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A mononuclear alkyne-stabilized Mo$^{(IV)}$O$_2$ moiety

Noelia Mansilla, Gerd Rheinwald, Heinrich Lang *

Technische Universität Chemnitz, Institut für Chemie, Lehrstuhl Anorganische Chemie, Straße der Nationen 62, D-09111 Chemnitz, Germany

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Abstract

Molybdenum(0) carbonyl complexes react with [Ti](C≡CSiMe$_3$)$_2$ {[Ti] = (η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti} in the presence of atmospheric oxygen to afford a novel alkyne-stabilized Mo$^{(IV)}$O$_2$ moiety. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Titanocenes; Alkyne; Molybdenum dioxide; Catalysis

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1. Introduction

In recent years, there has been considerable interest in the preparation, chemical and physical properties of molybdenum and tungsten complexes in high oxidation states [1]. In this respect, organometallic oxo species with one, two or even three oxygen atoms [2], oxo-peroxo [3], oxo-alkoxide [4] and oxo-halide complexes [5] are claimed to be model compounds for not only, e.g. olefin metathesis [6] and industrial oxidation processes [7], but also for oxygen transfer reactions in biological systems [8].

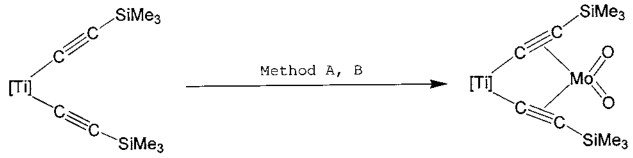
While the organometallic chemistry of Group VI oxides in the oxidation state +6 is well documented, only few examples in lower oxidation states are known [9]. To our knowledge, the existence of dioxo-M^{IV} complexes of this sort has only been observed in the formation of *trans*-M(CO)$_4$(O)$_2$ (M = Cr, Mo and W) by photooxidation of matrix-isolated M(CO)$_6$ [9a].

We report here the synthesis as well as structure and bonding, of the novel alkyne-stabilized Mo$^{(IV)}$O$_2$ complex {[Ti](C≡CSiMe$_3$)$_2$}MoO$_2$ {[Ti] = (η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti}.

2. Results and discussion

Reaction of [Ti](C≡CSiMe$_3$)$_2$ {[Ti] = (η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti} [10] (**1**) with stoichiometric amounts of Mo(CO)$_3$(CH$_3$C≡N)$_3$ (**2**) and subsequent oxidation by air in toluene at 25°C produces the alkyne-stabilized Mo$^{(IV)}$O$_2$ complex {[Ti](C≡CSiMe$_3$)$_2$}MoO$_2$ (**3**) in 43% yield.

Presumably, the first step in the synthesis of **3** is the formation of {[Ti](C≡CSiMe$_3$)$_2$}Mo(CO)$_4$ (**4**) as an intermediate, for which it is necessary to provide an extra carbonyl ligand. Thus, the preparation of **3** was optimized to 80% yield, when **1** was allowed to react with a two-fold excess of **2** under similar reaction conditions (Scheme 1). This result points to the fact that **4** is likely to be produced during the reaction of **1** with **2**. In order to prove this assumption, we reacted **1** with Mo(CO)$_4$(nbd) (nbd = norbornadiene) (**5**) in a 1:1 ratio under analogous conditions (vide supra) (Scheme 1). The course of the latter reaction was followed by IR spectroscopy. Since a typical CO absorption pattern for a *cis*-M(CO)$_4$ fragment (M = Cr, Mo, W), with four bands at 2030, 1933, 1921 and 1914 cm^{-1}, could be observed [11], the formation of **4** as intermediate is most likely.



1 **3**

Scheme 1. Preparation of {[Ti](C≡CSiMe$_3$)$_2$}MoO$_2$ (**3**). Method A: (i) Mo(CO)$_3$(CH$_3$C≡N)$_3$, toluene 25°C, (ii) O$_2$, 15 h. Method B: (i) Mo(CO)$_4$(nbd)$_3$, toluene 25°C, (ii) O$_2$, 20 h.

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* Corresponding author. Tel.: +49-371-5311200; fax: +49-371-5311833.

E-mail address: heinrich.lang@chemie.tu-chemnitz.de (H. Lang)

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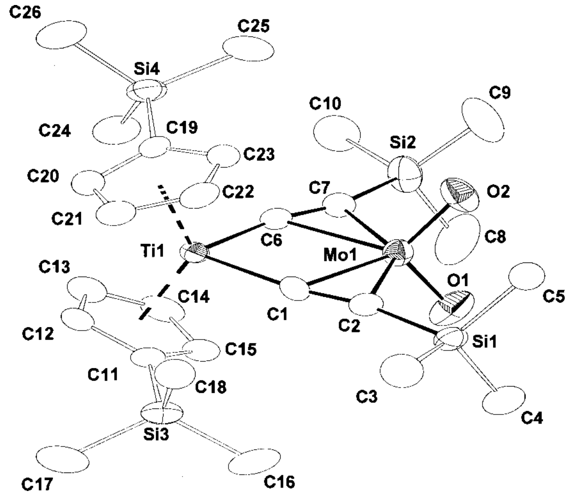

Fig. 1. ZORTEP drawing [12] (50% probability level) of **3**. Selected bond lengths (Å) and angles (°) are as follows: Ti(1)···Mo(1) 3.2698(8), Ti(1)–C(1) 2.051(4), Ti(1)–C(6) 2.048(5), C(1)–C(2) 1.254(6), C(6)–C(7) 1.257(6), Mo(1)–O(1) 1.698(3), Mo(1)–O(2) 1.709(3) Å; Ti(1)–C(1)–C(2) 166.3(4), Ti(1)–C(6)–C(7) 166.2(4), C(1)–Ti(1)–C(6) 88.90(16) C(1)–C(2)–Si(1) 161.4(4), C(6)–C(7)–Si(2) 161.8(4), O(1)–Mo(1)–O(2) 114.16(18)°.

Complex **3** is a brownish–red crystalline solid, which is remarkably soluble in most common non-polar organic solvents.

The molecular structure of **3** in the solid-state was determined by X-ray diffraction analysis (Fig. 1).

The result of the X-ray crystallographic analysis proves the existence of a mononuclear MoO_2 moiety, stabilized by the 3-titana-penta-1,4-diyne $Me_3SiC{\equiv}C$–[Ti]–$C{\equiv}CSiMe_3$ unit (Fig. 1).

Complex **3** adopts a somewhat distorted tetrahedral coordination sphere around Mo(1), defined by the oxygen atoms O(1) and O(2) as well as the π-coordinated alkyne units C(1)≡C(2) and C(6)≡C(7) [13]. The Mo–O(1) and Mo–O(2) distances of 1.698(3) and 1.709(3) Å, respectively, are in the range which is typical for Mo=O double bonds [14]. The oxygen atoms O(1) and O(2) are lying with -1.3548 and 1.5035 Å above or below the $Ti(C{\equiv}CSi)_2Mo$ plane. The $Ti(C{\equiv}CSi)_2$ array is almost perpendicular to the plane defined by Mo(1), O(1) and O(2).

Other crystallographic features of **3** closely resemble those so far reported in tweezer-like molecules of general type $\{[Ti](C{\equiv}CR)_2\}ML$ (ML = 10–12 valence-electron transition-metal fragments) [15].

The IR spectrum of this complex exhibits two strong absorptions at 932 and 889 cm^{-1}, which can be assigned to the asymmetric and symmetric stretching vibrations of the MoO_2 group. The $\nu_{M=O}$ frequencies are found in the same region, which is typical for molybdenum(VI) dioxygen species [16]. A further distinct absorption band is found at 2068 cm^{-1}, due to the C≡C stretching vibration of the $[Ti](C{\equiv}CSiMe_3)_2$ moiety [10].

The ^1H- and $^{13}C\{^1H\}$-NMR spectra of **3** are relatively simple and can be interpreted in a straightforward manner, as they greatly resemble those of other complexes $\{[Ti](C{\equiv}CR)_2\}ML$ (ML = 10–12 valence-electron transition-metal fragments) [15].

Complex **3** is the first example of a transition-metal complex which features a neutral mononuclear MoO_2 unit with molybdenum in the oxidation state $+4$ complexed by alkyne ligands. The structural data of **3** provide not only an excellent possibility for the evaluation of the nature of the alkyne-stabilized MoO_2 moiety (vide supra), but may also permit us to gain an insight into the mechanism of, e.g. oxygen-transfer reactions or polymerization processes by using well-defined mononuclear MoO_2 species.

3. Experimental

3.1. General conditions

All reactions were carried out under an atmosphere of N_2 using standard Schlenk techniques. Solvents were dried and distilled prior to use; Et_2O was refluxed with sodium/benzophenone ketyl and toluene with sodium. IR spectra were obtained with a Perkin–Elmer FT-IR 1000 spectrometer. ^1H and ^{13}C spectra were recorded on a Bruker Avance 250 spectrometer. Chemical shifts are reported in δ units (ppm) downfield from TMS with the solvent as reference signal. The C, H, N-microanalysis was performed by the Department of Organic Chemistry, Technical University of Chemnitz, using a Foss Heraeus Vario EL analysator.

3.2. Synthesis of $\{[Ti](C{\equiv}CSiMe_3)_2\}MoO_2$ (3)

Solid $Mo(CO)_3(CH_3C{\equiv}N)_3$ (0.46 g, 1.54 mmol) was added in one portion to $[Ti](C{\equiv}CSiMe_3)_2$ (0.40 g, 0.77 mmol) in toluene (40 cm^3) at 25°C. The resulting mixture was stirred for 15 h in the presence of atmospheric oxygen. Subsequently all the volatile materials were removed in vacuo. The brown residue obtained was extracted with diethylether (40 cm^3) and filtered through a pad of Celite. The filtrate was concentrated (20 cm^3) and cooled to -20°C to afford **3** (0.39 g, 80%) as a red–brown solid. Mp: 118°C dec. Anal. Calc. for $C_{26}H_{44}MoO_2Si_4Ti$ (644.88): C, 48.42; H, 6.89. Found: C, 48.30; H, 6.85%. IR (KBr): cm^{-1} 2068 (C≡C); 932, 889 (Mo=O). ^1H-NMR ($CDCl_3$): δ 0.28 (s, 18H, $SiMe_3$), 0.46 (s, 18H, $SiMe_3$), 5.11 (pt, 4H, C_5H_4, $J_{HH} = 2.2$ Hz), 5.60 (pt, 4H, C_5H_4, $J_{HH} = 2.2$ Hz). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 0.12 ($SiMe_3$), 0.67 ($SiMe_3$), 104.2 (TiC≡*C*), 107.6 (C_5H_4), 109.7 (C_5H_4), 112.4 (C_{ipso}, C_5H_4), 135.8 (Ti*C*≡C).

3.3. X-ray structure determination of **3**

Orange–red X-ray suitable crystals were obtained from diethyl ether at $-20°C$ ($0.2 \times 0.2 \times 0.15$ mm), orthorhombic, space group *Pbca*, with $a = 17.5243(3)$, $b = 15.4606(3)$, $c = 24.0470(4)$ Å, $V = 6515.2(2)$ Å^3, $Z = 8$, $D_{calc.} = 1.315$ g cm^{-3}, $\mu(\text{Mo–K}_\alpha) = 0.797$ mm^{-1}.

41 055 reflections (9207 independent reflections) ($1.69 < \theta < 30.55°$, ω-scan, $T = 174$ K) were measured on a Bruker Smart CCD using graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å), overall completeness 92.3%. Data were corrected for absorption using empirical methods (SADABS) [17], max. and min. transmission 0.897893 and 0.672399, respectively. The structure was solved by direct methods (SHELXS-97) [18] and refined by full-matrix least-squares methods (SHELXL-97/2) [18] to final *R* factors of $R_1 = 0.0659$, $wR_2 = 0.0878$, $S = 1.013$ for 4355 merged reflections with $I > 2\sigma(I)$. Hydrogen atoms were introduced on calculated positions and refined riding on their carrier atoms. All non-H atoms were refined with anisotropic thermal parameters. A final Fourier map showed no residual density outside -0.858 and 0.461 e Å^{-3} for **3**.

4. Supplementary material

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 139768. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road. Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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