Unusual room temperature activation of 1,2-dialkoxyalkanes by niobium and tantalum pentachlorides†

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The outcome of the reactions of MCl_5 (M = Nb, **1a**; M = Ta, **1b**) with 1,2-dialkoxyalkanes [*i.e.* $MeO(CH_2)_2OMe$ (dme), $EtO(CH_2)_2OEt$, $MeOCH_2CH(Me)OMe$, $MeO(CH_2)_2OCH_2Cl$, $MeO(CH_2)_2O(CH_2)_2OMe$ (diglyme)] depends strictly on the stoichiometry. In the 1 : 1 molar ratio reactions, single C–O bond cleavage occurs, resulting in formation of alkyl chloride and of the complexes $\overline{MCl_4[O(R)CH(R')CH_2O]}$ [M = Nb, R = Me, R′ = H, **3a**; M = Ta, R = Me, R′ = H, **3b**; M = Nb, R = Et, R′ = H, **5**; M = Nb, R = R′ = Me, **6**; M = Nb, R = CH_2Cl, R′ = H, **7**; M = Nb, R = $(CH_2)_2O(Me)NbCl_5$, R′ = H, **8**], which have been characterized spectroscopically. Moreover, minor amounts of the oxo-bridged adducts $MOCl_3(dme)MCl_5$ (M = Nb, **4a**; M = Ta, **4b**) have been isolated in the reactions involving dme. On the other hand, compounds **1** react with two (or more) equivalents of dme mainly *via* a multiple C–O bond cleavage process, affording $MOCl_3(dme)$ (M = Nb, **2a**; M = Ta, **2b**), 1,4-dioxane and methyl chloride. The oxychloride compounds $MOCl_3$ (M = Nb, **11a**; M = Ta, **11b**) have been efficiently obtained by addition of $TiCl_4$ to **2**. Compound **2a** is reduced in high yield to the Nb(III) species $NbCl_3(dme)$, **12**, upon treatment with $SnBu_3H$. The oxychloride $NbOCl_3(diglyme)$, **9**, 1,4-dioxane, CH_3Cl and the hexachloroniobate salt $[MeOCH_2CH_2OCH_2CH_2O(H)Me][NbCl_6]$, **10**, have been identified as products of the reaction of **1a** with two equivalents of diglyme. The 1 : 2 molar ratio reaction of **1a** with $MeOCH_2CH(Me)OMe$ gives 2,5-dimethyl-1,4-dioxane. Compound **1a** reacts with two equivalents of $EtO(CH_2)_2OEt$ or $MeO(CH_2)_2OCH_2Cl$ yielding $Cl(CH_2)_2OCH_2CH_3$ or $O(CH_2Cl)_2$ and diglyme, respectively, but not dioxane, suggesting that fragmentation pathways different from that found for dme are operating. The X-ray molecular structures of **4a**, **4b** and **10** have been determined.

Introduction

The activation of C–O bonds by low valent and electron-rich transition metal complexes has represented a key-step for a huge variety of organic syntheses.[1] Alternatively, the use of electron-poor metal derivatives is a less employed approach:[2] a significant example is given by the synthesis of esters by acylative cleavage of ethers, promoted by low valent early transition metal complexes.[3]

Otherwise, it has been reported that the stoichiometric reactions of ethers with compounds of strongly oxophilic metals (lanthanides, early transition elements in high oxidation states) usually afford stable metal alkoxides.[4] In such cases, the ether undergoes breaking into smaller fragments, rather than affording functionalized species. For instance, 1,2-dimethoxyethane, dme, a diether widely used as solvent in synthetic chemistry, reacts with various oxophilic metal complexes with cleavage of one or two O–CH_2 bonds, affording methoxy-derivatives.[4e–g,5] Ethylene production has been observed in some cases.[4e,g,5c–e]

We recently showed[6] that when niobium and tantalum pentahalides are allowed to react with ketones or aldehydes or aliphatic cyclic ethers different reactions can take place, beyond the formation of the expected acid–base adducts $MX_5(L)$, depending on the nature of the halide and the *O*-donor to metal molar ratios.

In the light of these considerations, we became interested in the reactivity of MCl_5 (M = Nb, **1a**; Ta, **1b**)[7] with open-chain ethers and we recently reported a short communication on the room temperature reaction of $NbCl_5$ with 1,2-dimethoxyethane, dme, which cleanly affords $NbOCl_3(dme)$, **2a**, CH_3Cl and 1,4-dioxane (eqn (1), $C_4H_{10}O_2$ = dme).[8]

$$NbCl_5 + 2C_4H_{10}O_2 \rightarrow \underset{\mathbf{2a}}{NbOCl_3\left(C_4H_{10}O_2\right)} + 2CH_3Cl + \tfrac{1}{2}C_4H_8O_2 \quad (1)$$

The result schematized in eqn (1) is notable for several reasons: (i) niobium pentachloride is a simple system effective in promoting the unusual transformation of dme into 1,4-dioxane and methyl chloride under mild conditions; (ii) the reaction proceeds through the unprecedented cleavage of three dme C–O bonds; (iii) preliminary studies indicate that the same reaction is extensible to 1,2-dialkoxyalkanes different from dme; (iv) other preparations previously reported for niobium oxytrihalide adducts mostly require high temperatures;[9] (v) some reductive complexations of group 5 metal pentahalides[10] and some organic syntheses mediated by MCl_5 (M = Nb, Ta)[2e,11] have been performed in dme solution, thus these processes might take place *via* the intermediate formation of oxo-complexes.

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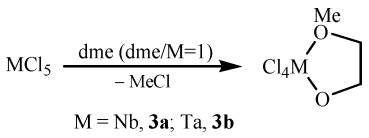
With respect to these points of interest, we decided to carry out a detailed study of the reactions of **1** with dme, and to extend this study to a variety of 1,2-dialkoxyalkanes. In the present paper, both the metal containing compounds and the organic products obtained by the different reactions will be presented, with particular reference to the stoichiometry employed in each case. Moreover, a novel room temperature synthesis of the oxychloride compounds $MOCl_3$ (M = Nb, Ta) will be described, and the role possibly played by oxo-compounds during the course of reductive reactions (see point v above) will be discussed.

Results and discussion

Reactivity of niobium and tantalum pentachlorides with 1,2-dialkoxyalkanes in 1 : 1 molar ratios

The reaction of $TaCl_5$, **1b**, with one equivalent of dme affords the alkoxyether adduct $TaCl_4[O(Me)CH_2CH_2O]$, **3b**, and methyl chloride in *ca.* 1 : 1 ratio, according to NMR evidence (see Experimental). The formation of **3b** is the result of single dme C–O bond cleavage, resembling what we reported in a recent communication about the 1 : 1 molar ratio reaction of **1a** with dme, see Scheme 1.[8]



Scheme 1

It is noteworthy that the complex $NbOCl_3$(dme), **2a** (see eqn (1)), formally derives from compound **3a** by addition of one dme and removal of one MeCl molecule and half dioxane unit. Actually we found that the treatment of **3a** with an excess of dme did cause partial transformation of **3a** into **2a**, CH_3Cl and 1,4-dioxane (see Experimental). This fact suggests that complexes **3** might act as intermediates during the reaction of **1** with large quantities of dme.

Compounds **3a–b** were obtained in optimal yields (*ca.* 80%) by reacting MCl_5, **1**, with one equivalent of $HOCH_2CH_2OMe$,[12] and were fully characterized by IR, NMR and elemental analyses. On the other hand, the reaction of **1** with one equivalent of dme afforded lower yields of **3** (55–60%). This is due to the fact that **3** is not the only metal-containing product obtainable by reacting **1** with dme in 1 : 1 molar ratio: another complex containing dme was isolated in 15–20% yield. This complex was characterized as the dinuclear species $MOCl_3$(dme)MCl_5 (*M–O–M*) (M = Nb, **4a**; M = Ta, **4b**), and more satisfactory yields for this were gained by reacting dme with a *ca.* 30% molar excess of **1**. The X-ray molecular structures of **4a–b** are represented in Fig. 1, and selected bond lengths and angles are reported in Table 1.

The molecules can be viewed as adducts of MCl_5 (M = Nb, Ta) with **2**, resembling in this the oxo bridged tetramers $[M_4O_2Cl_{18}]^{2-}$, M = Nb, Ta.[13] The geometry and bonding parameters of the $MOCl_3$(dme) units in **4a–b** are closely related to the ones discussed for **2a**,[8] apart from a detectable elongation of the M(1)–O(1) interaction [1.7579(14) Å in **4a** *vs.* 1.6939(18) Å in **2a**], which is a consequence of the further coordination of the oxo ligand to M(2).

Table 1 Selected bond lengths (Å) and angles (°) for $MOCl_3$(dme)MCl_5 (M = Nb, **4a**, M = Ta, **4b**)

	4a	**4b**
M(1)–O(1)	1.7579(14)	1.800(3)
M(1)–O(2)	2.1661(15)	2.158(3)
M(1)–O(3)	2.2898(14)	2.232(3)
M(1)–l(8)	2.2913(6)	2.2671(10)
M(1)–Cl(7)	2.3417(6)	2.3351(10)
M(1)–Cl(6)	2.3536(6)	2.3424(10)
M(2)–O(1)	2.1353(14)	2.030(3)
M(2)–Cl(2)	2.2778(6)	2.3272(10)
M(2)–Cl(5)	2.3120(6)	2.3201(10)
M(2)–Cl(1)	2.3284(6)	2.3407(10)
M(2)–Cl(4)	2.3311(6)	2.3348(10)
M(2)–Cl(3)	2.3423(6)	2.3521(10)
O(1)–M(1)–O(2)	96.67(6)	94.21(11)
O(1)–M(1)–O(3)	168.53(6)	167.03(11)
O(2)–M(1)–O(3)	72.37(5)	72.84(10)
M(1)–O(1)–M(2)	167.07(9)	164.15(16)
O(2)–C(2)–C(3)	107.09(17)	105.8(3)
C(3)–O(3)–M(1)	112.86(11)	114.1(2)
O(1)–M(2)–Cl(2)	178.76(4)	178.71(8)
O(1)–M(2)–Cl(5)	83.48(4)	87.47(8)
O(1)–M(2)–Cl(1)	86.67(4)	88.77(8)
O(1)–M(2)–Cl(4)	85.32(4)	86.91(8)
O(1)–M(2)–Cl(3)	85.23(4)	87.38(8)

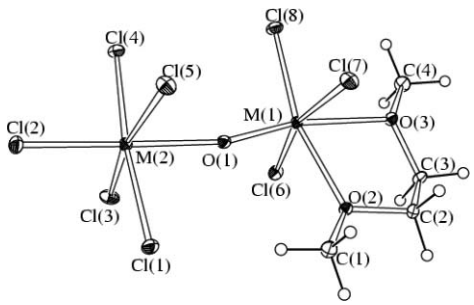


Fig. 1 View of the molecular structure of $MOCl_3$(dme)MCl_5 (M = Nb, **4a**, M = Ta, **4b**). Displacement ellipsoids are at the 30% probability level.

At variance to what is generally observed for μ-oxo derivatives of transition metals [see for example $(MCp_2X)_2O$,[14] $(Ta_2OCl_{10})^{2-}$,[13d,15] $[TaCl_2(NMe_2)_2(HNMe_2)]_2O$[16]], the M(1)–O(1)–M(2) angle deviates significantly from linearity [167.07(9)° in **4a** and 164.15(16)° in **4b**]; moreover the two M–O lengths differ considerably from each other [Nb(1)–O(1): 1.7579(14) Å *vs.* Nb(2)–O(1): 2.1353(14) Å; Ta(1)–O(1): 1.800(3) Å *vs.* Ta(2)–O(1): 2.030(3) Å]. The bond distances and angles regarding the bridging oxygen in **4** are better comparable to those reported for $NbOCl_3$,[17] the structure of which consists of dimeric units linked by asymmetric [Nb–O: 2.203(3) and 1.758(3) Å] and bent (Nb–O···Nb: 170.56°) bridges. The asymmetry of the bridge further corroborates the fact that **4a–b** can be viewed as the result of coordination of $MOCl_3$(dme) to the Lewis acid MCl_5.

We believe that the oxo-unit within compounds **4** originates *via* a O-abstraction reaction from dme (see eqn (1)). Accordingly, the formation of **4**, in the course of the 1 : 1 reaction between **1** and dme, should be accompanied by the formation of 1,4-dioxane. Although no dioxane was observed by monitoring these reactions *via* ^1H NMR, small amounts of that cyclic ether were detected (GC/MS) on the reaction mixtures after hydrolysis

(see Experimental). Presumably, under anhydrous conditions (*i.e.* the conditions of the NMR experiment), the sparingly soluble MCl_5(dioxane)[18] is formed, the lower solubility of this complex with respect to **3** preventing the detection of the former in solution.

In summary, the reactions of **1** with limited amounts of dme proceed *mainly via* single C–O bond cleavage affording **3**: nevertheless, further dme fragmentation takes place to a limited extent producing minor amounts of $MOCl_3$(dme), which gives **4** in the presence of excess MCl_5.

With the aim to extend the chemistry of **1** with dme to similar organic substrates, we decided to study the reactivity of $NbCl_5$, **1a**, with a series of 1,2-dialkoxyalkanes. The 1 : 1 molar ratio reactions proceed with cleavage of one external C–O bond, similar to the behaviour of dme (Scheme 1). In particular, compound **1a** reacts with $EtO(CH_2)_2OEt$ or $MeOCH_2CH(Me)OMe$ to give in good yield compounds of general formula $\overline{NbCl_4[O(R)CHR^1CH_2O]}$ (**5**, R = Et, R^1 = H; **6**, R = R^1 = Me), and alkyl chloride (in about 1 : 1 ratio with respect to the inorganic product, according to ^{1}H NMR evidence), see eqn (2).

$$NbCl_5 + ROCHR^1CH_2OR \rightarrow \overline{NbCl_4[O(R)CHR^1CH_2O]} + RCl \quad (2)$$

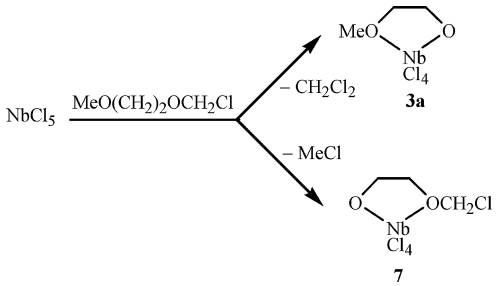
R = Et, R^1 = H, **5**
R = R^1 = Me, **6**

Compounds **5** and **6** have been characterized by NMR spectroscopy and elemental analyses. On the basis of the NMR features, the reaction of $NbCl_5$ with 1,2-dimethoxypropane affording **6** is highly chemoselective, since the alternative complex $\overline{NbCl_4[O(Me)CH_2CH(Me)O]}$, deriving from the cleavage of the O–Me bond at the most hindered side of the diether, has not been detected in solution. Complex **6** has been obtained as a mixture of two inseparable isomers, in 2 : 1 ratio, differing in the relative orientations of the substituents at the chiral centre (*i.e.*, H and Me). The ^{1}H NMR spectrum of the major isomer exhibits resonances at 5.24 and 5.08, 4.68, 3.98, 1.60 ppm, which have been assigned to the $NbOCH_2$, *CH*, O*Me* and CH*Me* protons, respectively. The ^{1}H NMR spectrum of the less abundant isomer displays a similar pattern.

Furthermore, the reactivity of $NbCl_5$, **1a**, with 1,2-dialkoxyethanes of generic formula $MeO(CH_2)_2OR$ [R = CH_2Cl, $(CH_2)_2OMe$ (diglyme)] has been explored in order to establish a possible influence of different R substituents on the reactivity.

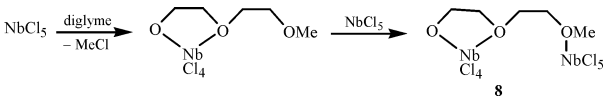
According to ^{1}H NMR data, the addition of one equivalent of $MeO(CH_2)_2OCH_2Cl$ to **1a** gives a mixture of $\overline{NbCl_4[O(Me)CH_2CH_2O]}$, **3a**, and $\overline{NbCl_4[O(CH_2Cl)CH_2CH_2O]}$, **7**, in *ca.* 5 : 2 ratio, which we have not been able to separate. The formation of these compounds is the consequence of the alternative cleavage of one of the two different external C–O bonds within 1-chloromethoxy-2-methoxyethane, $Me–O(CH_2)_2O–CH_2Cl$. In other words, two distinct potential fragmentation routes, consisting of breaking of one external C–O bond, are possible for this diether, and both are operating. Methyl chloride and methylene chloride should be expected as organic products, see Scheme 2, and these two substances have been actually found in the mixture at the end of reaction.

Otherwise, the reaction of **1a** with diglyme has yielded a complicated mixture containing prevalently the dinuclear complex **8**, Scheme 3. This compound, which has been isolated by fractional crystallization and identified by ^{1}H NMR spectroscopy and



Scheme 2

elemental analyses, is the result of the coordination of one diglyme to two $NbCl_5$ moieties, accompanied by cleavage of one O–Me bond and one Nb–Cl bond. In agreement, methyl chloride has been detected as a product of this reaction, *via* both NMR and GC/MS. In other words, the initial coordination of diglyme to **1a**, occurring presumably *via* two oxygen atoms in a "dme-fashion" (see Scheme 1), is then followed by MeCl elimination and consequent formation of a fragment which is still able to coordinate further $NbCl_5$.



Scheme 3

Complexes containing a bidentate, intact, diglyme ligand have been reported in the literature, and examples are: [Pb(hexafluoroacetyl-acetonato)$_2$(μ-η^3-η^1-diglyme)]$_2$,[19] $TiCl_2(OBut)_2$-(*O*,*O*′-diglyme),[20] and $TiCp_2$(*O*,*O*′-diglyme).[21]

Reactivity of niobium and tantalum pentachlorides with 1,2-dialkoxyalkanes in 1 : 2 molar ratios

It is worthy of mention that when a CH_2Cl_2 suspension of **4a** was reacted with dme, compound **2a** was isolated in very good yield. This indicates that the [MCl_5] moiety in **4** can be easily displaced from $MOCl_3$(dme) by addition of further dme, giving 2 equivalents of $MOCl_3$(dme), methyl chloride and 1,4-dioxane (eqn (3)).

$$\mathbf{4a} + 2C_4H_{10}O_2 \rightarrow 2\underset{\mathbf{2a}}{NbOCl_3(C_4H_{10}O_2)} + 2CH_3Cl + \tfrac{1}{2}C_4H_8O_2 \quad (3)$$

The oxytrichloride species $MOCl_3$(dme) (M = Nb, **2a**;[8] M = Ta, **2b**) were isolated in good yields by direct combination of MCl_5, **1**, with two equivalents of dme, eqn (4).

$$MCl_5 + 2C_4H_{10}O_2 \rightarrow \mathbf{2} + 2CH_3Cl + \tfrac{1}{2}1,4\text{-}C_4H_8O_2 \quad (4)$$

The spectroscopic features of **2b** resemble those already reported for **2a**.[8] The IR spectrum (recorded in the solid state) displays an intense absorption related to the Ta=O bond, at 910 cm^{-1} (954 cm^{-1} for Nb=O in **2a**).[8,22] The shift towards higher wavenumbers of the metal–oxygen stretching vibration in **2** with respect to **4** (876 cm^{-1} in **4a** and 872 cm^{-1} in **4b**) is a consequence of the enhancement of the metal–oxygen bond order, due to loss of the M–O–M interaction, which exists in **4**.

Moreover, the ^{1}H NMR resonances ($CDCl_3$ solution) accounting for the dme unit appear as singlets at 4.14 (CH_2) and 3.95 (CH_3) ppm. In agreement with the X-ray solid state structure determined for **2a**, the dme frame within complexes **2** is asymmetrically

coordinated to the metal centre; therefore, two pairs of resonances for non-equivalent CH_2 and CH_3 groups would be expected in the NMR spectra. The equivalence of the two CH_2 and of the two CH_3 groups suggests that a fast exchange phenomenon is operating in solution at room temperature. Analogous fluxionality was observed in similar mononuclear niobium adducts.[23] Unfortunately, low temperature NMR experiments could not be performed on complexes **2**, due to the low solubility in suitable deuterated solvents below 0 °C.

In order to focus on the formation of organic products deriving from the fragmentation of dme, the reactions of MCl_5 with two equivalents of dme were carried out in NMR tubes ($CDCl_3$ as solvent) and monitored by ^1H and ^{13}C NMR spectroscopies, in the presence of a known quantity of CH_2Cl_2 used as reference. Compounds **2**, CH_3Cl, MCl_5(1,4-dioxane)[18] and 1,4-dioxane, together with minor amounts of $[MCl_3(OCH_3)_2]_2$[24–26] and 1,2-dichloroethane, were seen in the final solutions (see Experimental). Coherently with the NMR features, the main reaction occurring when **1** is mixed with two equivalents of dme may be outlined according to eqn (4). This reaction implies the breaking of three of the four C–O bonds of dme. Beside that reaction, a secondary pathway of dme fragmentation seems to be operative concurrently: this pathway requires the cleavage of the two O–CH_2 bonds and would explain the formation of 1,2-dichlorethane and of $MCl_3(OCH_3)_2$ species, which have been reported to exist as dimers[26,25] (eqn (5)).

$$MCl_5 + C_4H_{10}O_2 \rightarrow \tfrac{1}{2}[MCl_3(OCH_3)_2]_2 + ClCH_2CH_2Cl \qquad (5)$$

The formation of CH_3Cl, 1.4-dioxane and 1,2-dichloroethane has been confirmed by GC/MS analyses. On the other hand, the presence in solution of MCl_5(1,4-dioxane), detected by NMR, is reasonable, since the dioxane produced by the main reaction (eqn (4)) should compete with dme in the coordination to the $MOCl_3$ moiety or to the still unreacted MCl_5. Interestingly, GC/MS and NMR analyses on the mixture obtained by reacting MCl_5 with a large excess of dme (10 equivalents or more) have allowed the identification of **2**, CH_3Cl and free dioxane, thus indicating that the main route (eqn (4)) is still effective even in correspondence of high dme/MCl_5 molar ratios. As expected, under these conditions, MCl_5(1,4-dioxane) is not generated, in view of the fact that dme is now largely predominant with respect to dioxane, and thus significantly favoured in coordinating the metal centre.

As stated in the Introduction, a number of examples have been reported of the activation of 1,2-dimethoxyethane by oxophilic metal complexes, which gives methoxy derivatives, as a consequence of the cleavage of two O–CH_2 bonds.[4,5]

Also, in connection with the chemistry described herein, some aluminium species promote the cleavage of the dme O–CH_3 bonds: for instance, $[(Me_3Si)_2CH]_2Al–Al[CH(SiMe_3)_2]_2$ reacts with potassium/dme affording the glycolato derivative $[(Me_3Si)_2CH]_2Al(OCH_2CH_2O)K(dme)$;[27] a similar aluminium compound, $[(Me_3SiCH_2)_2Al(OCH_2CH_2O)]_2$, has been isolated in attempting to prepare aluminium amides in dme solution.[28] Moreover, the species $[AlIMe(OCH_2CH_2OMe)]_2$ forms by reaction of dme with the "high-temperature molecule AlI", *via* single O–CH_3 bond breaking.[29]

Notwithstanding this, the dme fragmentation process summarized in eqn (4) is unprecedented in the sense it takes place *via* cleavage of three ethereal C–O bonds.

In contrast to that described about the reaction of **1a** with two equivalents of dme, which leads to the formation of **2a**, the reactions of **1a** with two (or more) equivalents of 1,2-diethoxyethane, 1,2-dimethoxypropane, 1-chloromethoxy-2-methoxyethane and diglyme appear to be less selective, and the inorganic products could not be identified, the only exception being $NbOCl_3$(*O*,*O*′-diglyme), **9**, which is characterized by a strong Nb=O stretching vibration at 934 cm^{-1}.

Concerning the organic products, 2,5-dimethyl-1,4-dioxane has been discovered by GC/MS in the reaction of **1a** with a two-fold excess of 1,2-dimethoxypropane: although a precise quantification of the yield has not been possible hitherto, a new potential way for the facile preparation of methyl-substituted dioxanes is given.

The nature of the alkoxy groups is crucial in determining the fragmentation pathway followed by the 1,2-dialkoxyalkane $ROCH_2CH_2OR$, when this is reacted with $NbCl_5$ in 2 : 1 molar ratio. Interestingly, $MeO(CH_2)_2OCH_2Cl$ gives $O(CH_2Cl)_2$ and diglyme, while $Cl(CH_2)_2OCH_2CH_3$ has been recognised in the final mixture of the reaction of **1a** with two equivalents of $EtO(CH_2)_2OEt$ (see Experimental). As a matter of fact, neither 1,4-dioxane nor 1,2-dichloroethane have been found as products in these two cases.

On the other hand, 1,4-dioxane is produced in good yield when **1a** is reacted with diglyme in *ca.* 1 : 2 molar ratio. Nevertheless, when monitoring the 1 : 2 reaction of **1a** with diglyme by NMR, a complicated ^1H NMR spectral pattern was seen, indicating that, under these conditions, diglyme probably reacts with **1a** following several fragmentation pathways. In particular, we observed a downfield resonance ($\delta = 8.72$ ppm, see Experimental), which suggested to us the possible formation of some stabilized *O*-protonated organic species. Indeed, the study of the chemistry of the halides MX_5 (M = Nb, Ta) with ketones and acetylacetones has demonstrated that $[MX_6]^-$ salts of the protonated organic substrates can form as secondary products, for which the O–*H* protons can give rise to ^1H NMR downfield resonances.[6] In order to verify the possibility, we made several attempts to grow X-ray quality crystals from the reaction liquor. A successful attempt gave crystals suitable for X-ray analysis which were identified as the hexachloroniobate salt of protonated diglyme, *i.e.* $[MeOCH_2CH_2OCH_2CH_2O(H)Me][NbCl_6]$, **10**, which OH hydrogen atom might come from some diglyme C–H bond activation. Water cannot be excluded in principle as the source of the OH hydrogen, although this possibility appears unlikely since the reaction has been carried out in strictly anhydrous conditions. The molecular structure of **10** is represented in Fig. 2, and selected bond lengths and angles are reported in Table 2. Further characterization of **10** was supported by IR spectroscopy (in solid), showing the O–H stretching vibration at 3175 cm^{-1}.

The molecular structure of **10** consists of an octahedral $[NbCl_6]^-$ anion and a protonated diglyme cation $[MeOCH_2CH_2O–CH_2CH_2O(H)Me]^+$. The unit cell contains twelve anions and twelve cations, one and a half of which being independent (the complete second anion and cation are generated by an inversion centre). The *O*-bonded hydrogen atoms in the protonated diglyme have been located in the Fourier map and their positions are in agreement with the formation of an extended network of hydrogen bonds, which generates an infinite chain of H-bonded cations. In order to obtain this polymeric structure, protonation occurs on the terminal –OMe groups of each diglyme molecule [O(1),

Table 2 Selected bond distances (Å), angles (°) and hydrogen bond parameters for $[MeOCH_2CH_2OCH_2CH_2O(H)Me][NbCl_6]$, **10**

Bond distances			
Nb(1)–Cl(2)	2.3297(8)	Nb(1)–Cl(6)	2.3356(8)
Nb(1)–Cl(1)	2.3422(8)	Nb(1)–Cl(4)	2.3471(8)
Nb(1)–Cl(5)	2.3562(8)	Nb(1)–Cl(3)	2.3768(8)
Nb(2)–Cl(7)	2.3483(8)	Nb(2)–Cl(9)	2.3462(8)
Nb(2)–Cl(8)	2.3542(7)		

Angles			
Cl(2)–Nb(1)–Cl(6)	90.19(3)	Cl(2)–Nb(1)–Cl(1)	90.71(3)
Cl(6)–Nb(1)–Cl(1)	91.17(3)	Cl(2)–Nb(1)–Cl(4)	90.25(3)
Cl(6)–Nb(1)–Cl(4)	91.36(3)	Cl(1)–Nb(1)–Cl(4)	177.29(3)
Cl(2)–Nb(1)–Cl(5)	179.23(3)	Cl(6)–Nb(1)–Cl(5)	89.16(3)
Cl(1)–Nb(1)–Cl(5)	89.72(3)	Cl(4)–Nb(1)–Cl(5)	89.35(3)
Cl(2)–Nb(1)–Cl(3)	91.04(3)	Cl(6)–Nb(1)–Cl(3)	178.73(3)
Cl(1)–Nb(1)–Cl(3)	89.11(3)	Cl(4)–Nb(1)–Cl(3)	88.34(3)
Cl(5)–Nb(1)–Cl(3)	89.60(3)		
C(1)–O(1)–C(2)	116.2(2)	O(1)–C(2)–C(3)	111.4(2)
O(2)–C(3)–C(2)	109.2(2)	C(4)–O(2)–C(3)	111.9(2)
O(2)–C(4)–C(5)	108.7(2)	O(3)–C(5)–C(4)	110.6(2)
C(5)–O(3)–C(6)	115.3(2)	O(4)–C(7)–C(8)	107.6(2)
O(5)–C(8)–C(7)	110.4(2)	C(9)–O(5)–C(8)	116.4(2)

Hydrogen bonds parameters				
D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(3)–H(3)···O(3)#3	0.845(10)	1.550(16)	2.388(4)	171(8)
O(5)–H(5)···O(1)	0.844(10)	1.578(15)	2.413(2)	170(3)
O(1)–H(1)···O(5)	0.848(10)	1.574(15)	2.413(2)	170(7)

Symmetry transformations used to generate equivalent atoms: #3 − *x*, *y*,−*z* + 1/2.

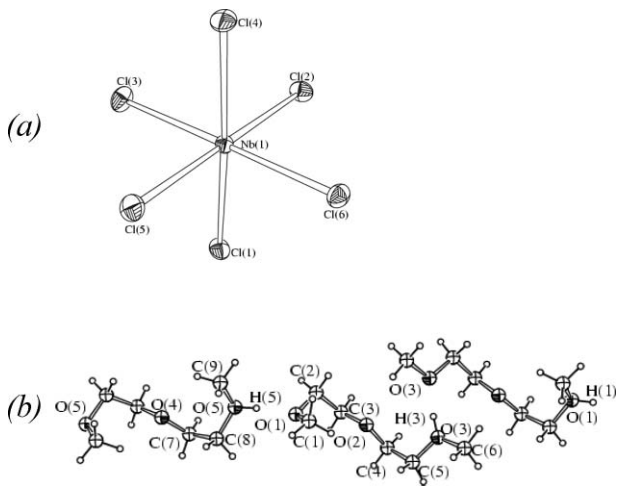


Fig. 2 View of the molecular structure of $[MeOCH_2CH_2OCH_2CH_2O(H)Me][NbCl_6]$, **10**: (*a*) the octahedral $[NbCl_6]^-$ anion (only one of the two independent anions has been drawn). (*b*) the $[MeOCH_2CH_2OCH_2CH_2O(H)Me]^+$ cation for which part of the infinite H-bonded chain is represented. Displacement ellipsoids are at the 30% probability level. Only independent atoms are labelled.

O(3) and O(5)], and not on the central oxygens [O(2) and O(4)]. In order to have one H^+ per diglyme molecule and to avoid the simultaneous presence of two OH groups on the same H-bond, an occupancy factor of 0.5 has been assigned to H(1), H(3) and H(5). Therefore, hydrogen bonds exist between all O(3)···O(3) and O(1)···O(5) contacts, but because of disorder protons are alternatively present on one or the other oxygen atom. As a consequence of protonation, all C–O bonds involving protonated oxygens [C(1)–O(1) 1.446(3) Å, C(2)–O(1) 1.455(3) Å, C(5)–O(3) 1.444(3) Å, C(6)–O(3) 1.446(3) Å, C(8)–O(5) 1.461(3) and C(9)–O(5) 1.454(3) Å] are markedly elongated compared to the non protonated ones [C(3)–O(2) 1.423(3) Å, C(4)–O(2) 1.422(3) Å, C(7)–O(4) 1.423(3) Å]. All other C–C and C–O contacts are in keeping with normal single bonds present in unsaturated organic molecules.[30]

Room temperature synthesis of niobium and tantalum oxytrichlorides

The oxygen-abstraction reaction leading to $MOCl_3(dme)$, **2**, occurs smoothly at room temperature, whereas the syntheses of the oxyhalides MOX_3 (M = Nb, Ta; X = Cl, Br) generally require temperatures between 60 and 130 °C,[9,31] as described for analogous compounds of the sp-block, such as AlOX.[32]

Therefore, we became interested in finding the way to prepare the known $MOCl_3$ from **2**. Interestingly, we saw that the addition of an excess of $TiCl_4$ to dichloromethane solutions of crystalline **2** resulted in the almost instantaneous precipitation of the colourless oxychloride compounds $MOCl_3$, **11**, from yellow solutions containing $TiCl_4(dme)$ (eqn (6)).

$$\underset{\mathbf{2}}{MOCl_3(dme)} + TiCl_4 \rightarrow \underset{\mathbf{11}}{MOCl_3} + TiCl_4(dme) \quad (6)$$

This observation indicates a room temperature pathway for the preparation of $MOCl_3$ (M = Nb, **11a**; Ta, **11b**), starting from MCl_5. Unfortunately, attempts to obtain **11** by a one-pot synthesis, *i.e.* treating MCl_5 with excess dme and then with $TiCl_4$, led to clean solutions of $TiCl_4(dme)$, but the solids **11a–b** resulted contaminated by organic impurities, according to IR and elemental analyses data.

Niobium and tantalum oxytrichlorides as precursors of M(III) species

The fact that **2** may possibly play a role in synthetic procedures which make use of niobium and tantalum pentahalides and dme[10] has been already mentioned (see Introduction, point v). According to the literature, the tantalum(III)–alkyne complexes $TaCl_3(alkyne)$ are obtained by zinc reduction of $TaCl_5$ in the presence of dme, and successive treatment with alkyne. These compounds, which represent important precursors for a variety of interesting organic preparations,[2e,11] might derive from initial formation of the oxychloride species $TaOCl_3dme$, **2b**, in agreement with eqn (4). Furthermore, with reference to the reduction of $NbCl_5$ to $NbCl_3(dme)$ by $SnBu_3H$ in dme,[10a] we observed that the treatment of a suspension of crystalline **2a** with $SnBu_3H$ resulted in the fast formation of a brick-red solid, identified as $NbCl_3(dme)$, **12** (eqn (7)).

$$\underset{\mathbf{2a}}{NbOCl_3(dme)} + SnBu_3H \rightarrow \underset{\mathbf{12}}{NbCl_3(dme)} + \text{"}SnBu_3OH\text{"} \quad (7)$$

This evidence supports the idea that the formation of $NbOCl_3(dme)$ may be really the first step in the course of the tin hydride reduction of Nb(V) to Nb(III) by $SnBu_3H$ in dme.

Conclusions

Although the chemistry of niobium and tantalum pentahalides with oxygen-containing organics was scarcely developed in the past,[6] the results presented herein show that such halides are efficiently capable of promoting clean reactions on 1,2-dialkoxyalkanes at room temperature, proceeding through the cleavage and the establishment of C–O bonds. The fact that 1,2-dimethoxyethane, dme, is not stable in the presence of MCl_5 is particularly meaningful when considering that dme has been widely employed as solvent in preparative inorganic chemistry and in metal-directed organic synthesis involving group 5 pentahalides. Our observations suggest that M(v) oxo-complexes (M = Nb, Ta) might behave as intermediates in reactions involving the reduction of MCl_5, carried out in dme solution.

We have shown that the outcomes of the reactions of MCl_5 (M = Nb, Ta) with 1,2-dialkoxyalkanes depend strictly on the stoichiometry used. In more detail, when MCl_5 and the diether react in *ca.* 1 : 1 molar ratio, single C–O bond activation occurs, with consequent formation of alkoxyether complexes and alkyl chlorides. Minor amounts of the dinuclear μ-oxo bridged species $MOCl_3(dme)MCl_5$ have been isolated in the reactions involving dme.

On the other hand, the 1 : 2 ratio reactions between MCl_5 and 1,2-dialkoxyalkanes are strongly influenced by the nature of the latter. In the cases of dme and diglyme, unprecedented activation of three ethereal C–O bonds takes place, resulting in formation of the oxychloride species $MOCl_3$(*O*,*O*′-ligand) and 1,4-dioxane. Analogously, the 2 : 1 ratio reaction of 1,2-dimethoxypropane with $NbCl_5$ indicates a potential strategy for the expeditious synthesis of a methyl-substituted dioxane. Alternative fragmentation pathways, which do not lead to dioxanes, are followed by different 1,2-dialkoxyalkanes.

Finally, the oxytrichlorides $MOCl_3$(dme) are revealed as convenient precursors for $MOCl_3$, thus indicating a novel room temperature route for the preparation of $MOCl_3$ starting from MCl_5.

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. MCl_5 (M = Nb, **1a**; M = Ta, **1b**) were commercial products (Aldrich), sublimed at 100–110 °C and 10^{-2} Torr before use. $TiCl_4$, $SnBu_3H$, 2-methoxyethanol and 1-chloromethoxy-2-methoxyethane were commercial products (Aldrich), stored under argon atmosphere as received. CH_2Cl_2, CD_2Cl_2, $CDCl_3$, 1,2-dimethoxyethane (dme), 1,2-dimethoxypropane, 1,2-diethoxyethane and $MeO(CH_2)_2O(CH_2)_2OMe$ (diglyme) were distilled before use under argon atmosphere from P_4O_{10}, while pentane was distilled from $LiAlH_4$. Infrared spectra were recorded at 298 K on a FT IR-Perkin Elmer Spectrometer, equipped with a UATR sampling accessory. NMR measurements were recorded on Mercury Plus 400 instrument at 298 K, unless otherwise specified. The chemical shifts for ^1H and ^{13}C were referenced to the non-deuterated aliquot of the solvent. 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 at the Dipartimento di Chimica Farmaceutica of the University of Pisa 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 chlorine content was determined by the Volhard method[33] after exhaustive hydrolysis of the sample. The metal was analyzed as M_2O_5 obtained by hydrolysis of the sample followed by calcination in a platinum crucible. The halogen and the metal analyses were repeated twice in order to get reproducible results.

Preparation of $MOCl_3$(dme), M = Nb, Ta. The preparation of **2b** is described in detail; compound **2a** was obtained by analogous procedure.[8] A suspension of **1b** (0.180 g, 0.502 mmol) in CH_2Cl_2 (20 mL), was treated with dme (0.12 mL, 1.15 mmol), and the resulting mixture was stirred at room temperature for 5 h, during which progressive dissolution of the solid and darkening of the solution were noticed. Hence, the volatile materials were removed under vacuum. Crystallization of the residue from CH_2Cl_2/pentane at room temperature gave a pale yellow microcrystalline solid corresponding to **2b**. Yield: 0.136 g (69%). Anal. Calcd for $C_4H_{10}Cl_3O_3Ta$: C, 12.21; H, 2.56; Ta, 45.99; Cl, 27.03. Found: C, 12.10; H, 2.69; Ta, 45.61; Cl, 26.45%. IR (solid state): 910 s [$\nu_{Ta=O}$] cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.14 (s, 2H, CH_2), 3.95 ppm (s, 3H, CH_3).

In a different experiment, CH_2Cl_2 (0.0321 mL, 0.500 mmol) and dme (0.055 mL, 0.53 mmol) were introduced into a NMR tube containing a suspension of compound **1b** (0.090 g, 0.251 mmol) in $CDCl_3$ (0.80 mL). The tube was sealed, and a light brown solution formed in 3 h time. Subsequent ^1H and ^{13}C NMR analyses (recorded at 243 K and at 298 K) revealed the presence of CH_2Cl_2, compound **2b**, CH_3Cl (^1H NMR: 3.00 ppm[34]), $TaCl_5$(1,4-dioxane),[18] 1,4-dioxane, 1,2-dichloroethane and $[TaCl_3(OCH_3)_2]_2$[24,25] in *ca.* 20 : 9 : 16 : 3 : 2 : 1 : 1 ratio. CH_3Cl, 1,4-dioxane and 1,2-dichloroethane were also detected by GC/MS analysis carried out on an aliquot of the mixture at the end of reaction. When complex **1b** (0.25 mmol) was reacted with dme (2.8 mmol) in $CDCl_3$, compound $TaCl_5$(1,4-dioxane) was not ascertained by ^1H NMR spectroscopy.

Analogous results were achieved by NMR and GC/MS investigations on the reactions of **1a** with dme in different stoichiometric ratios.

*$NbOCl_3$(dme), **2a**.* Anal. Calcd for $C_4H_{10}Cl_3O_3Nb$: C, 15.71; H, 3.30; Nb, 30.44; Cl, 34.82. Found: C, 15.93; H, 3.24; Nb, 29.82; Cl, 33.97%. IR (solid state): 2946 w, 1466 m, 1448 m-s, 1277 w-m, 1238 w-m, 1188 w, 1123 w, 1071 m, 1016 s, 984 s, 954 vs [$\nu_{Nb=O}$], 927 ms, 854 vs, 818 s cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2): δ = 4.20 (s, 2H, CH_2), 3.98 ppm (s, 3H, CH_3). ^{13}C NMR (400 MHz, CD_2Cl_2): δ = 74.0 (CH_2), 63.5 ppm (CH_3).

Preparation of $\overline{MCl_4[O(Me)CH_2CH_2O]}$, M = Nb, Ta. The preparation of **3a** is described in detail; compound **3b** was obtained by analogous procedure. Liquid $MeO(CH_2)_2OH$ (0.068 mL, 0.86 mmol) was added to a suspension of **1a** (0.230 g, 0.851 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for 30 min at room temperature, during which progressive dissolution of the solid and gas evolution (HCl) were observed. Compound **3a** was obtained

as a colourless microcrystalline solid from a dichloromethane solution layered with pentane, at –20 °C. Yield: 0.211 g (80%). Anal. Calcd for $C_3H_7Cl_4NbO_2$: C, 11.63; H, 2.27; Nb, 29.99; Cl, 45.77. Found: C, 11.48; H, 2.35; Nb, 30.25; Cl, 44.98%. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.23$ (t, $^3J_{HH} = 5.86$ Hz, 2H, CH_2ONb), 4.43 (t, $^3J_{HH} = 5.86$ Hz, 2H, CH_2OMe), 4.02 ppm (s, 3H, Me). ^{13}C NMR (400 MHz, $CDCl_3$): $\delta = 78.7$ (CH_2ONb), 78.3 (CH_2OMe), 65.2 ppm (Me).

*$TaCl_4[O(Me)CH_2CH_2O]$, **3b**.* Colourless, air sensitive solid; 79% yield from **1b** (0.180 g, 0.502 mmol) and $MeO(CH_2)_2OH$ (0.040 mL, 0.51 mmol). Anal. Calcd for $C_3H_7Cl_4O_2Ta$: C, 9.06; H, 1.77; Ta, 45.48; Cl, 35.64. Found: C, 9.21; H, 1.82; Ta, 45.30; Cl, 34.95%. IR (solid): 2944 w, 2891 w, 2846 w, 1597 w-m, 1455 m, 1260 *m*-s, 1228 m, 1061 vs, 1007 s, 988 s, 932 s, 843 vs, 797 vs cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.34$ (t, $^3J_{HH} = 5.86$ Hz, 2H, CH_2OTa), 4.51 (t, $^3J_{HH} = 5.86$ Hz, 2H, CH_2OMe), 4.19 ppm (s, 3H, Me). ^{13}C NMR (400 MHz, $CDCl_3$): $\delta = 81.2$ (CH_2OTa), 74.1 (CH_2OMe), 66.2 ppm (Me).

Reactivity of MCl_5, 1a–b, with dme (dme/M molar ratio = 1 : 1). The reactions of **1** (0.40 mmol), in CH_2Cl_2 (7 mL), with dme (0.40 mmol) in Schlenk tubes afforded clear solutions, which were layered with pentane. Compounds **3a–b** were obtained as microcrystalline solids after 12 h at –20 °C, in 55–60% yields.

In a different experiment, the pentachloride (0.30 mmol) was suspended in $CDCl_3$ (0.8 mL) in a NMR tube, and then treated with dme (0.30 mmol). The tube was sealed, and progressive dissolution of the solid was observed. ^{1}H-NMR spectrum, recorded 30 min after mixing, showed the presence of CH_3Cl (3.00 ppm) and **3**, in about 1 : 1 ratio. GC/MS carried out on aliquots of the solutions, after hydrolysis and filtration on alumina, showed the presence of 2-methoxyethanol, methyl chloride and minor amounts of 1,4-dioxane.

Reaction of 3a with dme: formation of $NbOCl_3$(dme), 2a, CH_3Cl and 1,4-dioxane. Compound **3a** (0.25 mmol) was dissolved in $CDCl_3$ (0.7 mL) in a NMR tube and treated with dme (0.50 mmol). After 3 d, a mixture of **3a**, **2a**,[8] CH_3Cl and 1,4-dioxane (10 : 20 : 15 : 8 ratio) was detected.

Preparation of $MOCl_3$(dme)MCl_5 (*M–O–M*), M = Nb, Ta. The preparation of **4a** is described in detail; compound **4b** was obtained by analogous procedure. A suspension of $NbCl_5$ (0.350 g, 1.30 mmol) in CH_2Cl_2 (25 mL) was treated with dme (0.10 mL, 0.96 mmol), and the yellow mixture was stirred at room temperature for 45 min, during which progressive dissolution of the solid occurred. Hence, the mixture was filtered and layered with pentane. Pale yellow crystals of **4a** suitable for X-ray analysis were obtained after 24 h at room temperature. Yield: 0.058 g (21% yield). Anal. Calcd for $C_4H_{10}Cl_8Nb_2O_3$: C, 8.34; H, 1.75; Nb, 32.28; Cl, 49.28. Found: C, 8.09; H, 1.81; Nb, 32.05; Cl, 48.72%. IR (solid state): 2943 w, 2885 w, 2833 w, 1462 m, 1454 m-s, 1447 m-s, 1274 m, 1239 m, 1185 m, 1126 w, 1062 m-s, 1008 s, 996 s, 976 s, 956 m-s, 876 s [$\nu_{Nb-O-Nb}$], 836 vs, 811 vs cm^{-1}.

*$TaOCl_3$(dme)$TaCl_5$ (*Ta–O–Ta*), **4b**.* Colourless, air sensitive solid; 15% yield from **1b** (0.360 g, 1.00 mmol) and dme (0.080 mL, 0.77 mmol). Anal. Calcd for $C_4H_{10}Cl_8O_3Ta_2$: C, 6.39; H, 1.34; Ta, 48.15; Cl, 37.73. Found: C, 6.25; H, 1.38; Ta, 47.80; Cl, 37.19%. IR (solid): 2962 w, 2916 vw, 1400 br-m, 1260 ms, 1074 br-s, 1013 vs, 872 s [$\nu_{Ta-O-Ta}$], 797 vs cm^{-1}.

Reaction of $NbOCl_3$(dme)$NbCl_5$ (*Nb–O–Nb*) with dme. The reaction of crystalline **4a** (0.050 g, 0.087 mmol) with dme (0.020 mL, 0.19 mmol), in CH_2Cl_2 (8 mL), afforded a dark yellow solution in 3 h time. The solution was layered with pentane: crystals of compound **2a** formed overnight in nearly 80% yield. The identity of **2a** was checked by IR (strong absorption at 954 cm^{-1}), whereas GC/MS analysis of the liquor pointed out the presence of CH_3Cl and 1,4-dioxane.

Reactivity of $NbCl_5$ with 1,2-diethoxyethane. Preparation of $NbCl_4[O(Et)CH_2CH_2O]$, 5. A suspension of **1a** (0.150 g, 0.555 mmol) in CH_2Cl_2 (10 mL) was treated with 1,2-diethoxyethane (0.070 mL, 0.50 mmol), and stirred at room temperature for 30 min. The final mixture was filtered in order to remove some solid, then it was layered with pentane. Compound **5** was obtained as a yellow solid after 12 h at –20 °C. Yield: 0.125 g (77%). Anal. Calcd for $C_4H_9Cl_4NbO_2$: C, 14.84; H, 2.80; Nb, 28.69; Cl, 43.79. Found: C, 14.65; H, 2.71; Nb, 28.45; Cl, 43.21%. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.25$ (t, 2H, $^3J_{HH} = 5.86$ Hz, CH_2ONb), 4.53 (q, 2H, $^3J_{HH} = 6.59$ Hz, OCH_2CH$_3$), 4.52 (t, 2H, $^3J_{HH} = 5.86$ Hz, CH_2OEt), 1.51 ppm (t, 3H, $^3J_{HH} = 6.59$ Hz, OCH$_2$CH_3). ^{13}C NMR (400 MHz, $CDCl_3$): $\delta = 78.9$ (CH_2ONb), 76.0 (CH_2OEt), 40.9 (OCH_2CH$_3$), 19.1 ppm (OCH$_2$CH_3). GC/MS analysis on an aliquot of the mixture at the end of reaction revealed the presence of ethyl chloride. The reaction of $NbCl_5$ (0.105 g, 0.389 mmol) with 1,2-diethoxyethane (0.12 mL, 0.85 mmol), in a mixture of $CDCl_3$ (0.65 mL) and CH_2Cl_2 (0.0256 mL, 0.400 mmol), gave a solution which was analyzed by ^{1}H NMR and GC/MS: CH_2Cl_2, EtCl and $Cl(CH_2)_2OCH_2CH_3$ were detected in *ca.* 10 : 20 : 15 ratio (^{1}H NMR), together with some unreacted 1,2-diethoxyethane.

Reactivity of $NbCl_5$ with 1,2-dimethoxypropane. Preparation of $NbCl_4[O(Me)CH(Me)CH_2O]$, 6. To a suspension of **1a** (0.205 g, 0.759 mmol) in CH_2Cl_2 (15 mL) 1,2-dimethoxypropane (0.079 mL, 0.65 mmol) was added, and the mixture was stirred at room temperature for additional 30 min. The final red mixture was filtered in order to remove some solid, then the filtrated solution was layered with pentane. Dark-red microcrystalline compound **6** was obtained as a mixture of two isomeric forms after 12 h at –20 °C. Yield: 0.181 g (82%). Anal. Calcd for $C_4H_9C_{l4}NbO_3$: C, 14.14; H, 2.67; Nb, 27.34; Cl, 41.73. Found: C, 14.04; H, 2.70; Nb, 26.91; Cl, 41.02%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (major isomer) = 5.24, 5.08 (m, 2H, NbOCH_2), 4.68 (m, 1H, C*H*), 3.98 (s, 3H, O*Me*), 1.60 ppm (d, 2H, $^3J_{HH} = 6.23$ Hz, CH*Me*); δ (minor isomer) = 5.29, 5.02 (m, 2H, NbOCH_2), 4.45 (m, 1H, C*H*), 4.02 (s, 3H, O*Me*), 1.53 ppm (d, 2H, $^3J_{HH} = 5.86$ Hz, CH*Me*). Isomer ratio = 2 : 1. ^{13}C NMR (400 MHz, $CDCl_3$): δ (major isomer) = 87.7 (NbOCH_2), 84.6 (*C*H), 63.1 (O*Me*), 15.6 ppm (CH*Me*); δ (minor isomer) = 87.5 (NbOCH_2), 83.6 (*C*H), 62.4 (O*Me*), 16.8 ppm (CH*Me*).

When the reaction of **1a** (0.65 mmol) with 1,2-dimethoxypropane (0.52 mmol) was carried out in $CDCl_3$ inside a NMR tube, ^{1}H NMR spectroscopy revealed the presence of methyl chloride, in *ca.* 1 : 1 ratio with respect to **6**.

The reaction of **1a** (0.110 g, 0.407 mmol) with 1,2-dimethoxypropane (0.11 mL, 0.90 mmol), in $CDCl_3$, gave a mixture which was analyzed by ^{1}H NMR and GC/MS: MeCl, 2,5-dimethyl-1,4-dioxane and some unreacted 1,2-dimethoxypropane were detected.

Reactivity of $NbCl_5$ with 1-chloromethoxy-2-methoxyethane. Preparation of $\overline{NbCl_4[O(CH_2Cl)CH_2CH_2O]}$, 7. A suspension of **1a** (0.209 g, 0.774 mmol) in CH_2Cl_2 (15 mL) was treated with 1-chloromethoxy-2-methoxyethane (0.070 mL, 0.61 mmol), and the mixture was stirred at room temperature for additional 45 min. The final yellow mixture was filtered in order to remove some solid, then it was layered with pentane. Compounds **3a** and **7** were obtained in admixture as a dark-yellow solid, after 12 h at –20 °C. Complex **7**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.60 (s, 2H, CH_2Cl), 5.28 (t, 2H, $^3J_{HH}$ = 5.86 Hz, CH_2ONb), 4.64 ppm (t, 2H, $^3J_{HH}$ = 5.86 Hz, CH_2OCH$_2$Cl). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 84.8 (*C*H$_2$Cl), 79.7 (*C*H$_2$OCH$_2$Cl), 74.0 ppm (*C*H$_2$ONb).

When the reaction of **1a** (0.70 mmol) with $ClCH_2O(CH_2)_2OCH_3$ (0.60 mmol) was carried out in $CDCl_3$ in a NMR tube, ^{1}H NMR spectroscopy revealed the presence of methyl chloride, **3a** and **7** in *ca.* 3 : 5 : 2 ratio.

The reaction of **1a** (0.110 g, 0.407 mmol) with $ClCH_2O(CH_2)_2OCH_3$ (0.10 mL, 0.88 mmol), in a mixture of $CDCl_3$ (0.70 mL) and CH_2Cl_2 (0.0260 mL, 0.405 mmol), gave a solution which was analyzed by ^{1}H NMR and GC/MS: CH_2Cl_2, $O(CH_2Cl)_2$, diglyme (100 : 18 : 17 molar ratio) and unreacted 1-chloromethoxy-2-methoxyethane were detected.

Reactivity of MCl_5 with diglyme. Isolation and characterization of $\overline{NbCl_4[OCH_2CH_2O}(CH_2)_2O(Me)NbCl_5]$, 8, $NbOCl_3$(diglyme), 9, and $[MeO(CH_2)_2O(CH_2)_2O(H)Me][NbCl_6]$, 10. A suspension of **1a** (0.140 g, 0.518 mmol) in CH_2Cl_2 (15 mL) was treated with diglyme (0.055 mL, 0.38 mmol), and the mixture was stirred at room temperature for additional 20 min. The final yellow mixture was filtered in order to remove some solid, then the filtrated solution was layered with pentane. Compound **8** was obtained as an ochre-yellow microcrystalline solid, after 48 h at room temperature. Yield: 0.079 g (49%). Anal. Calcd for $C_5H_{11}Cl_9Nb_2O_3$: C, 9.62; H, 1.78; Nb, 29.78; Cl, 51.13. Found: C, 9.71; H, 1.75; Nb, 29.54; Cl, 50.81%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.51 (m, 2H, CH_2ONb), 4.8 (m-br, 6H, CH_2), 4.31 ppm (s, 3H, Me).

When the reaction of **1a** (0.50 mmol) with diglyme (0.40 mmol) was carried out in $CDCl_3$ in a NMR tube, ^{1}H NMR spectroscopy revealed the presence of **8**, **3a** and methyl chloride, in about 10 : 1 : 20 ratio.

The reaction of **1a** (0.085 g, 0.31 mmol) with diglyme (0.095 mL, 0.66 mmol), in $CDCl_3/CH_2Cl_2$ ($CDCl_3$ 5.0 mL, CH_2Cl_2 0.308 mmol), afforded a solution which was analyzed by ^{1}H NMR and GC/MS: CH_2Cl_2, MeCl, $MeOCH_2CH_2Cl$, 1,4-dioxane, 1,2-dichloroethane were detected in 20 : 30 : 5 : 7 : 1 ratio (^{1}H NMR). Compound **9** was isolated by layering the $CDCl_3$ solution with pentane, at –20 °C. Yield: 0.043 g (40%). Anal. Calcd for $C_6H_{14}Cl_3NbO_4$: C, 20.62; H, 4.04; Nb, 26.59; Cl, 30.44. Found: C, 20.51; H, 4.11; Nb, 26.22; Cl, 29.88%. IR (solid): 934 vs [$\nu_{Nb=O}$] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.42 (m, 2H, CH_2), 3.95 (m, 4H, CH_2), 3.7 ppm (m-br, 8H, CH_2 and CH_3).

In a second attempt of crystallization, at –20 °C, X-ray quality crystals of **10** were collected: yield 12% from **1a** (0.090 g, 0.33 mmol) and diglyme (0.049 mL, 0.34 mmol). Anal. Calcd for $C_6H_{15}Cl_6NbO_3$: C, 16.35; H, 3.43; Nb, 21.08; Cl, 48.26. Found: C, 16.02; H, 3.34; Nb, 21.05; Cl, 48.43%. IR (solid): 3175 w [ν_{O-H}] cm^{-1}.

Preparation of $MOCl_3$, M = Nb, Ta. The preparation of **11a** is described in detail; compound **11b** was obtained by analogous procedure. Crystalline $NbOCl_3$(dme), **2a** (0.120 g, 0.393 mmol), was added to CH_2Cl_2 (15 mL), hence the mixture was treated with $TiCl_4$ (0.065 mL, 0.59 mmol). Precipitation of colourless **11a** occurred nearly instantaneously from a yellow solution. Yield: 0.071 g, 84%. Anal. Calcd for Cl_3NbO: Nb, 43.16; Cl, 49.41. Found: Nb, 43.02; Cl, 48.90%. The yellow solution was dried under vacuum, and an aliquot of the residue was dissolved in $CDCl_3$ (0.5 mL): ^{1}H NMR analysis revealed the presence of $TiCl_4$(dme) [δ = 4.28 (s, 2H, CH_2), 4.08 ppm (s, 3H, CH_3)].[35] A second aliquot of the residue was dissolved in CH_2Cl_2, and the solution was layered with pentane. Crystals of $TiCl_4$(dme), which were identified by X-ray analysis, were collected after 24 h at room temperature.

*$TaOCl_3$, **11b**.* Colourless, air sensitive solid; 80% yield from **2b** (0.160 g, 0.407 mmol) and $TiCl_4$ (0.070 mL, 0.64 mmol). Anal. Calcd for Cl_3OTa: Ta, 59.66; Cl, 35.07. Found: Ta, 59.20; Cl, 34.95%.

Preparation of $NbCl_3$(dme), 12. Crystalline $NbOCl_3$(dme), **2a** (0.060 g, 0.20 mmol), was added to CH_2Cl_2 (8 mL), thus the mixture was treated with $SnBu_3H$ (0.12 mL, 0.45 mmol). A brick-red solid, corresponding to $NbCl_3$(dme), **12**, quickly formed. The solid was recovered by filtration, washed with pentane (2 × 10 mL) and dried under reduced pressure. Yield: 0.050 g, 87%. Anal. Calcd for $C_4H_{10}Cl_3NbO_2$: C, 16.60; H, 3.48; Nb, 32.10; Cl, 36.75. Found: C, 16.78; H, 3.56; Nb, 31.77; Cl, 36.31%.

X-Ray crystallography

Crystal data and collection details for $NbOCl_3$(dme)$NbCl_5$ (*Nb–O–Nb*), **4a**, $TaOCl_3$(dme)$TaCl_5$ (*Ta–O–Ta*), **4b**, and $[MeO(CH_2)_2O(CH_2)_2O(H)Me][NbCl_6]$, **10**, are listed in Table 3. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector and using Mo-Kα radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).[36] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[36] The asymmetric unit of **10** contains one independent $[NbCl_6]^-$ anion located on a general position and half of a second $[NbCl_6]^-$ anion located on an inversion centre, as well as one fully independent $[MeO(CH_2)_2O(CH_2)_2O(H)Me]^+$ cation and a second one located on an inversion centre. All non-hydrogen atoms were refined with anisotropic displacement parameters.

H-atoms bonded to carbons were placed in calculated positions and treated isotropically using the 1.2 fold U_{iso} value of the parent atom except methyl protons, which were assigned the 1.5 fold U_{iso} value of the parent *C*-atom. The *O*-bonded hydrogen atoms in **10** [H(1), H(3) and H(5)] were located in the Fourier map and refined isotropically using the 1.2 fold U_{iso} value of the parent *O*-atom. Restraints were applied to the O–H distances. The O(3)–H(3) group is located close to an inversion centre and forms a hydrogen bond to a symmetry generated O(3) atom. Therefore, H(3) appears to be disordered over two symmetry related positions with 0.5 occupancy factor each. As a consequence of this fact, in order to maintain one protonated oxygen atom per diglyme molecule, the hydrogen atom involved in the H-bond between O(1) and O(5) has been split into two equally populated positions, one

Table 3 Crystal data and experimental details for $NbOCl_3(dme)NbCl_5$ (*Nb–O–Nb*), **4a**, $TaOCl_3(dme)TaCl_5$ (*Ta–O–Ta*), **4b**, and $[MeO(CH_2)_2O(CH_2)_2O(H)Me][NbCl_6]$, **10**

Complex	**4a**	**4b**	**10**
Formula	$C_4H_{10}Cl_8Nb_2O_3$	$C_4H_{10}Cl_8O_3Ta_2$	$C_6H_{15}Cl_6NbO_3$
Fw	575.54	751.62	440.79
λ/Å	0.71073	0.71073	0.71073
T/K	100(2)	100(2)	100(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/n$	$C2/c$
a/Å	7.0287(5)	6.6388(3)	21.528(3)
b/Å	13.5297(9)	26.0083(13)	15.3879(19)
c/Å	17.5555(12)	9.9726(5)	17.492(2)
β/°	90	103.1160(10)	124.665(2)
Cell volume/Å^3	1669.5(2)	1676.99(14)	4766.1(10)
Z	4	4	12
D_c/g cm^{-3}	2.290	2.977	1.843
μ/mm^{-1}	2.644	14.305	1.756
$F(000)$	1104	1360	2616
Crystal size/mm	$0.21 \times 0.15 \times 0.12$	$0.16 \times 0.14 \times 0.12$	$0.22 \times 0.19 \times 0.15$
θ limits/°	1.90–27.00	1.57–27.00	1.75–25.03
Reflections collected	9274	18476	11126
Independent reflections	3564 ($R_{int} = 0.0173$)	3666 ($R_{int} = 0.0354$)	4066 ($R_{int} = 0.0276$)
Data/restraints/parameters	3564/0/156	3666/0/156	4066/2/228
Goodness on fit on F^2	1.068	1.053	1.017
$R1$ [$I > 2\sigma(I)$]	0.0138	0.0194	0.0247
w$R2$ (all data)	0.0327	0.0428	0.0499
Largest diff. peak/hole, e Å^{-3}	0.255/–0.401	1.336/–0.702	0.407/–0.399

directly bonded to O(1) and the other to O(5). Therefore, one *O*-bonded H^+ is present on each diglyme molecule, which is located alternatively on one or the other of the two terminal methoxy groups in each independent cation.

CCDC reference numbers 691886–691888 contain the supplementary crystallographic data for this paper. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b810210d

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