A systematic study on the activation of simple polyethers by $MoCl_5$ and WCl_6†

Sara Dolci,[a] Fabio Marchetti,‡[a] Guido Pampaloni*[a] and Stefano Zacchini[b]

Received 22nd January 2010, Accepted 13th April 2010
First published as an Advance Article on the web 7th May 2010
DOI: 10.1039/c001377c

$MoCl_5$, **1a**, and WCl_6, **1b**, activate 1,3-dioxolane at room temperature in chlorinated solvents: the compound $[MoOCl_3\{O{=}C(H)OCH_2CH_2Cl\}]_2$, **2**, has been isolated from $MoCl_5$/dioxolane. The mixed oxo-chloro species $WOCl_4$, **1c**, reacts with 1,3-dioxolane, selectively giving the coordination adduct $WOCl_4(\kappa^1\text{-}C_3H_6O_2)$, **3**. Dimethoxymethane, $CH_2(OMe)_2$, undergoes activation including C–H bond cleavage when reacted with **1a** to give the molybdenum complexes $[MoOCl_3\{O{=}C(H)OMe\}]_2$, **4**, and $Mo_2Cl_5(OMe)_5$, **5**. The reactions of **1b** with $CH_2(OR)_2$ (R = Me, Et) proceed *via* *O*-abstraction with formation of the oxo-derivatives $WOCl_4[O(R)CH_2Cl]$ (R = Me, **6a**; R = Et, **6b**) in admixture with equimolar amounts of RCl. The reactions of **1a**,**b** with $CMe_2(OMe)_2$ lead to mesityl oxide, $MeC(O)CH{=}C(Me)_2$. A series of simple diethers of general formula $ROCH_2(CHR')OR''$ are activated by **1a**,**b** in $CDCl_3$, usually *via* cleavage of C–O bonds at high temperature. The complex $WCl_5(OCH_2CH_2OMe)$, **7**, has been detected in solution as an intermediate species in the course of the degradation of 1,2-dimethoxyethane (dme) by **1b**. The activation of $CH(OMe)_3$ by **1** is limited to C–O bonds and selectively gives methyl chloride and methylformate, which has been found coordinated in $WOCl_4[O{=}C(H)OMe]$, **8**. The organic fragments produced in the reactions have been detected by GC-MS and NMR analyses, upon hydrolysis of the reaction mixtures. Compounds **2** and **5**, which have had their molecular structures ascertained by X-ray diffraction, represent rare examples of crystallographically-characterized dinuclear Mo(V) species containing both halides and oxygen ligands.

Introduction

Early transition metal halides in high oxidation states have been efficiently employed in a huge number of metal-directed reactions.[1-3]

In this context, the most accessible halides of the group 6 heavier metals in high oxidation state, *i.e.* $MoCl_5$, **1a**, and WCl_6, **1b**, have found application as catalytic precursors in a variety of processes, including polymerization of alkynes,[4] alkenes[5] and cyclic esters,[6] alkene metathesis,[7] ROMP polymerization,[8] alkene fluorination,[9] thioacetalizations,[10] and oxidative coupling of sulfides.[11] In particular, the high oxophilicity of **1a** and **1b** has been exploited for performing different types of transformations involving oxygen species; relevant examples are oxidative coupling of alkoxyarenes,[12] chlorination of alcohols, aldehydes and epoxides,[13] *N*-acylation of sulfonamides,[14] acylative cleavage of ethers,[15] deoxygenation,[16] C–C coupling,[17] and conversion of ketones into vinyl-chlorides.[18]

In spite of the interesting performances that compounds **1a** and **1b** may exhibit in catalysis, their coordination chemistry is still far from being well elucidated.[19] There are some factors which complicate the comprehension of this chemistry: (a) the high air- and moisture-sensitivity of **1**, providing difficulties in the storage and in the manipulation of these materials; (b) when organic substrates are allowed to contact with **1**, activation of the former may take place even at room temperature;[20] and (c) compounds **1** may reduce to lower oxidation states by reaction with different types of ligands.[21] More specifically, the behaviour of $MoCl_5$ in oxygen-containing organic solvents, L, was subject to investigation a long time ago.[22] It was proposed that two main reactivity patterns could be followed depending on L:[20b] (*i*) *O*-abstraction from L (see point (b) above), resulting in formation of chloro-oxo derivatives $MoOCl_3L_2$;[23] and (*ii*) metal reduction with consequent generation of adducts $MoCl_4L_2$ (see point (c) above). It may sound impressive that only two crystallographically-characterized compounds, *i.e.* $WCl_6(S_8)$,[24] and $MoCl_5(OPCl_3)$,[20c] as obtained by simple Lewis-base addition to compounds **1a** and **1b**, have been reported.

A better knowledge of the stoichiometric chemistry of **1** may help the understanding and, hopefully, improve the catalytic processes. This is particularly true on considering that the catalytic activity of **1** is often reported to be associated with the presence of an "oxygen modifier" (ether, amide, DMSO, *etc.*) acting as a promoter.[4d,5,13c] For example, the ring opening polymerization of various cyclic olefins has been efficiently performed in the presence of oxygen Lewis bases.[25] Nevertheless, no information about the interaction of the modifier with the metal species has been provided.

In recent years, we have carried out a systematic study on the reactivity of the heavier group 5 pentahalides MX_5 (M = Nb, Ta; X = F, Cl, Br) with controlled amounts of oxygen

---

[a] *Università di Pisa, Dipartimento di Chimica e Chimica Industriale, Via Risorgimento 35, I-56126, Pisa, Italy. E-mail: pampa@dcci.unipi.it; Fax: +39 050 2219246; Tel: +39 050 2219219*
[b] *Università di Bologna, Dipartimento di Chimica Fisica e Inorganica, Viale Risorgimento 4, I-40136, Bologna, Italy*

† CCDC reference numbers 758020 and 758021. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c001377c

‡ Born in Bologna (Italy) in 1974.

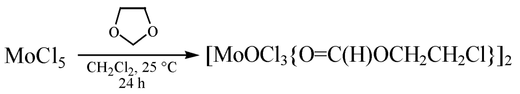
species.[26] The study has pointed out interesting features, in particular we have found that simple diethers may undergo unusual, noticeable transformations, when allowed to react with MX_5 in chlorinated solvents.[27] Therefore, we decided to extend our investigation, concerning the chemistry of oxophilic metal halides with oxygen species, to molybdenum pentachloride, **1a**, and tungsten hexachloride, **1b**.[28] The purpose is to increase the knowledge about the direct interaction of the halides **1a** and **1b** with oxygen-containing compounds, in the view of contributing to the development of the exploitation of these metal derivatives in organic synthesis.

The present paper focuses on the reactions of **1a** and **1b** with a variety of simple, multifunctional, oxygen molecules, including 1,1-dialkoxyalkanes $[CRR'(OR'')_2]$,[29] 1,2-dialkoxyalkanes $[ROCH_2CH(R')OR'']$, and trimethoxymethane $[CH(OMe)_3]$. The structural and spectroscopic features of the isolated metal-containing products will be presented, moreover the fragmentations operative in the various reactions will be discussed. The clear detection of the organic fragments generated in the distinct cases has been practicable upon hydrolysis of the reaction mixtures, and the quantification has been based on NMR analyses using CH_2Cl_2 as standard.

Results and discussion

Activation of 1,3-dioxolane by means of molybdenum and tungsten chlorides

When $MoCl_5$ was treated with two equivalents of 1,3-dioxolane in CH_2Cl_2, slow turning of the mixture from brown to green was observed. The successive work-up afforded moderate yields of the dinuclear oxo-chloroethylformate complex $[MoOCl_3\{O{=}C(H)OCH_2CH_2Cl\}]_2$, **2**, see Scheme 1. The product has been characterized by elemental analysis, IR spectroscopy and X-ray diffraction.



$$MoCl_5 \xrightarrow[CH_2Cl_2,\ 25\ ^\circ C,\ 24\ h]{} [MoOCl_3\{O{=}C(H)OCH_2CH_2Cl\}]_2$$

2

Scheme 1 Synthesis of compound **2**.

Fig. 1 represents a view of the molecular structure of **2**, while a selection of bond distances and angles is reported in Table 1.

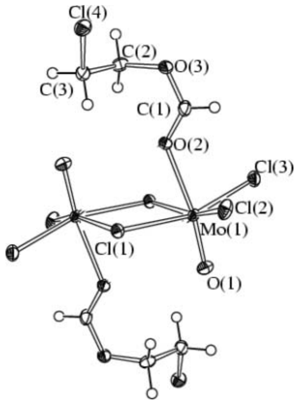


Fig. 1 View of the molecular structure of **2**. Displacement ellipsoids are at the 50% probability level. Only independent atoms are labelled.

Table 1 Selected bond distances (Å) and angles (°) for **2**

Mo(1)–O(1)	1.6532(14)	Mo(1)–O(2)	2.2924(14)
Mo(1)–Cl(1)	2.4749(6)	Mo(1)–Cl(1)#1	2.4790(6)
Mo(1)–Cl(2)	2.3029(6)	Mo(1)–Cl(3)	2.3170(6)
O(2)–C(1)	1.217(3)	C(1)–O(3)	1.311(3)
O(3)–C(2)	1.455(3)	C(2)–C(3)	1.496(3)
Cl(4)–C(3)	1.799(2)		
Cl(1)–Mo(1)–Cl(1)#1	83.826(18)	Cl(2)–Mo(1)–Cl(3)	92.75(2)
O(1)–Mo(1)–O(2)	169.59(6)	O(2)–C(1)–O(3)	123.9(2)
O(3)–C(2)–C(3)	110.68(17)	C(2)–C(3)–Cl(4)	110.87(15)

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + 2, -z + 2$.

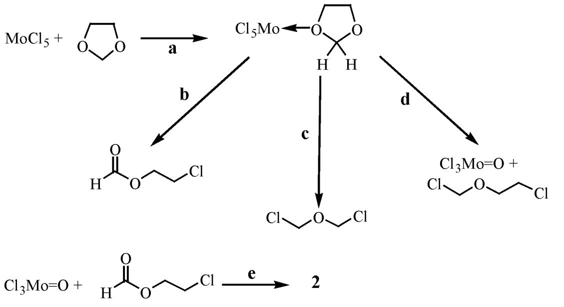
Only half of **2** is present within the asymmetric unit, the rest of the molecule being generated by an inversion centre. The Mo(V)-centres display distorted octahedral geometry being coordinated by four chloride ligands (two of which are in the bridging position), one oxo and a chloroethylformate ligand. The $Mo_2(\mu\text{-}Cl)_2$ core of the dimer is perfectly planar, and the terminal chloride ligands lie considerably out of the plane [Cl(2) 0.623 Å and Cl(3) 0.666 Å]. Due to the long separation [3.687(3) Å] between the molybdenum centres, no bonding has to be envisaged between them. The oxo and the chloroethylformate ligands, bound respectively to distinct metal centres, are in a relative *trans* position. The Mo(1)–O(1) distance [1.6532(14) Å] is considerably shorter than Mo(1)–O(2) [2.2924(14) Å], in view of the double bond character of the former. Dimolybdenum complexes of general formula $[MoOX_3L]_2$ (X = halogen; L = neutral ligand) are rarely discussed in the literature, and to the best of our knowledge the X-ray structure determined for **2** is the first one reported for this class of compounds. The derivatives $[MoOCl_3L]_2$ may form *via* reaction of $MoCl_5$ with two equivalents of the oxygen donor ligand L (including *O*-abstraction regarding one equivalent), and can be considered as precursors of mononuclear $MoOCl_3L_2$ species, which have already been described (see Introduction).

Interestingly, it was reported that the 1 : 2 molar ratio reaction of $MoCl_5$ with ethanol afforded the stable pentacoordinated $MoOCl_3(EtOH)$, whose solid state structure was determined.[30] This adduct is actually an example of a mononuclear equivalent of $[MoOCl_3L]_2$ (see above).

Salient IR features for **2** (see Experimental) are given by two strong absorptions at 1644 and 1000 cm^{-1}, which have been associated with the coordinated carbonyl group and the Mo=O moiety,[20b,31] respectively.

The presence of the chloroethylformate unit in **2** is clearly the result of dioxolane ring opening, proceeding with the activation of C–O and C–H bonds (Scheme 2, pathway b). This feature is not entirely new, since the generation of non-cyclic esters from dioxolanes by means of acidic transition-metal species was formerly proposed.[32]

On account of the fact that **2** is obtained in relatively modest amount, the reaction was also carried out in $CDCl_3$ and monitored by NMR. However, certain recognition of the products was not possible due to the presence of paramagnetic centres. Therefore, the mixture was hydrolyzed with the aim to clearly detect the organic products. Indeed this procedure, which favours the isolation of an organic phase consisting of the *O*-substrates released from the metal centres, has proved to be effective in



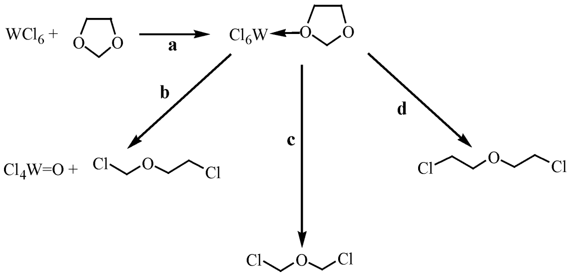
Scheme 2 Reaction of 1,3-dioxolane with $MoCl_5$, **1a**.

related studies regarding group 5 pentahalides.[27a-c,33] The solution resulting from treatment with water was analyzed by NMR and GC-MS: $O(CH_2Cl)_2$ and $O(CH_2Cl)(CH_2CH_2Cl)$ were identified in admixture with minor amounts of $HCO_2CH_2CH_2Cl$ and MeCl. This result has suggested that the fragmentation of the dioxolane molecule by means of $MoCl_5$ is not selective, and might proceed according to several pathways.

On considering that the reactions have been carried out in strictly anhydrous conditions, we believe that the oxo unit found in complex **2** reasonably originates from the organic material, rather than from adventitious water (Scheme 2, pathways d and e). Coherently with this point, the formation of $O(CH_2Cl)(CH_2CH_2Cl)$ could be the consequence of *O*-abstraction by molybdenum and chloride transfer from molybdenum to the organic substrate (Scheme 2, pathway d). Likewise, $O(CH_2Cl)_2$ might generate *via* C–O and C–C bond breaking, and chloride transfer (Scheme 2, pathway c). Notwithstanding it should not be ruled out in principle the possibility that alternative routes are operative to give the Cl-ethers, including the formation of paramagnetic metal compounds containing the alkoxo unit M–OR. This latter may afford chloroalkanes, Cl–R, upon treatment with water (HCl is produced during the hydrolysis).

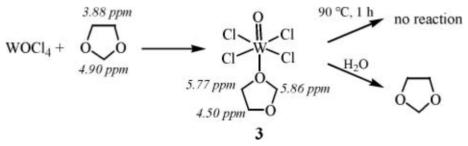
The reaction of WCl_6 with dioxolane in $CDCl_3$ could be monitored by NMR spectroscopy, in view of the diamagnetism of the W(VI) system. Hence the uncoordinated ethers $O(CH_2Cl)_2$, $O(CH_2CH_2Cl)_2$ and $O(CH_2Cl)(CH_2CH_2Cl)$ were identified, in admixture with presumably a W(VI) complex containing the alkoxo frame [–$O(CH_2)_2OCH_2Cl$], derived from dioxolane single C–O bond breaking. The complete characterization of the latter complex failed (see Experimental).

The same ethers were recovered after hydrolysis, and, in contrast with the reaction involving $MoCl_5$, no chloroethylformate was found. Reasonable pathways for the non-selective activation of 1,3-dioxolane by WCl_6 are given in Scheme 3. Interestingly, C–C breaking could be a process operative in the course of the activation (Scheme 3, pathway c), like we have seen for $MoCl_5$/dioxolane (see above). On the other hand, the possibility exists that the symmetric ethers $O(CH_2Cl)_2$ and $O(CH_2CH_2Cl)_2$ form from some interaction with $O(CH_2Cl)(CH_2CH_2Cl)$ molecules with the metal species involved in the process, through C–O bond cleavages and couplings, according to the reaction $2ORR' \rightarrow OR_2 + OR'_2$. Actually $O(CH_2Cl)_2$ and $O(CH_2CH_2Cl)_2$ have been found in comparable amounts in the mixture after hydrolysis.



Scheme 3 Reaction of 1,3-dioxolane with WCl_6, **1b**.

The behaviour of 1,3-dioxolane with WCl_6, **1b**, has been compared with that of the tungsten(VI) oxychloride $WOCl_4$, **1c**. This latter adds dioxolane to give the coordination compound **3**, see Scheme 4, which has been characterized in $CDCl_3$ solution by NMR spectroscopy. The spectra display three resonances [*e.g.* in the ^1H NMR spectrum: 5.86 (OCH_2O), 5.77, 4.50 ppm (CH_2CH_2)], thus indicating that 1,3-dioxolane acts here as a monodentate, non-symmetric, oxygen ligand. It is noteworthy that compound **3** is stable upon thermal treatment in $CDCl_3$ solution, and uncoordinated 1,3-dioxolane has been cleanly recovered after hydrolysis.



Scheme 4 Reaction of 1,3-dioxolane with $WOCl_4$, **1c.**

Although $WOCl_4$ contains a tungsten centre in +6 oxidation state, the presence of one oxo-unit makes **1c** less oxophilic than **1b**, and considerably less efficient for the activation of C–O bonds. Similar results were reported for the reactivity of azoxybenzenes with WCl_6/$WOCl_4$: N–O bond activation was achieved only by using WCl_6.[34]

When considering that $NbCl_5$ is not effective in activating 1,3-dioxolane at room temperature,[27b] the results reported in this section indicate that $MoCl_5$ is more efficient than the corresponding group 5 congener in promoting C–O bond activation. This agrees with the fact that a prominent feature of the chemistry of molybdenum and tungsten is the formation of numerous polymolybdate(VI) and polytungstate(VI) salts; the corresponding group 5 elements show this tendency to a more limited extent.[35]

C–O and C–H bond activation in the reaction of $MoCl_5$ with $CH_2(OMe)_2$

Molybdenum pentachloride, **1a**, reacts with one equivalent of dimethoxymethane in dichloromethane solution at room temperature, affording a dark-green solution. By layering with heptane, a mixture of dark-green microcrystals and red crystals was obtained. The two solids were separated mechanically, thus the dark-green one was analyzed by IR spectroscopy and elemental analyses. The IR spectrum exhibited two strong absorptions at 1643 cm^{-1} and 987 cm^{-1}, the latter within the range typical of the Mo=O bond. The absorption at 1643 cm^{-1} has been assigned to the C=O stretching vibration of coordinated methylformate. Really this molecule has been identified by NMR after dissolution of the solid in $CDCl_3$ followed by addition of water. Crystals were obtained after several attempts, but their low quality prevented an accurate crystal structure determination. Nevertheless, the connectivity was

Table 2 Selected bond distances (Å) and angles (°) for **5**

Cl(1)–Mo(1)	2.4876(6)	Cl(1)–Mo(2)	2.4196(6)
Mo(1)–O(1)	2.0154(16)	Mo(2)–O(1)	2.0285(16)
Cl(2)–Mo(1)	2.3297(6)	Cl(4)–Mo(2)	2.3905(7)
Cl(3)–Mo(1)	2.3902(6)	Cl(5)–Mo(2)	2.3881(6)
Mo(1)–O(2)	1.8157(16)	Mo(2)–O(4)	1.8153(16)
Mo(1)–O(3)	1.8157(16)	Mo(2)–O(5)	1.8115(16)
Mo(1)–Mo(2)	2.8509(3)	C(1)–O(1)	1.439(3)
C(2)–O(2)	1.414(3)	C(4)–O(4)	1.413(3)
C(3)–O(3)	1.426(3)	C(5)–O(5)	1.421(3)
O(1)–Mo(1)–Cl(1)	98.73(5)	O(1)–Mo(2)-Cl(1)	100.58(5)
Cl(2)–Mo(1)–Cl(3)	88.02(2)	Cl(5)–Mo(2)–Cl(4)	86.69(2)
O(3)–Mo(1)–O(2)	165.11(8)	O(5)–Mo(2)–O(4)	170.37(7)

established to be that of [MoOCl$_3${O=C(H)OMe}]$_2$, **4**, a dinuclear Mo(V) species analogous to **2**.

We were also able to characterize the minor component of the solid mixture which, on the basis of a single-crystal X ray diffraction study, resulted in the mixed chloro-methoxy complex Mo$_2$Cl$_4$(μ-Cl)(μ-OMe)(OMe)$_4$, **5**. The X ray molecular structure is drawn in Fig. 2, and the main bond distances and angles are reported in Table 2.

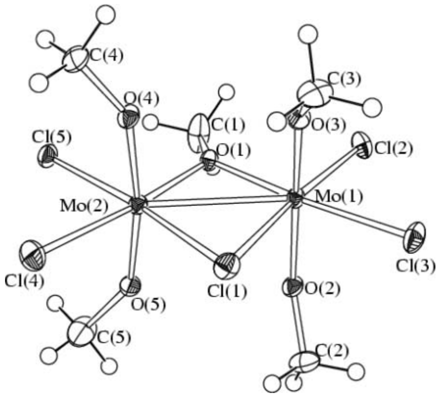
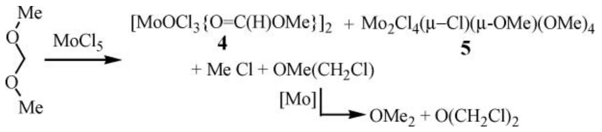


Fig. 2 View of the molecular structure of **5**. Displacement ellipsoids are at the 50% probability level.

Compound **5** belongs to the restricted family of crystallographically-characterized mixed halo-alkoxo compounds of Mo(V), the only previously reported examples being Mo$_2$Cl$_2$(OMe)$_8$,[36] Mo$_2$Cl$_4$(OMe)$_6$,[37] Mo$_2$Cl$_4$(OPh)$_6$,[38] and Mo$_2$X$_4$(O^{i}Pr)$_6$ (X = Cl, Br).[39] The Mo$_2$(μ-Cl)(μ-OMe)Cl$_4$ core of the dinuclear species is almost planar [mean deviation from the least square plane Mo(1) Mo(2) Cl(1) Cl(2) Cl(3) Cl(4) Cl(5) O(1) 0.0156 Å], with the two terminal alkoxo ligands in a relative *trans* position. The Mo(1)–Mo(2) contact [2.8509(3) Å] is indicative for a Mo–Mo single bond.[36-40] The Mo–O contacts with terminal alkoxide ligands fall in the range 1.8115(16)–1.8157(16) Å, and are significantly shorter compared to the Mo–O(bridging) distances [2.0154(16)–2.0285(16) Å]. Moreover, the former contacts are intermediate between the distances found in **2** for Mo=O [1.6532(14) Å] and Mo–O(chloroethylformate) [2.2924(14) Å].

The formation of the units Cl$_3$Mo=O and O=C(H)OMe, found in complex **4**, and of the methoxy-containing derivative **5**, indicates that more than one fragmentation pathway are concurrent when CH$_2$(OMe)$_2$ is treated with MoCl$_5$. Indeed the treatment with water of the reaction mixture gave a solution containing O=C(H)OMe, MeCl, OMe$_2$, OMe(CH$_2$Cl) and O(CH$_2$Cl)$_2$ (see Experimental and Scheme 5). This suggests that C–O bond cleavage is the main process operative in the course of the reaction. For the symmetric ethers OMe$_2$ and O(CH$_2$Cl)$_2$, these may form by C–O cleavages and couplings starting from OMe(CH$_2$Cl), analogously to what was discussed above for the WCl$_6$/dioxolane interaction. Besides, the generation of O=C(H)OMe requires a C–H breaking step.

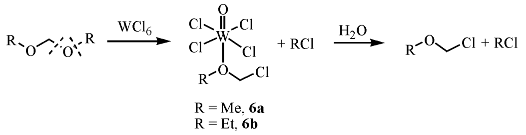


Scheme 5 Reaction of dimethoxymethane with MoCl$_5$, **1a**.

The reactivity of WCl$_6$ with dialkoxymethanes: formation of oxo-ether compounds

The reactions of WCl$_6$, **1b**, with CH$_2$(OR)$_2$ (R = Me, Et), in 1 : 2 molar ratio, afford the complexes WOCl$_4$[O(R)CH$_2$Cl] (R = Me, **6a**; R = Et, **6b**) in good yields. The latter have been isolated as microcrystalline solids and characterized by IR and NMR spectroscopy and elemental analysis.[41] A common feature in the IR spectra is the typical absorption due to the W=O interaction (*e.g.* at 980 cm^{-1} in the case of **6b**).[20h,42] The NMR spectra (in CDCl$_3$) display the resonances due to the coordinated chloromethyl-alkyl ether, for instance the [CH$_2$Cl] moiety is seen as a singlet at *ca.* 5.70 ppm in the ^{1}H NMR spectra.

The reactions leading to **6a** and **6b** seemed to be quite selective, and we were interested in understanding what kind of fragmentation was operative. In order to investigate the point, we carried out the reactions of **1b** with CH$_2$(OR)$_2$ (R = Me, Et) in CDCl$_3$. The ether ROCH$_2$Cl and the alkylchloride RCl were the only compounds present in the mixtures after hydrolysis, in comparable ratio. This feature suggests that the reaction of CH$_2$(OR)$_2$ with WCl$_6$ proceeds selectively *via* oxygen abstraction by the metal centre. The abstraction takes place with contextual chlorine transfer from tungsten to the organic fragments, affording RCl and ROCH$_2$Cl, with the latter capable of coordination to the newly formed WOCl$_4$ moiety (see Scheme 6).

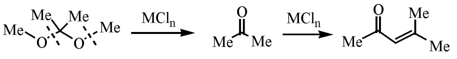


Scheme 6 Reaction of dioxyalkanes with WCl$_6$, **1b**.

Interestingly, fragmentation routes completely different from that presented in Scheme 6 occur when using MoCl$_5$ in the place of WCl$_6$. The non-selective reaction of MoCl$_5$ with CH$_2$(OMe)$_2$ has been discussed in the previous paragraph. Otherwise, the reaction of MoCl$_5$ with CH$_2$(OEt)$_2$ gave a mixture of unidentified products, and EtCl was recognised as the major component after hydrolysis (see Experimental).

C–C bond formation in the reactions of 1a and 1b with 2,2-dialkoxypropanes

The reactivity of $CMe_2(OMe)_2$ with equimolar amounts of **1a** and **1b** was investigated. The mixtures of the reactions carried out in $CDCl_3$ in sealed NMR tubes gave, after treatment with water, solutions for which GC-MS analysis evidenced the presence of MeCl and mesityl oxide, $Me_2C{=}CHC(O)Me$, see Scheme 7. The first step is presumably the formation of acetone, that is a well-known reaction in the field of ketal to ketone transformations promoted by acidic species.[43] Then, mesityl oxide is produced by successive aldol condensation of acetone.



Scheme 7 Reaction of 2,2-dimethoxypropane with **1a** and **1b**.

The possibility that mesityl oxide is generated during hydrolysis should be discharged on the basis of the fact that the IR spectra of the solid mixtures isolated from the reactions before hydrolysis display absorptions ascribable to the $Me_2C{=}CHC(O)Me$ unit (see Experimental).

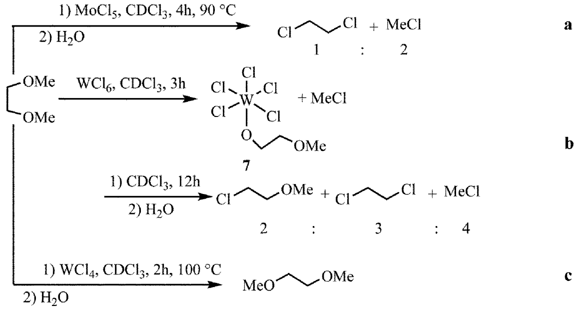
Analogously, the reaction of **1a** with $CHMe(OEt)_2$ afforded a dark-green solid after work-up. The solid was dried, dissolved in $CDCl_3$ and treated with water. Thus, NMR/GC-MS analyses evidenced the presence of a mixture of ethyl chloride and several carbonylic compounds. Among the latter, *trans*-2-butenal, $HC(O)C(H){=}C(H)Me$, was detected unambiguously in small amounts. The formation of *trans*-2-butenal may take place by a two-step process, including the formation of acetaldehyde, and resembling that shown in Scheme 7. On the other hand, the presence of ethyl chloride suggests the previous formation of Mo-ethoxide species, which afford EtCl upon hydrolysis.

The reactivity of 1a and 1b with 1,2-dialkoxyalkanes, $ROCH_2(CHR')OR''$

The reactivity of **1a** and **1b** with a series of 1,2-dialkoxyalkanes, $ROCH_2(CHR')OR''$ ($R = R'' = Me$, $R' = H$ (dme); $R = R' = R'' = Me$; $R = Me$, $R' = H$, $R'' = CH_2Cl$), was investigated.

It is known that $MoCl_5$ undergoes reduction in the presence of dme, affording the Mo(IV) derivative $MoCl_4(\kappa^2\text{-dme})$.[21a] We have confirmed this result and we have investigated the stability of this product in $CDCl_3$ solution. After being stored at room temperature for several days, the mixture was treated with water, giving a solution containing dme, $Cl(CH_2)_2Cl$ and MeCl, in 9 : 2 : 4 ratio (see Scheme 8(a)). This fact points out that the compound $MoCl_4(\kappa^2\text{-dme})$ is not indefinitely stable in solution, thus slow degradation of the organic moiety takes place *via* multiple C–O bond cleavage. The degradation is complete in 4 h at 90 °C, then $Cl(CH_2)_2Cl$ and MeCl have been recognized in *ca.* 1 : 2 ratio in the final mixture after hydrolysis (see Experimental).

The reaction between WCl_6 and dme in $CDCl_3$ was monitored by NMR spectroscopy. After a few hours, the starting materials had disappeared, and the NMR spectra revealed the probable formation of the alkoxo-complex $WCl_5(OCH_2CH_2OMe)$, **7**, in admixture with MeCl, as a result of single C–O bond cleavage (Scheme 8(b)). However, compound **7** is not stable in solution: after 12 days NMR evidenced the absence of **7** and the formation of non-identified products. The mixture was hydrolyzed, then compounds $MeO(CH_2)_2Cl$, $Cl(CH_2)_2Cl$ and MeCl were detected (Scheme 8(b)).



Scheme 8 Reactions of **1a**, **1b** and **1d** with dme.

The possibility to activate dme by means of a group 6 halide was also evaluated by using WCl_4, **1d**. The reaction was carried out in $CDCl_3$ in a sealed NMR tube heated at 100 °C for 2 h. Successive hydrolysis gave a solution containing dme only, thus indicating that the W(IV) species **1d** is not effective in performing fragmentation of dme (Scheme 8(c)).

The study of the reactivity of **1a** and **1b** with 1,2-dialkoxyalkanes was extended to $MeOCH_2CH(Me)OMe$ and $MeOCH_2CH_2OCH_2Cl$. At room temperature in $CDCl_3$, only partial fragmentation of $MeOCH_2CH_2OCH_2Cl$ was observed, whereas $MeOCH_2CH(Me)OMe$ was recovered nearly quantitatively from the respective reaction mixtures after treatment with water. These reactions were repeated at 90 °C (see Experimental): in these conditions, fragmentation of the diethers took place in a few hours. NMR analyses did not allow to identify unambiguously the inorganic products. Conversely, organic substrates derived from the fragmentation reactions could be detected after hydrolysis. The products recognized after hydrolysis of the reaction mixtures obtained by high temperature reactions of **1a** and **1b** with 1,2-dialkoxyalkanes are listed in Table 3.

According to the results shown in Table 3, the fragmentations of 1,2-diethers by means of the group 6 chlorides **1a** and **1b** generally proceed at high temperatures *via* the cleavage of C–O bonds. The higher reactivity of $MeOCH_2CH_2OCH_2Cl$ is manifested in the room temperature, non-selective, reaction with WCl_6, which may include the coupling of C–O bonds. These outcomes can be compared to the chemistry exhibited by niobium and tantalum pentahalides with $MeOCH_2CH_2OMe$. The unique behaviour of such group 5 derivatives determines the selective activation of dme,

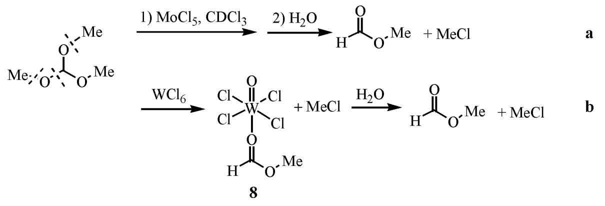
Table 3 Compounds detected by NMR/GC-MS after hydrolysis of the reaction mixtures obtained from **1**/$ROCH_2(CHR')OR''$

Metal compound	1,2-Dialkoxyalkane	Products of the fragmentation
$MoCl_5$, **1a**	$MeOCH_2CH_2OMe$	MeCl, $ClCH_2CH_2Cl$
WCl_6, **1b**	$MeOCH_2CH_2OMe$	MeCl, $ClCH_2CH_2Cl$, $OMe(CH_2CH_2Cl)$
WCl_4, **1d**	$MeOCH_2CH_2OMe$	$MeOCH_2CH_2OMe$
$MoCl_5$, **1a**	$MeOCH_2CH(Me)OMe$	MeCl, $ClCH_2CH(Me)Cl$
WCl_6, **1b**	$MeOCH_2CH(Me)OMe$	MeCl, $ClCH_2CH(Me)Cl$, $MeOCH_2CH(Me)OH$, $HOCH_2CH(Me)OMe$
$MoCl_5$, **1a**	$MeOCH_2CH_2OCH_2Cl$	MeCl, $ClCH_2CH_2Cl$
WCl_6, **1b**	$MeOCH_2CH_2OCH_2Cl$	MeCl, $ClCH_2CH_2Cl$, $O(CH_2Cl)_2$, $OMe(CH_2Cl)$, $O(CH_2CH_2Cl)_2$, OMe_2

consisting of multiple C–O bond cleavage followed by C–O coupling.[27a,d]

The reactivity of 1a and 1b with trimethylformate, $CH(OMe)_3$

The study of the reactivity of chlorides **1a** and **1b** with polyethers was extended to trimethoxymethane. The reactions proceed selectively through multiple C–O bond cleavage, including probable *O*-abstraction by the metal centre, see Scheme 9. Indeed, methyl formate and methyl chloride have been found in *ca.* 1 : 2 ratio in the reaction mixtures, see Experimental. Moreover, the complex $WOCl_4[O{=}C(H)OMe]$, **8**, has been isolated as a brown solid in good yield from the reaction of **1b** with a two-fold excess of $CH(OMe)_3$ (Scheme 9(b)).



Scheme 9 Reaction of trimethylformate with **1a** and **1b**.

Major features of the IR spectrum (solid state) are two intense bands at 1652 cm^{-1} and 1056 cm^{-1}, attributed to the coordinated carbonyl and the W=O moiety, respectively. The NMR spectra show the resonances related to the methylformate ligand at higher chemical shifts with respect to the uncoordinated molecule [*e.g.* for the ^1H spectrum: $\delta = 8.67$ (CH), 4.19 (CH_3) ppm].

Conclusions

This paper reports the systematic investigation on the reactivity of the highly oxophilic early transition metal chlorides $MoCl_5$ and WCl_6 towards simple polyethers, such as acetals, ketals, 1,2-dialkoxyalkanes and trimethylformate. The reactions result in fragmentation of the organic species, and the two metal compounds behave similarly in most cases. It is remarkable that the room temperature reactions of acetals and ketals with **1a** and **1b** do not generally follow the usual pathway expected on the basis of the acidity of **1**, *i.e.* generation of the "deprotected" carbonylic compound. Conversely, more complicated reaction patterns are operative, including cleavage of C–H and, possibly, C–C bonds, and formation of new C–C bonds.

Interestingly, $MoCl_5$ and WCl_6 show higher reactivity towards 1,3-dioxolane than the corresponding pentahalides of group 5, namely $NbCl_5$ and $TaCl_5$. The compound $[MoOCl_3\{O{=}C(H)OCH_2CH_2Cl\}]_2$, resulting from a dioxolane ring-opening reaction, represents the first crystallographically-characterized dimeric oxo-chloro Mo(V) derivative.

The results presented here may provide more information in the reactivity of the highly oxophilic $MoCl_5$ and WCl_6 with oxygen substrates, in order to further exploit these easily-accessible materials in metal-directed syntheses involving oxygen species. Development in this area is really desirable, on account of the availability of such metal compounds and of the substantial low-toxicity of the elements.

Experimental

General

All manipulations of air and/or moisture sensitive compounds were performed under an atmosphere of pre-purified argon using standard Schlenk techniques. The reaction vessels were oven dried at 150 °C prior to use, evacuated (10^{-2} mmHg) and then filled with argon. $MoCl_5$, **1a**, WCl_6, **1b**, $WOCl_4$, **1c**, and WCl_4, **1d**, were commercial products (Aldrich) of the highest purity available, stored under argon atmosphere as received. 1,3-Dioxolane, $CH_2(OMe)_2$, $CH_2(OEt)_2$, $CMe_2(OMe)_2$, $CHMe(OEt)_2$, $MeOCH_2CH(Me)OMe$, $MeO(CH_2)_2OCH_2Cl$ and $CH(OMe)_3$ were commercial products (Aldrich) stored under argon atmosphere as received. CH_2Cl_2, $CDCl_3$ and 1,2-dimethoxyethane (dme) were distilled before use under argon atmosphere from P_4O_{10}, while pentane and heptane were distilled from $LiAlH_4$. Infrared spectra were recorded at 293 K on a Spectrum One Perkin Elmer Spectrometer, equipped with a UATR sampling accessory. NMR measurements were recorded on Varian Gemini 200BB instrument at 293 K. The chemical shifts of ^1H and ^{13}C NMR spectra were referenced to the non-deuterated aliquot of the solvent. Ratios were calculated on the basis of ^1H NMR peak integrals. GC-MS analyses were performed on a HP6890 instrument, interfaced with MSD-HP5973 detector and equipped with a Phenonex Zebron column. Carbon and hydrogen analyses were performed on a Carlo Erba mod. 1106 instrument, paying particular attention to the more sensitive compounds which were weighed and directly introduced into the analyzer. The halide content was determined by the Volhardt method[44] after exhaustive hydrolysis of the sample. The halogen analyses were repeated twice in order to check for reproducibility.

Reactivity of 1a–c with 1,3-dioxolane; synthesis and isolation of $[MoOCl_3\{O{=}C(H)OCH_2CH_2Cl\}]_2$, 2, and detection in solution of $WOCl_4(\kappa^1\text{-}C_3H_6O_2)$, 3

1,3-Dioxolane (80 μL, 1.1 mmol) was added to $MoCl_5$, **1a** (0.150 g, 0.549 mmol), in CH_2Cl_2 (12 mL). The resulting brown mixture was stirred at room temperature for 24 h, during which progressive turning to green was observed. The final solution was layered with heptane (15 mL) and stored at −30 °C, thus green crystals of **2** suitable for X ray analysis were collected after some days. Yield: 0.072 g, 40%. Anal. Calcd. for $C_6H_{10}Cl_8Mo_2O_6$: C, 11.03; H, 1.54; Cl, 43.39. Found: C, 11.17; H, 1.49; Cl, 43.16. IR (solid state): ν = 2968 w, 1644 m-s ($\nu_{C=O}$), 1614 s, 1440 m, 1429 w-m, 1391 w-m, 1374 m, 1302 s, 1288 s, 1271 s, 1238 m-s, 1196 m, 1065 w-m, 1000 s ($\nu_{Mo=O}$), 959 m, 942 s, 825 w-m, 805 m, 782 w-m, 736 w-m, 661 s cm^{-1}.

In a different experiment, $MoCl_5$, **1a** (0.075 g, 0.28 mmol), in $CDCl_3$ (0.75 mL) inside an NMR tube, was treated firstly with CH_2Cl_2 (0.018 mL, 0.28 mmol) and then with 1,3-dioxolane (21 μL, 0.30 mmol). The tube was sealed, briefly shaken so to homogenize the content, and stored at room temperature for 72 h. Afterwards, the tube was cooled to −20 °C, opened, and water (*ca.* 5 mmol) was added. A dark-green solid precipitated from a green solution; the solution was analysed by NMR/GC-MS, which evidenced the presence of CH_2Cl_2, CH_3Cl, $O(CH_2Cl)_2$, $Cl(CH_2)_2OCH_2Cl$ and $HCO_2(CH_2)_2Cl$ (ratio 20 : 2 : 7 : 10 : 1).

The 1 : 1 reactions of 1,3-dioxolane (0.50 mmol) with WCl_6, **1b**, or $WOCl_4$, **1c**, in $CDCl_3$ (0.75 mL) were carried out by the same procedure described for **1a**. The ^1H NMR spectrum of the mixture obtained from **1b** and dioxolane, after 8 days, showed the presence of CH_2Cl_2, $O(CH_2Cl)_2$, $O(CH_2CH_2Cl)_2$, $Cl(CH_2)_2OCH_2Cl$ and, presumably, a W(VI) complex containing the ligand [–$OCH_2CH_2OCH_2Cl$] (ratio 10 : 3 : 2 : 1 : 3). The resonances related to the latter appeared as follows: ^1H NMR δ = 5.84 (s, 2 H, CH_2Cl), 5.74 (t, 2 H, $^3J_{HH}$ = 5.5 Hz, OCH_2CH_2O), 4.48 (t, 2 H, $^3J_{HH}$ = 5.5 Hz, OCH_2CH_2O) ppm; ^{13}C NMR{^1H} δ = 80.6 (CH_2Cl), 78.1 (OCH_2CH_2O), 70.5 (OCH_2CH_2O) ppm.

After treatment with water, a light-yellow solution was separated from a blue precipitate and analysed by NMR/GC-MS: CH_2Cl_2, $O(CH_2Cl)_2$, $O(CH_2CH_2Cl)_2$ and $Cl(CH_2)_2OCH_2Cl$ were found in 10 : 3 : 3 : 4 ratio. Compound $WOCl_4(\kappa^1\text{-}C_3H_6O_2)$, **3**, and CH_2Cl_2 were detected by ^1H NMR in *ca.* 1 : 1 ratio in the yellow solution obtained from **1c** (0.25 mmol), 1,3-dioxolane (0.25 mmol) and CH_2Cl_2 (0.25 mmol) after 12 days. ^1H NMR ($CDCl_3$): δ = 5.86 (s, 2 H, OCH_2O), 5.77, 4.50 (t, 4 H, $^3J_{HH}$ = 5.5 Hz, CH_2CH_2) ppm. ^{13}C NMR{^1H} ($CDCl_3$): δ = 80.6 (OCH_2O), 78.2, 70.9 (CH_2CH_2) ppm. 1,3-Dioxolane was recovered cleanly after hydrolysis. Complex **3** in $CDCl_3$ in a sealed tube was unchanged after thermal treatment at 90 °C for 60 min.

Reactivity of 1a with $CH_2(OMe)_2$; synthesis and isolation of $[MoOCl_3\{O{=}C(H)OMe\}]_2$, 4, and $Mo_2Cl_5(OMe)_5$, 5

$MoCl_5$, **1a** (0.168 g, 0.615 mmol), CH_2Cl_2 (7 mL) and $CH_2(OMe)_2$ (0.615 mmol) were introduced into a Schlenk tube. The mixture was stirred for 20 h, then it was filtrated in order to remove some solid. The filtrated dark-green solution was layered with heptane and stored at −30 °C for 7 days. Hence, a mixture of a few red X-ray quality crystals and a dark-green microcrystalline solid was obtained. Part of this mixture was dissolved in $CDCl_3$ and treated with water: a solution containing HCO_2Me and MeOH (ratio 10 : 1, ^1H NMR) was obtained. The red crystals of compound $Mo_2Cl_5(OMe)_5$, **5**, were separated mechanically from the solid mixture and studied by X-ray diffraction and elemental analysis. Anal. Calcd. for $C_5H_{15}Cl_5Mo_2O_5$: C, 11.45; H, 2.88; Cl, 33.81. Found: C, 11.36; H, 2.73; Cl, 32.90. The dark green solid consisted of $[MoOCl_3\{O{=}C(H)OMe\}]_2$, **4**. Yield: 0.068 g (40%). Anal. Calcd. for $C_4H_8Cl_6Mo_2O_6$: C, 8.63; H, 1.45; Cl, 38.21. Found: C, 8.50; H, 1.39; Cl, 37.60. IR (solid state): ν = 2967 w, 1643 m-s ($\nu_{C=O}$), 1445 w-m, 1429 m, 1369 m, 1285 s, 1174 w, 1044 m, 987 m-s ($\nu_{Mo=O}$), 963 s, 884 s, 794 m, 730 w cm^{-1}.

The reaction of **1a** (0.20 mmol) with $CH_2(OMe)_2$ (0.20 mmol), in $CDCl_3$ (0.70 mL) in a sealed NMR tube, afforded a green-brown mixture after 24 h. Hydrolysis gave a light-green solution of HCO_2Me, MeCl, OMe_2, $OMe(CH_2Cl)$ and $O(CH_2Cl)_2$ (ratio 10 : 60 : 12 : 6 : 8).

Reactivity of 1a and 1b with $CH_2(OR)_2$; synthesis and isolation of $WOCl_4[O(R)CH_2Cl]$ (R = Me, 6a; R = Et, 6b). General procedure

$CH_2(OR)_2$ (0.74 mmol) was added to WCl_6, **1b** (0.145 g, 0.366 mmol), in CH_2Cl_2 (15 mL), and the resulting mixture was stirred overnight. Hence, the final yellow solution was layered with heptane (15 mL) and stored at room temperature. Thus, compound **6** was obtained as a light-green microcrystalline solid after 3 days.

6a. Yield: 0.102 g, 66%. Anal. Calcd. for $C_2H_5Cl_5O_2W$: C, 5.69; H, 1.19; Cl, 41.99. Found: C, 5.76; H, 1.13; Cl, 41.77. IR (solid state): ν = 2955 w, 1442 m, 1374 m-s, 1152 m, 1109 m, 1068 s, 999 m, 970 vs ($\nu_{W=O}$) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 5.71 (s, 2 H, CH_2), 3.82 (s, 3 H, CH_3) ppm. ^{13}C NMR{^1H} ($CDCl_3$): δ = 84.8 (CH_2), 57.7 (CH_3) ppm.

6b. Yield: 0.109 g, 68%. Anal. Calcd. for $C_3H_7Cl_5O_2W$: C, 8.26; H, 1.62; Cl, 40.64. Found: C, 8.31; H, 1.59; Cl, 40.15. IR (solid state): ν = 2963 w, 1441 m, 1396 m, 1379 m, 1351 m, 1260 s, 1086 m-s, 1018 s, 980 m-s ($\nu_{W=O}$), 935 m-s, 934 m-s, 855 s, 793 vs cm^{-1}. ^1H NMR ($CDCl_3$): δ = 5.69 (s, 2 H, CH_2), 4.48 (q, $^3J_{HH}$ = 5 Hz, 2 H, CH_2), 1.41 (t, $^3J_{HH}$ = 5 Hz, 3 H, CH_3) ppm. ^{13}C NMR{^1H} ($CDCl_3$): δ = 84.0 (CH_2), 69.8 (CH_2), 14.4 (CH_3) ppm.

All the attempts to isolate products from the reaction of $MoCl_5$ with $CH_2(OEt)_2$ gave brown, very air-sensitive, oily-solids which could not be characterised. $MoCl_5$, **1a** (0.25 mmol), in $CDCl_3$ (0.75 mL), was treated in an NMR tube with CH_2Cl_2 (0.25 mmol) and then with $CH_2(OEt)_2$ (0.25 mmol). The tube was sealed, shaken so to homogenize the content, and stored at room temperature for *ca.* 7 days. After cooling at *ca.* −30 °C, the tube was opened, and water (*ca.* 5 mmol) was added. A brown solid precipitated from a brown solution. The solution was analysed by NMR/GC-MS: CH_2Cl_2, CH_3Cl and EtCl were found in 10 : 1 : 8 ratio.

The reactions of WCl_6, **1b**, with $CH_2(OR)_2$ (R = Me, Et), in $CDCl_3$ (0.75 mL), were carried out by the same procedure described above for the reaction of **1a** with $CH_2(OEt)_2$. ^1H NMR/GC-MS analyses of the mixture obtained from **1b** and $CH_2(OMe)_2$, after 2 days, showed the presence of CH_3Cl and $WOCl_4[O(Me)CH_2Cl]$, **6a** (ratio *ca.* 1 : 1) After treatment with water, a brown solution was separated from a colourless precipitate, and analysed by NMR/GC-MS: CH_3Cl and $MeOCH_2Cl$ were found in *ca.* 1 : 1 ratio. Instead, ^1H NMR/GC-MS analyses of the mixture obtained from **1b** and $CH_2(OEt)_2$, after 12 days, showed the presence of CH_2Cl_2, EtCl, $ClCH_2OEt$, $WOCl_4[O(Et)CH_2Cl]$, **6b**. After treatment with water, a light-brown solution was separated from a yellow precipitate and analysed by NMR/GC-MS: CH_2Cl_2, EtCl, $ClCH_2OEt$ were found in *ca.* 10 : 8 : 9 ratio.

Reactivity of 1a and 1b with $CMe_2(OMe)_2$. General procedure

$CMe_2(OMe)_2$ (0.550 mmol) was added to **1a** or **1b** (0.500 mmol), in CH_2Cl_2 (20 mL), and the mixture was stirred for *ca.* 24 h. Hence, the resulting orange-brown solution was layered with heptane (30 mL) and stored at −30 °C for 10 days. Thus, the final products were obtained as dark solids, which were analyzed by IR spectroscopy. From **1a** and $CMe_2(OMe)_2$, IR (solid state): ν = 2954 w-m, 2844 w, 1584 s ($\nu_{C=O}$), 1519 m ($\nu_{C=C}$), 1484 m, 1448 m-s, 1428 m, 1361 m-s, 1337 m-s, 1302 m-s, 1299 w-m, 1101 m, 978 s ($\nu_{Mo=O}$), 893 m, 735 m cm^{-1}. From **1b** and $CMe_2(OMe)_2$, IR (solid state): ν = 2941 w, 1595 s ($\nu_{C=O}$), 1506 s ($\nu_{C=C}$), 1453 m, 1437 m, 1403 w-m, 1378 w, 1342 m-s, 1294 w-m, 1029 w-m, 981 s ($\nu_{W=O}$), 932 m, 872 vs, 847 m, 792 m, 733 m cm^{-1}.

An NMR tube was charged with $MoCl_5$, **1a** (0.180 mmol), $CDCl_3$ (0.65 mL), CH_2Cl_2 (0.180 mmol) and $CMe_2(OMe)_2$ (0.185 mmol). The tube was sealed and shaken in order to obtain a homogeneous mixture. The tube was stored at room temperature for 7 days, obtaining an orange solution. Then the tube was cooled to *ca.* −20 °C and opened. A large excess of water (*ca.* 5 mmol) was added, so producing a dark precipitate and a light-yellow solution. The latter was analyzed by NMR/GC-MS: CH_2Cl_2, MeCl (ratio 1 : 1, ^{1}H NMR) and MeC(O)CH=C(Me)$_2$ (GC-MS) were clearly identified.

The reaction of **1b** (0.250 mmol) and CMe$_2$(OMe)$_2$ (0.253 mmol), in sealed NMR tube, was carried out similarly. After 6 days, the reaction mixture was hydrolysed, thus CH_2Cl_2, MeCl (ratio 1 : 1, ^{1}H NMR) and MeC(O)CH=C(Me)$_2$ (GC-MS) were found in the resulting solution.

Reactivity of 1a and 1b with CHMe(OEt)$_2$. General procedure

CHMe(OEt)$_2$ (0.550 mmol) was added to **1a** or **1b** (0.500 mmol), in CH_2Cl_2 (20 mL), and the mixture was stirred for *ca.* 24 h. Hence, the resulting solution was layered with heptane (30 mL) and stored at −30 °C for 72 h. Precipitation of a solid occurred. The solid was dried under vacuo, dissolved in $CDCl_3$ (0.80 mL) and treated with a large excess of H_2O. The resulting mixture was analyzed by GC-MS and NMR spectroscopy. From **1a** and CHMe(OEt)$_2$: *trans*-HC(O)C(H)=C(H)CH$_3$ and EtCl (ratio 2 : 3). From **1b** and CHMe(OEt)$_2$: EtCl.

Reactivity of 1a, 1b and 1d with ROCH$_2$(CHR′)OR″ (R = R″ = Me, R′ = H (dme); R = R′ = R″ = Me; R = Me, R′ = H, R″ = CH$_2$Cl). General procedure

CH_2Cl_2 (0.300 mmol) and ROCH$_2$(CHR′)OR″ (0.300 mmol) were added to a suspension of **1** (0.300 mmol) in $CDCl_3$ (0.70 mL), in an NMR tube. Then the tube was sealed, shaken in order to homogenize the mixture, and maintained at different temperatures for variable times. Hence, the tube was cooled to −20 °C and opened, then H_2O (*ca.* 5 mmol) was added causing the precipitation of a solid from a solution. Combined GC-MS/NMR analysis of the latter was carried out.

From **1a** and MeOCH$_2$CH$_2$OMe (reaction time: 4 h; temperature: 90 °C): CH_2Cl_2, MeCl and Cl(CH$_2$)$_2$Cl (3 : 4 : 2 ratio).

From **1b** and MeOCH$_2$CH$_2$OMe (12 d, room temperature): CH_2Cl_2, MeO(CH$_2$)$_2$Cl, Cl(CH$_2$)$_2$Cl and MeCl (7 : 2 : 3 : 8).

From **1d** and MeOCH$_2$CH$_2$OMe (2 h, 100 °C): CH_2Cl_2 and MeOCH$_2$CH$_2$OMe (1 : 1).

From **1a** and MeOCH$_2$CH(Me)OMe (10 h, 110 °C): CH_2Cl_2, MeCl and ClCH$_2$CH(Me)Cl (5 : 8 : 4).

From **1b** and MeOCH$_2$CH(Me)OMe (3 h, 100 °C): CH_2Cl_2, MeCl, ClCH$_2$CH(Me)Cl, MeOCH$_2$CH(Me)OH and HOCH$_2$CH(Me)OMe (10 : 8 : 2 : 3 : 3).

From **1a** and MeOCH$_2$CH$_2$OCH$_2$Cl (2 h, 90 °C): CH_2Cl_2, MeCl and Cl(CH$_2$)$_2$Cl (5 : 3 : 2).

From **1b** and MeOCH$_2$CH$_2$OCH$_2$Cl (12 h, room temperature): CH_2Cl_2, MeCl, Cl(CH$_2$)$_2$Cl, O(CH$_2$Cl)$_2$, MeOCH$_2$Cl, O(CH$_2$CH$_2$Cl)$_2$ and Me$_2$O (50 : 15 : 15 4 : 2 : 13 : 6).

The NMR spectra of the mixture obtained from **1b** and dme, before hydrolysis, exhibited resonances attributed to the compound WCl$_5$(OCH$_2$CH$_2$OMe), **7** (ratio CH_2Cl_2 : **7** : CH_3Cl = 10 : 8 : 9). ^{1}H NMR($CDCl_3$): δ = 5.72 (t, 2 H, $^3J_{HH}$ = 5.0 Hz, WOCH$_2$), 4.27 (t, 2 H, $^3J_{HH}$ = 5.0 Hz, CH$_2$), 4.03 (s, 3 H, Me) ppm. ^{13}C NMR{^{1}H} ($CDCl_3$): δ = 79.0 (WOCH$_2$), 75.6 (CH$_2$), 63.5 (Me) ppm.

Reactivity of 1a and 1b with CH(OMe)$_3$: synthesis of WOCl$_4$[O=C(H)OMe], 8. General procedure

Trimethylformate (0.65 mmol) was added to **1a** or **1b** (0.32 mmol), in $CDCl_3$ (0.70 mL)/CH_2Cl_2 (0.35 mmol) in an NMR tube. The tube was shaken to homogenize the mixture, and then maintained at room temperature for 24 h. The final mixture was treated with water (*ca.* 5 mmol): immediate precipitation of a green solid from a solution took place. NMR analysis of the latter pointed out the presence of CH_2Cl_2, MeCl and HCO$_2$Me (ratio from **1a**: 1 : 2 : 1; ratio from **1b**: 5 : 7 : 4). NMR spectrum of the mixture obtained from **1b** and CH(OMe)$_3$, before hydrolysis, evidenced the presence of complex **8**. The latter was isolated according to the following procedure: WCl$_6$, **1b** (0.180 g, 0.454 mmol), in CH_2Cl_2 (15 mL), was treated with CH(OMe)$_3$ (0.100 mL, 0.914 mmol). The mixture was stirred for 18 h. Thus, the final orange solution was layered with heptane and stored at −30 °C for 10 days. A brown solid corresponding to **8** was collected. Yield: 0.137 g, 75%. Anal. Calcd. for $C_2H_4Cl_4O_3W$: C, 5.98; H, 1.00; Cl, 35.30. Found: C, 6.06; H, 1.04; Cl, 35.06. IR (solid state): ν = 2963 w, 1652 s ($\nu_{C=O}$), 1431 m, 1417 m, 1371 w-m, 1289 s, 1262 m, 1148 m, 1056 s ($\nu_{W=O}$), 986 s, 886 vs, 808 vs, 675 s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 8.67 (CH), 4.19 (CH$_3$) ppm. ^{13}C NMR{^{1}H} ($CDCl_3$): δ = 170.5 (CH), 55.8 (CH$_3$) ppm.

X-Ray crystallographic study

Crystal data and collection details for [MoOCl$_3${O=C(H)-OCH$_2$CH$_2$Cl}]$_2$, **2**, and Mo$_2$Cl$_5$(OMe)$_5$, **5**, are reported in Table 4. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector using Mo-Kα radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS)[45] Structures were solved by direct methods and refined by

Table 4 Crystal data and experimental details for [MoOCl$_3${O=C(H)-OCH$_2$CH$_2$Cl}]$_2$, **2**, and Mo$_2$Cl$_5$(OMe)$_5$, **5**

	2	**5**
Formula	$C_6H_{10}Cl_8Mo_2O_6$	$C_5H_{15}Cl_5Mo_2O_5$
Fw	653.62	524.30
λ/Å	0.71073	0.71073
Temperature/K	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$
a/Å	21.043(4)	12.7518(9)
b/Å	6.1669(10)	12.8342(9)
c/Å	14.915(3)	10.3363(7)
β/°	93.412(2)	109.041(1)
Cell volume/Å^3	1932.0(6)	1599.1(2)
Z	4	4
D_c/g cm^{-3}	2.247	2.178
μ/mm^{-1}	2.421	2.406
F(000)	1256	1016
θ limits/°	1.94–26.00	1.69–26.00
Reflections collected	6369	15987
Independent reflections	1900 (R_{int} = 0.0228)	3142 (R_{int} = 0.0159)
Data/restraints/parameters	1900/1/103	3142/68/154
Goodness on fit on F^2	1.176	1.117
R_1 ($I > 2\sigma(I)$)	0.0181	0.0188
wR_2 (all data)	0.0417	0.0468
Largest diff. peak and hole/e Å^{-3}	0.303 and −0.682	0.651 and −0.480

full-matrix least-squares based on all data using F^2.[46] Hydrogen atoms bonded to C-atoms were fixed at calculated positions and refined by a riding model, except H(1) in **2** which was located in the Fourier map and refined isotropically using the 1.2 fold U_{iso} value of the parent C(1) atom; the C(1)–H(1) distance was restrained to 0.93 Å [s.u. 0.01]. The asymmetric unit of **2** contains only half of a molecule, the rest being generated by an inversion centre. Rigid bond restraints were applied to all atoms in **5** (s.u. 0.005).

Acknowledgements

The authors wish to thank the Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR, Roma), Programmi di Ricerca Scientifica di Notevole Interesse Nazionale 2007-2008, for financial support.

References

1 Some recent references are: (*a*) V. Rodriguez-Cisterna, C. Villar, P. Romea and F. Urpí, *J. Org. Chem.*, 2007, **72**, 6631; (*b*) C. Mamat, S. Büttner, T. Trabhardt, C. Fischer and P. Langer, *J. Org. Chem.*, 2007, **72**, 6273; (*c*) D. Basavaiah and K. R. Reddy, *Org. Lett.*, 2007, **9**, 57; (*d*) V. T. H. Nguyen, E. Bellur, B. Appel and P. Langer, *Synthesis*, 2006, 1103; (*e*) L. Anastasia, E. Giannini, G. Zanoni and G. Vidari, *Tetrahedron Lett.*, 2005, **46**, 5803.

2 G. Smitha, S. Chandrasekhar and C. S. Reddy, *Synthesis*, 2008, 829, and the reference therein.

3 (*a*) Y. Hayashi, M. Nakamura, S. Nakao, T. Inoue and M. Shoji, *Angew. Chem., Int. Ed.*, 2002, **41**, 4079; (*b*) M. Shoji, J. Yamaguchi, H. Kakeya, H. Osada and Y. Hayashi, *Angew. Chem., Int. Ed.*, 2002, **41**, 3192.

4 (*a*) T. Masuda, K. Hasegawa and T. Higashimura, *Macromolecules*, 1974, **7**, 728; (*b*) Y.-S. Gal, *J. Macromol. Sci.*, 1997, **A34**, 377; (*c*) G. Zhang and M. Neuenschwander, *Macromol. Rapid Commun.*, 1994, **15**, 777; (*d*) T. Masuda, K.-Q. Thieu and T. Higashimura, *Polym. J.*, 1978, **10**, 269.

5 (*a*) B. Düz, C. K. Elbistan, A. Ece and F. Sevin, *Appl. Organomet. Chem.*, 2009, **23**, 359; (*b*) F. E. Naylor, *U.S. Patent* 3,336,280 (to Phillips Petroleum Co.), 1967.

6 J. E. Baéz and A. Martínez-Richa, *Polymer*, 2005, **46**, 12118.

7 (*a*) V. I. Bykov, E. M. Khmarin, B. A. Belyaev, T. A. Butenko and E. Sh. Finkel'shtein, *Kinet. Catal.*, 2008, **49**, 11; (*b*) L. Hocks, A. Noels, A. Hubert and P. Teyssie, *J. Org. Chem.*, 1976, **41**, 1631; (*c*) F. Quignard, M. Leconte, J.-M. Basset, L.-Y. Hsu and J. J. Alexander, *Inorg. Chem.*, 1987, **26**, 4272.

8 (*a*) O. Dereli, B. Düz and Y. Imamoglu, *Eur. Polym. J.*, 2006, **42**, 368; (*b*) S. Çetinkaya, S. Karabulut, B. Düz and Y. Imamoglu, *Appl. Organomet. Chem.*, 2005, **19**, 347.

9 A. E. Feiring, *J. Fluorine Chem.*, 1979, **14**, 7.

10 S. Goswami and A. C. Maity, *Tetrahedron Lett.*, 2008, **49**, 3092.

11 A. Spurg, G. Schnakenburg and S. R. Waldvogel, *Chem. Eur. J.*, 2009, **15**, 13313.

12 (*a*) S. Kumar and M. Manickam, *Chem. Commun.*, 1997, 1615; (*b*) S. R. Waldvogel, *Synlett*, 2002, 622; (*c*) B. Kramer, R. Fröhlich, K. Bergander and S. R. Waldvogel, *Synthesis*, 2003, 91.

13 (*a*) E. M. Coe and C. J. Jones, *Polyhedron*, 1992, **11**, 3123; (*b*) H. Firouzabadi and F. Shirini, *Tetrahedron*, 1996, **52**, 14929; (*c*) H. Firouzabadi, N. Iranpoor and B. Karimi, *Synlett*, 1998, 739; (*d*) M. E. Jung and J. M. Murphy, *Tetrahedron Lett.*, 2007, **48**, 8388.

14 C. R. Reddy, B. Mahipal and S. R. Yaragorla, *Tetrahedron Lett.*, 2007, **48**, 7528.

15 (*a*) Q. Guo, T. Miyaji, G. Gao, R. Hara and T. Takahashi, *Chem. Commun.*, 2001, 1018; (*b*) Q. Guo, T. Miyaji, R. Hara, B. Shen and T. Takahashi, *Tetrahedron*, 2002, **58**, 7327.

16 (*a*) B. W. Yoo, M. C. Park and M. S. Song, *Synth. Commun.*, 2007, **37**, 4079; (*b*) B. W. Yoo, J. W. Choi and S. Park, *Bull. Korean Chem. Soc.*, 2008, **29**, 909.

17 (*a*) Y. Fujivara, R. Ishikawa, F. Akiyama and S. Teranishi, *J. Org. Chem.*, 1978, **43**, 2477; (*b*) C. R. Reddy, N. N. Rao and A. Sudhakar, *Lett. Org. Chem.*, 2008, **5**, 473; (*c*) J. R. Graham and L. H. Slaugh, *Tetrahedron Lett.*, 1971, **12**, 787; (*d*) Q. Guo, L. Li, L. Chen, Y. Wang, S. Ren and B. Shen, *Energy Fuels*, 2009, **23**, 51; (*e*) T. Hirao, S. Kohno, J. Enda, Y. Ohshiro and T. Agawa, *Tetrahedron Lett.*, 1981, **22**, 3633.

18 M. E. Jung and J. I. Wasserman, *Tetrahedron Lett.*, 2003, **44**, 7273.

19 (*a*) C. D. Garner and J. M. Charnock, Molybdenum(III), (IV) and (V), in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 3, pp. 1329–1374; (*b*) Z. Dori, Tungsten in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 3, pp. 973–1022; (*c*) C. G. Young, Molybdenum in *Comprehensive Coordination Chemistry II*, ed. J. A. McCleverty and T. J. Meyer, Pergamon, Oxford, 2003, Vol 4, pp. 415–527; (*d*) T. Okamura and N. Ueyama, Tungsten in *Comprehensive Coordination Chemistry II*, ed. J. A. McCleverty and T. J. Meyer, Pergamon, Oxford, 2003, Vol 4, pp. 529–573.

20 $MoCl_5$: (*a*) M. L. Larson, *J. Am. Chem. Soc.*, 1960, **82**, 1223; (*b*) D. L. Kepert and R. Mandyczewsky, *J. Chem. Soc. A*, 1968, 530; (*c*) T. Ernst, A. El-Kholi, U. Müller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1988, **566**, 7; (*d*) J. Hyde, L. Magin and J. Zubieta, *Chem. Commun.*, 1980, 204; (*e*) S. M. Horner and S. Y. Tyree, Jr., *Inorg. Chem.*, 1962, **1**, 122. WCl_6: (*f*) B. J. Brisdon, G. W. A. Fowles and B. P. Osborne, *J. Chem. Soc.*, 1962, 1330; (*g*) C. M. Mikulski, L. L. Pytlewski and N. M. Karayannis, *Inorg. Nucl. Chem. Lett.*, 1977, **13**, 165; (*h*) H. Balcar, A. Dosedlová and B. Matyska, *Coll. Czech. Chem. Commun.*, 1986, **51**, 753; (*i*) J. Levisalles, H. Rudler and D. Villemin, *J. Organomet. Chem.*, 1979, **164**, 251.

21 (*a*) E. Hey-Hawkins and H. G. von Schnering, *Z. Naturforsch.*, 1991, **46B**, 307; (*b*) E. Carmona, L. Sanchez and M. L. Poveda, *Polyhedron*, 1983, **2**, 797; (*c*) C. Redshaw, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1992, 555; (*d*) P. M. Boorman, N. N. Greenwood, M. A. Hildon and R. V. Parish, *J. Chem. Soc. A*, 1968, 2002; (*e*) C. Persson and C. Andersson, *Polyhedron*, 1991, **10**, 2089; (*f*) D. Zeng and M. J. Hampden-Smith, *Polyhedron*, 1992, **11**, 2585; (*g*) C. Persson and C. Andersson, *Inorg. Chim. Acta*, 1993, **203**, 235.

22 W. Wardlaw and H. W. Webb, *J. Chem. Soc.*, 1930, 2100.

23 K. Feenan and G. W. A. Fowles, *Inorg. Chem.*, 1965, **4**, 310.

24 F. A. Cotton, P. A. Kibala and R. B. W. Sandor, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1989, **45**, 1287.

25 (*a*) G. Pampus and G. Lehnert, *Makromol. Chem.*, 1974, **175**, 2605; (*b*) G. Lehnert, D. Maertens, G. Pampus and M. Zimmermann, *Makromol. Chem.*, 1974, **175**, 2617; (*c*) D. T. Laverty, M. A. McKervey, J. J. Rooney and A. Stewart, *J. Chem. Soc., Chem. Commun.*, 1976, 193; (*d*) P. O. Nubel, C. A. Lutman and H. B. Yokelson, *Macromolecules*, 1994, **27**, 7000.

26 (*a*) F. Marchetti, G. Pampaloni and S. Zacchini, *Dalton Trans.*, 2007, 4343; (*b*) F. Marchetti, G. Pampaloni and S. Zacchini, *Inorg. Chem.*, 2008, **47**, 365; (*c*) F. Marchetti, G. Pampaloni and S. Zacchini, *Polyhedron*, 2008, **27**, 1969; (*d*) F. Marchetti, G. Pampaloni and S. Zacchini, *Eur. J. Inorg. Chem.*, 2008, 453.

27 (*a*) R. Bini, C. Chiappe, F. Marchetti, G. Pampaloni and S. Zacchini, *Inorg. Chem.*, 2010, **49**, 339; (*b*) F. Marchetti, G. Pampaloni and S. Zacchini, *Dalton Trans.*, 2009, 6759; (*c*) F. Marchetti, G. Pampaloni and S. Zacchini, *Dalton Trans.*, 2009, 8096; (*d*) F. Marchetti, G. Pampaloni and S. Zacchini, *Chem. Commun.*, 2008, 3651; (*e*) F. Marchetti, G. Pampaloni and S. Zacchini, *Dalton Trans.*, 2008, 7026.

28 The hexachloride of tungsten(VI), WCl_6, has a mononuclear structure both in the solid state and in the vapour phase. The pentachloride of molybdenum(V) is dinuclear in the solid state and mononuclear in the vapour phase [A. F. Wells, *Structural Inorganic Chemistry*, 5th Edition, Clarendon Press, Oxford, 1993]. For the sake of simplicity, the latter compound will be mentioned in this paper by the empirical formula $MoCl_5$.

29 S. R. Waldvogel, A. R. Wartini, P. H. Rasmussen and J. Rebeck Jr, *Tetrahedron Lett.*, 1999, **40**, 3515.

30 C. Limberg, R. Boese and B. Schiemenz, *J. Chem. Soc., Dalton Trans.*, 1997, 1633.

31 E. I. Stiefel, Molybdenum(VI), in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 3, pp. 1375–1420.

32 P. Mastagli and M. De Nanteuil, *Compt. Rend., Serie C, Chemical Sciences*, 1972, **268**, 1970.

33 F. Marchetti, G. Pampaloni and S. Zacchini, *Polyhedron*, 2009, **28**, 1235.

34 A. Greco, F. Pirinoli and G. Dall'Asta, *J. Organomet. Chem.*, 1974, **69**, 293.

35 (*a*) F. A. Cotton, G. Wilkinson, C. A. Murillo and M. Bochmann, *Advanced Inorganic Chemistry*, Wiley, New York, 1999, 6th Ed., p. 926; (*b*) W. A. Nugent and J. M. Mayer, *Metal–Ligand Multiple Bonds*, Wiley, New York, 1988; (*c*) M. T. Pope and B. W. Dale, *Q. Rev. Chem. Soc.*, 1968, **22**, 527.

36 N. V. Bardina, T. A. Bazhenova, K. A. Lyssenko, M. Yu. Antipin, Y. M. Shulga, T. A. Filina and A. F. Shestakov, *Mendeleev Commun.*, 2006, **16**, 307.

37 B. Kamenar, B. Korpar-Collig, M. Penavic and M. Cindric, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1990, **46**, 195.

38 B. Kamenar and M. Penavic, *J. Chem. Soc., Dalton Trans.*, 1977, 356.

39 M. H. Chisholm, C. K. Kirkpatrick and J. C. Huffman, *Inorg. Chem.*, 1981, **20**, 871.

40 (*a*) C. Limberg, S. Parsons, A. J. Downs and D. J. Watkin, *J. Chem. Soc., Dalton Trans.*, 1994, 1169; (*b*) F. A. Cotton, *J. Less Common Met.*, 1977, **54**, 3; (*c*) C. Limberg, M. Büchner, K. Heinze and O. Walter, *Inorg. Chem.*, 1997, **36**, 872.

41 All the attempts to isolate products from the reactions of $MoCl_5$ with $CH_2(OR)_2$ ($R = Me, Et$) gave brown oily-solids, very air-sensitive, which could not be characterized.

42 S. M. Humphrey, C. Redshaw, K. E. Holmes and M. R. J. Elsegood, *Inorg. Chim. Acta*, 2005, **358**, 222.

43 (*a*) R. C. Larock, *Comprehensive Organic Transformations*, 2nd Edition, Wiley-VCH, New York, 1999; (*b*) M. B. Smith and J. March, *March's Advanced Organic Chemistry*, 5th Edition, J. Wiley, New York, 2001; (*c*) G. Balme and J. Goré, *J. Org. Chem.*, 1983, **48**, 3336; (*d*) M. E. Jung, W. A. Andrus and P. L. Ornstein, *Tetrahedron Lett.*, 1977, **18**, 4175; (*e*) A. H. Schmidt, *Aldrichim. Acta*, 1981, **14**, 31; (*f*) M. G. Voronkov, E. I. Dubinskaya and V. G. Komarov, *Russ. J. Gen. Chem.*, 1990, **60**, 1212; (*g*) A. K. Mandal, P. Y. Shrotri and A. D. Ghogare, *Synthesis*, 1986, 221.

44 D. A. Skoog and D. M. West, *Fundamentals of Analytical Chemistry*, 2nd Edition, Holt, Rinehart and Winston, Chatham, UK, 1974, p. 233.

45 G. M. Sheldrick, *SADABS*, University of Göttingen, Göttingen, Germany.

46 G. M. Sheldrick, *SHELX97*, University of Göttingen, Göttingen, Germany.