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COMMUNICATION

ᵗBuO—SiMe$_3$, A FACILE OXYGEN-TRANSFER REAGENT. PREPARATION OF WOCl$_4$, WOCl$_3$dme, MoOCl$_3$dme, [WOCl$_2$dme]$_2$O AND [MoOCl$_2$dme]$_2$O BY OXYGEN-TRANSFER REACTIONS (dme = 1,2-DIMETHOXYETHANE)

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Abstract—Monomeric and μ-oxo bridged dimeric oxohalide complexes of tungsten(V) and molybdenum(V) are conveniently prepared using ᵗbutyl-trimethylsilyl ether as an oxygen-transfer reagent.

The reactions of high valent metal halides with silylated alcohols,[1] RO—SiMe$_3$, and silylated amines,[2] $R_{3-n}N$—(SiMe$_3$)$_n$ ($n = 1, 2$), to form M—OR, M—NR$_2$ or M=NR and XSiMe$_3$ are well-established preparative methods to introduce these functionalities on a metal atom. Reports describing the use of MeO—SiMe$_3$ for the introduction of the oxo group have been published[3,4] but more recent findings[5–7] have shown that Me$_3$Si—O—SiMe$_3$ (**I**) is a more convenient reagent for this purpose. Presently we are studying molybdenum and tungsten complexes in relation to the olefin metathesis reaction and in conjunction with that we are carrying out preparative studies on molybdenum(V) and tungsten(V). Attempted chloride–ᵗbutoxide exchange in MoOCl$_3$(dme) using ᵗBuO—SiMe$_3$ (**II**) as a reactant led to an unexpected product, shown to be the known[8] dimer [MoOCl$_2$dme]$_2$O. This contains the metal-oxo core, $Mo_2O_3^{4-}$, frequently found in molybdenum(V) aqueous chemistry.[9] To screen the oxygen-transfer properties of **II** and to compare it with that of **I** further studies, as outlined in Table 1, were carried out.

For the halide complexes of Table 1 oxygen-transfer takes place to yield WOCl$_4$, WOCl$_3$(dme) and MoOCl$_3$(dme), respectively, concomitant with the formation of ClSiMe$_3$ and ᵗBuCl. In all these reactions the main difference using reagent **I** or **II** is the somewhat longer reaction time needed for **I** as compared to **II**, e.g. the reaction with WCl$_6$ is complete within minutes after addition of **II**. Because of the sensitivity of WOCl$_3$(dme) in solution, longer reaction times tend to give more by-products and a lower yield. The organic products, ClSiMe$_3$ and ᵗBuCl, in these reactions and the high reactivity of **II** parallel previous observations in the reaction of WCl$_6$ with the sulphur-analogue ᵗBuS—SiMe$_3$.[10] Both WOCl$_3$(dme) and MoOCl$_3$(dme) are known compounds prepared previously from isolated MOCl$_3$ (M = Mo, W) and dme.[11,12]

In the reaction of the oxo-halide complexes with **II** dimeric oxygen-bridged complexes are formed [eq. (1)].

$$\underset{(M = Mo,\ W)}{2\,MOCl_3(dme)} + \underset{\mathbf{II}}{2\,{}^tBuO\text{—}SiMe_3} \longrightarrow [MOCl_2(dme)]_2O + 2\,{}^tBuCl + \underset{\mathbf{I}}{Me_3Si\text{—}O\text{—}SiMe_3} \quad (1)$$

These complexes have been identified by analytical means (Table 1) and by an IR spectroscopic comparison with an authentic sample of [MoOCl$_2$(dme)]$_2$O, prepared by an alternative route as described previously.[8]

The IR spectrum of the new tungsten complex is very similar to that of the molybdenum complex with only small shifts in the position of the main

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Table 1. Preparation[a] of oxohalide complexes of molybdenum and wolfram

Reactants	Solvent/ligand	Product	Yield %	Analysed % Found (Calc.)
WCl_6+**II**	CH_2Cl_2/none	$WOCl_4$	85	Cl, 41.7 (41.5); W, 53.4 (53.8)
$WCl_5(OEt_2)^b$+**I**	CH_2Cl_2/dme	$WOCl_3$(dme)	45	C, 12.1 (12.1); H, 2.4 (2.5); Cl, 27.3 (26.8)
$WCl_5(OEt_2)$+**II**	CH_2Cl_2/dme	$WOCl_3$(dme)	88	C, 11.7 (12.1); H, 2.5 (2.5); Cl, 26.9 (26.8)
$MoCl_5$+**I**	CH_2Cl_2/dme	$MoOCl_3$(dme)	91	C, 15.5 (15.6); H, 3.2 (3.3); Cl, 34.1 (34.5)
$WOCl_3$(dme)+**II**	dme/dme	$[WOCl_2(dme)]_2O$	87	C, 13.1 (13.0); H, 2.8 (2.7); Cl, 19.4 (19.2); W, 49.4 (49.8)
$MoOCl_3$(dme)+**II**	CH_2Cl_2/dme	$[MoOCl_2(dme)]_2O$	76	C, 16.8 (17.1); H, 3.4 (3.6); Cl, 25.7 (25.2)

[a] Preparative methods applied in the study are exemplified by the synthesis of tetrachlorobis (1,2-dimethoxyethan)-μ-oxodioxiditungsten as follows: ^tBuO—$SiMe_3$ (0.74 g, 5.0 mmol) was added to a solution of $WOCl_3$(dme) (2.0 g, 5.0 mmol) in dme (10 cm^3). Stirring the resulting dark green solution for a short period gave a dark green precipitate. More product was obtained by further reaction overnight followed by the addition of diethyl ether (25 cm^3). The fine grained solid was collected by Schlenk-filtration.

[b] Prepared according to ref. 14.

bands, indicating structural similarities in both complexes.

GC-MS analysis of the organic phase after reaction revealed the organic reaction products ^tBuCl and **I**. The formation of **I** as a product in eq. (1) suggests that the μ-oxo group is formed in a bimolecular elimination reaction from intermediates containing the M—$OSiMe_3$ group (M = Mo, W). In accordance with observations in the present study the formation of **I** also implies that **I** cannot be used to prepare the dimeric μ-oxo complexes. Additionally, we have, however, observed that the molybdenum dimer is formed in a very slow reaction using EtO—$SiMe_3$ as the reagent.

The reaction [eq. (1)] is critically dependent on the choice of solvent. The molybdenum complex can be prepared in CH_2Cl_2 but not in neat dme, while the opposite holds for the tungsten complex. If an exchange of the dme-ligand for **II** is supposed to be the initial step in the reaction sequence leading to the product the influence of solvent indicates a stronger binding of the dme-ligand in the molybdenum complex as compared to the tungsten complex. Attempts to further simplify the preparation of the dimers by a one-pot reaction from MCl_5 (M = Mo, W) and one equivalent of **I**, followed by one equivalent of **II**, were unsuccessful, indicating some negative effect of $ClSiMe_3$ in the second oxygen-transfer reaction.

The dimeric complexes are relatively stable and can be exposed to air for a short period. The dme ligand in these complexes undergoes facile ligand-displacement by other bidentate donors enabling the syntheses of a wide variety of other complexes containing the $M_2O_3{}^{4-}$ anion. The molybdenum complex reacts with thf to yield $[\{MoOCl_2(thf)_2\}_2O]$ but attempts to prepare the tungsten analogue have only led to decomposition to products supposed to be the outcome of a disproportionation to tungsten(IV) and tungsten(VI), as observed in similar systems.[13]

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