+$ ; 429,  $(\text{C}_{15}\text{H}_{20}\text{MoTiO}_3\text{Cl})^+$ ,  $((\text{C}_5\text{H}_5)(\text{C}_5\text{Me}_5)\text{MoTiO}_3\text{Cl})^+$ ; 393,  $(\text{C}_{15}\text{H}_{20}\text{MoTiO}_3)^+$ ,  $((\text{C}_5\text{H}_5)(\text{C}_5\text{Me}_5)\text{MoTiO}_3)^+$ . Mass spectrum (EI, high resolution): observed 524.9924,  $(\text{C}_{20}\text{H}_{27}\text{MoTi}_2\text{O}_4)^+$ ,  $((\text{C}_5\text{H}_5)_2(\text{C}_5\text{Me}_5)\text{MoTi}_2\text{O}_4 + 2\text{H})^+$ , calculated 524.9930; 523.9966,  $(\text{C}_{20}\text{H}_{26}\text{MoTi}_2\text{O}_4)^+$ ,  $((\text{C}_5\text{H}_5)_2(\text{C}_5\text{Me}_5)\text{Ti}_2\text{MoO}_4 + \text{H})^+$  524.1172; 429.9715,  $(\text{C}_{15}\text{H}_{21}\text{MoTiO}_3\text{Cl})^+$ ,  $((\text{C}_5\text{H}_5)(\text{C}_5\text{Me}_5)\text{MoTiO}_3\text{Cl} + \text{H})^+$ , 429.9727.

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