Further Insights into the Chemistry of Niobium and Tantalum Pentahalides with 1,2-Dialkoxyalkanes: Synthesis of Bromo- and Iodoalkoxides, Spectroscopic and Computational Studies

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Abstract

The room temperature reactions of a series of 1,2-dialkoxyalkanes $ROCH_2CH(R')OR''$ with MX_5 (M = Nb, Ta; X = Br, I) in 1:1 ratio result in single C–O bond cleavage and high-yield formation of the halo-alkoxides $MBr_4[\kappa^2\text{-}OCH_2CH(R')OR'']$ or $[NbI_4\{\kappa^1\text{-}OCH_2CH(R')OR''\}]_2$, and equimolar amounts of the corresponding alkyl halides RX. The reaction of $NbBr_5$ with 1,2-dimethoxyethane, dme, proceeds with preliminary formation of the ionic species $[NbBr_4(\kappa^2\text{-dme})(\kappa^1\text{-dme})][NbBr_6]$, **3b**, which has been identified by solution NMR at low temperature and conductivity analyses. The gas-phase structure of **3b** has been optimized by DFT calculations, confirming that the dme ligands adopt bidentate and monodentate coordination, respectively. Although the formation of $NbOBr_3$(dme), **4b**, 1,4-dioxane and MeBr from $NbBr_5$/dme (ratio 1:2) is an exoergonic process (calculated $\Delta G_r° = -115.96$ kcal·mol^{-1}), it is inhibited at room temperature. High temperature conditions enhance the production of 1,4-dioxane at the expense of selectivity. The dinuclear species $NbOBr_3$(dme)$NbBr_5$ *(Nb–O–Nb)*, **5b**, (X-ray) has been isolated in modest yield as byproduct of the room temperature reaction of $NbBr_5$ with dme. In general, the 1:2 molar reactions of NbX_5 (X = Br, I) with $ROCH_2CH(R')OR''$ occur with the exclusion of nearly one equivalent of organic reactant.

Keywords: Niobium / Tantalum / Diethers / C–O bond activation / Oxygen abstraction.

1. Introduction

Among early transition metal halides, the coordination chemistry of the pentahalides of niobium and tantalum, MX_5 (M = Nb: X = F, **1a**; X = Cl, **1b**; X = Br, **1c**; X = I, **1d**; M = Ta: X = F, **1e**; X = Cl, **1f**; X = Br, **1g**) [1], has not been exhaustively explored so far. This is probably related to the moisture-sensitivity of these oxophilic materials, which makes their preparation and storage difficult.

Nevertheless, an increasing interest in the use of **1** in metal-mediated synthesis has grown up in the recent years [2]; this is consequence of the unusual and striking behaviour exhibited by such complexes, in comparison with other early transition metal halides [3].

In view of the paucity of information available on the reactivity of **1**, some years ago we started a research project aimed to clarify the main features of the coordination chemistry of **1** with oxygen donor ligands [4]. We have found that the reactions with limited amounts of *O*-donors lead to coordination adducts which, under appropriate conditions, may evolve as result of C–Y bond activation (Y = H, O) [4b-d,f,5]. The outcomes of these reactions are strictly associated with the nature of the halide, while the metal (niobium or tantalum) does not play a crucial role. More remarkably, we have reported that the reactions of MX_5 (M = Nb, Ta; X = F, Cl) with simple bifunctional *O*-donors may proceed giving uncommon transformations. In particular, the room temperature reaction of **1b**,**f** with a two-fold excess of dme leads to selective conversion into $MOCl_3$(dme), methyl chloride and 1,4-dioxane [5d-e]. This outcome is unprecedented, on account of the fact that 1,4-dioxane formation implies the establishment of new C–O bonds, other than C–O cleavages. Actually the activation of ethers or diethers, by means of oxophilic metal derivatives, is generally limited to the breaking down of the organic substrate into smaller fragments [5d,e].

On the other hand, the fluorides **1a,e** are able to activate dme affording 1,4-dioxane and dimethyl ether at high temperature [5a]; the process does not affect the [MF_5] frame and occurs also in catalytic conditions.

In consideration of the interesting results achieved by studying the direct interaction of **1** with limited amounts of bifunctional oxygen substrates, we moved to see the reactivity of the heavier niobium and tantalum pentahalides, *i.e.* **1c,d,g**, with diethers of the type $ROCH_2CH(R')OR''$. It has to be noted that such metal species were even less studied in the past than the lighter congeners [3a,b,6]. This is certainly associated with the extreme moisture-sensitivity, due to the relatively low M–X (M = Nb, Ta; X = Br, I) bond energy.

Our purpose is to expand the knowledge on the role possibly played by **1** in organic reactions, with the aim to contribute to develop the use of these oxygen-affine materials in metal-directed syntheses. Advancements in this field should be desirable also taking into account that niobium and tantalum are essentially disposable [7] and are considered biocompatible elements [8]. The experimental results discussed herein have been accompanied by computational analyses, carried out by B3LYP/LANL2DZ method; the latter has previously revealed to be effective in predicting some chemistry of MX_5 (M = Nb, Ta; X = F, Cl) with dme [5a].

2. Results and Discussion

The 1:1 reactions of MX_5 (M = Nb, Ta; X = Br, I) with 1,2-dialkoxyalkanes: synthesis of haloalkoxides.

A number of mixed haloalkoxides having formula $MX_4[OCH_2CH(R')OR'']$ have been efficiently prepared by room-temperature treatment of the parent compounds MX_5 (**1c,d,g**) with one molar equivalent of 1,2-dialkoxyalkanes, $ROCH_2CH(R')OR''$, see Scheme 1.

Scheme 1 about here

NMR experiments have pointed out that the formation of **2** takes place with contextual production of equimolar amount of alkyl halide, RX (see Experimental). The products **2a-g** have been characterized by spectroscopic and analytical techniques.

The NMR spectra ($CDCl_3$) of **2a,b** display the resonance due to the two equivalent methoxy units at *ca.* 4.1 ppm (^{1}H) and 66 ppm (^{13}C), respectively. On considering that the –OMe moiety resonates at 3.39 (^{1}H) and 59.0 ppm (^{13}C) in uncoordinated dme, and at 3.52 ppm (^{1}H) and 59.5 ppm (^{13}C) in the complex $NbF_5[\kappa^1$-$O(H)CH_2CH_2OMe]$ (where –OMe does not coordinate niobium) [9], the methoxy fragment in **2a,b** should be involved in the coordination to the metal centre. Thus, compounds **2a,b** are mononuclear with the $[–OCH_2CH_2OMe]$ group acting as a bidentate ligand. This is coherent with what found for the chloro derivatives $MCl_4[\kappa^2$-$OCH_2CH_2OMe]$ (M = Nb, Ta) [5e,10,11].

In a similar manner, the [OR″] frame of **2c,d** gives NMR resonances which are significantly shifted to high frequencies, with respect to what observed in the corresponding uncoordinated diethers [$EtOCH_2CH_2OEt$ and $MeOCH_2CH(Me)OMe$]. For instance, the methylene unit in **2c** resonates at 4.21 (^{1}H) and 72.8 (^{13}C) ppm respectively, to be compared with the values 3.54 (^{1}H) and 66.7 (^{13}C) ppm reported for uncoordinated 1,2-diethoxyethane. All these information suggest that, as well as **2a**,**b**, the alkoxide compounds **2c,d** exist in solution as monomers comprising a bidentate $–OCH_2CH(R')OR''$ ligand (see Scheme 1).

The reaction of $NbBr_5$ with 1,2-dimethoxypropane might proceed in principle with cleavage of either Me–OCH_2 or Me–OCH(Me) bond, resulting in formation of two different regioisomers (see Scheme 2). Notwithstanding, according to NMR data, the reaction is almost regiospecific, and compound $NbBr_4$[OCH_2CH(Me)OMe], **2d**, forms selectively (no traces of $NbBr_4$[OCH(Me)CH_2OMe] have been detected). NMR analysis of **2d** has evidenced the presence of two stereoisomers differing in the orientation of the substituents (H and Me) on the asymmetric carbon of the five-membered cycle (Scheme 2). This feature reflects what seen for the analogous chloro-complex $NbCl_4$[κ^2-OCH_2CH(Me)OMe] [5e].

Scheme 2 about here

The preparation of the iodo-derivatives **2e-g** has required much longer reaction times with respect to **2a-d**, in agreement with the inertness usually exhibited by niobium and tantalum pentaiodides on reacting with ethers [12]. A careful analysis of the NMR spectra of **2e-g** suggests that the [OR″] unit does not coordinate the metal centre. For example, the –OMe unit in the ^{1}H NMR spectrum of **2e** resonates at 3.60 ppm, which is relatively close to the value 3.39 ppm related to uncoordinated 1,2-dimethoxyethane, see above. Since the iodo-derivatives **2e-g** contain monodentate oxygen ligands, they presumably hold dinuclear structure in order to provide octahedral coordination around each niobium, with the two metal centres sharing two bridging ligands. It is noteworthy that dinuclear structures are generally adopted by $M(OR)_5$ alkoxides [13] and $MX_n(OR)_{5-n}$ halo-alkoxides (M = Nb, Ta; n = 1÷3). In the latter, monodentate oxygen ligands occupy preferentially bridging sites rather than terminal ones [5c,14].

The reactions of **1c,d,g** with $ROCH_2CH(R')OR''$ described in this Section occur selectively with breaking of one terminal C–O bond. In view of this, the reaction of NbI_5, **1d**, with the unsymmetrical $MeO(CH_2)_2OCH_2Cl$ might proceed basically with cleavage of either Me–O or

$ClCH_2$–O bond, leading to a mixture of products. In reality selective cleavage of the Me–O bond takes place, resulting in exclusive formation of $NbI_4[OCH_2CH_2OCH_2Cl]$, **2g**, and MeI. The alternative products **2e**/CH_2ClI (derived from $ClCH_2$–O cleavage) have not been recognized in the reaction medium. In agreement with these observations, the $[OCH_2Cl]$ group has been found by NMR in the final metal compound [$\delta(^1H, CDCl_3) = 5.80$ ppm; $\delta(^{13}C, CDCl_3) = 83.0$ ppm].

The mononuclear structure adopted by **2a-d** is the consequence of the possibility for the □–$OCH_2CH(R')OR''$ ligand to behave as bidentate, so forming a stable five-membered ring. On the other hand, in **2e-g** the five-membered ring is not stable with respect to the dinuclear structure containing monodentate alkoxyethers, presumably due to the steric hindrance exerted by the iodides.

In conclusion, we would like to remark that the reactions of MX_5 (X = Cl, Br, I) with 1,2-dialkoxyalkanes (see Scheme 1 and reference [5e]) represent a new and straightforward route for the preparation of a vast series of monoalkoxo-tetrahalo compounds of Nb(V) and Ta(V). The simple synthetic procedure that we propose may give an impulse to the development of the use of Nb(V) and Ta(V) alkoxy-derivatives in metal-directed reactions.

The reactivity of MX_5 (M = Nb, Ta; X = Cl, Br, I) with dme: NMR, computational and crystallographic results.

We have previously reported that the room-temperature reaction of $NbCl_5$ with 1,2-dimethoxyethane leads to different outcomes depending on the stoichiometry employed. More specifically, the mononuclear compound $NbCl_4(OCH_2CH_2OMe)$, **2h**, is obtained in good yield by using strictly 1:1 molar ratio (Scheme 3, pathway a) [5e]. On the other hand, the use of an excess

(two or more equivalents) of dme gives selectively $NbOCl_3(dme)$, **4a**, and 1,4-dioxane, *via* multiple C–O bond activation (Scheme 3, pathway b) [5d]. The initial formation of the ionic intermediate $[NbCl_4(dme)_2][NbCl_6]$, **3a**, is common to the two pathways.

Although the way to **2h** is largely favoured when equimolar quantities of reagents (*i.e.* $NbCl_5$ and dme) are engaged, advanced ether activation occurs to a low extent under these conditions and minor amounts of 1,4-dioxane and of the oxo-bridged complex $NbOCl_3(dme)NbCl_5$, **5a**, may form (see Scheme 3).

Scheme 3 about here

With the aim to see the possibility to increase the production of 1,4-dioxane in the 1:1 reaction of $NbCl_5$ with dme, we have carried out this reaction in $CDCl_3$ in sealed tubes at progressively increasing temperatures but a reasonable dme $\rightarrow$ 1,4-dioxane conversion has not been achieved (see Experimental for details). We also have tested the reactivity of **2h** with dme in $CDCl_3$ (see Scheme 3). Clean formation of **4a**/1,4-dioxane has not been observed even at high temperatures, suggesting that **2h** cannot be considered as intermediate in the course of the 1:2 Nb/dme reaction.

In the previous Section, we have seen that $NbBr_5$ reacts with dme in 1:1 ratio yielding the monoalkoxo complex **2a**. The reaction proceeds with preliminary formation of the ionic adduct $[NbBr_4(\kappa^2\text{-dme})(\kappa^1\text{-dme})][NbBr_6]$, **3b**, as indicated by ^{1}H NMR experiment in $CDCl_3$ at –60°C. The spectrum displays two resonances due to bidentate dme [δ = 4.00 (CH_2), 3.68 (CH_3) ppm] and four resonances ascribable to monodentate dme ligand [δ = 4.61 ($NbOCH_2$), 4.24 (CH_3ONb), 3.90 (CH_2), 3.41 (CH_3) ppm]. Moreover, the ionic nature of **3b** has been corroborated by solution conductivity measurement (see Experimental).

In view of the fact that the B3LYP/LANL2DZ computational method allowed to predict the structures of compounds **3a** and **4a** [5a], we have optimized the gas-phase structure of **3b** by the same computational method. Making reference to Figure 1, a selection of bond lengths (Å) and angles (deg) is reported in Table 1. Although the calculations referred to the gas phase, they could be satisfactorily extended to the solid state and to solutions of non-polar solvents.

Figure 1 and Table 1 about here

The computer outcome obtained for **3b** is in agreement with the NMR data (see above), showing the two dme ligands in the cation adopting respectively monodentate and bidentate coordination mode. As a matter of fact, three calculated Nb–O distances are within bond-length [Nb(2)–O(3) 2.292, Nb(2)–O(5) 2.213, Nb(2)–O(6) 2.199 Å]. Conversely, the remaining Nb–O distance value points the absence of interaction [Nb(2)···O(4) 4.350 Å]. This situation resembles well that described for the chloro analogues **3a** [5e], and contrasts with what found for the fluoro $[NbF_4(dme)_2]^+$ where both dme ligands are bidentate [5a] The structure difference between $[NbF_4(dme)_2]^+$ and $[NbX_4(dme)_2]^+$ (X = Cl, Br) seems to be the result of the higher steric demand of the heavier halides with respect to the small fluoride ion.

The oxo-complex $NbOCl_3(dme)$, **4a**, can be obtained expeditiously by reaction of $NbCl_5$ with two equivalents of dme (see above). In principle, the analogous reaction of $NbBr_5$ with dme could afford $NbOBr_3(dme)$, **4b**. Indeed DFT results indicate that the formation of **4b** from $NbBr_5$ is exoergonic with $\Delta G°_r$ comparable to that calculated for the transformation **1b** → **4a** (eqn. (1)).

$$\underset{\textbf{1b,c}}{Nb_2X_{10}} + 4dme \rightarrow 2\underset{\textbf{4a,b}}{NbOX_3(dme)} + 1,4\text{-dioxane} + 4MeX \qquad (1)$$

$\Delta G_r°$ (X = Cl) = –106.25 kcal·mol^{-1}
$\Delta G_r°$ (X = Br) = –115.96 kcal·mol^{-1}

Somehow surprisingly, the combination of $NbBr_5$ with a two-fold excess of dme leaves one equivalent of organic material unreacted, thus **2a** is obtained as main metal product (see Scheme 4). In other terms, the pathway leading to **4b** and 1,4-dioxane from **1c**/dme (eqn. (1)) is almost not practicable at room temperature. Indeed very little 1,4-dioxane has been recognized after hydrolysis of the $CDCl_3$ mixture maintained for 15 days at room temperature (see Experimental and Scheme 5).

Scheme 4 about here

The mixture obtained from treatment of $NbBr_5$ with an excess of dme was layered with pentane, hence few X-ray quality crystals of the dinuclear complex $NbOBr_3(dme)NbBr_5$ *(Nb–O–Nb)*, **5b**, were collected (see Scheme 4). The low-yield isolation of **5b**, together with the NMR identification of small amounts of 1,4-dioxane in the same reaction (see above), confirm that the $NbBr_5$-mediated transformation dme → 1,4-dioxane is operative to a limited extent only. It has to be remarked that the μ-oxo unit found in complexes of the type $MOX_3(O–O)MX_5$ (M = Nb, Ta; X = Cl, Br; *O–O* = bidentate oxygen ligand) commonly results from oxygen-abstraction from the organic reactant rather than being imputable to adventitious water [5b].

Salient spectroscopic feature of **5b** is given by the IR absorption at 857 cm^{-1}, accounting for the Nb=O interaction (the corresponding value calculated for the gas phase is 892 cm^{-1}). In addition, the ^1H NMR spectrum (in $CDCl_3$) shows the two peaks due to the dme ligand, falling at 4.30 (CH_2) and 3.93 ppm (CH_3).

The molecular structure of **5b** is in Figure 2, whereas selected bond lengths and angles are reported in Table 2. The asymmetric unit of **5b** contains two independent molecules located in general positions. In view of the very similar bonding parameters, only the parameters of one

molecule will be discussed. The structure is closely related to the ones previously reported for $MOCl_3(dme)MCl_5$ (M = Nb, Ta) [5e], and it can be viewed as the result of the coordination of the oxo complex $[Nb(=O)Br_3(dme)]$ to the Lewis acid $NbBr_5$. In agreement with this, the oxo-bridge displays a considerable asymmetry, being double bonded to Nb(2) [Nb(2)-O(1) 1.747(5) and 1.755(6) Å for the two independent molecules] and single bonded to Nb(1) [Nb(1)-O(1) 2.137(5) and 2.120(6) Å for the two independent molecules].

Compound **5b** represents one of the rare examples of crystallographically-characterized M(V) derivative (M = Nb, Ta) containing bromide ligands[5d, 14].

Figure 2 and Table 2 about here

Figure 3 depicts the computer-optimized structure of compound **5b**. A comparison of geometric parameters (X-ray vs. DFT) is shown in Table 2, evidencing good agreement between experimental data for the solid state and calculated values for the gas phase.

Figure 3 about here

Attempting to force the thermodynamically-allowed conversion of dme into 1,4-dioxane (eqn. (1)), a 1:2 mixture of $NbBr_5$ and dme in $CDCl_3$ was heated at *ca.* 80°C for 12 hours. Although the final mixture resulted enriched in 1,4-dioxane, significant amounts of 1,2-dibromoethane and methanol were detected after hydrolysis (see Scheme 5 and Experimental), thus suggesting that high temperatures favour the conversion dme $\rightarrow$ 1,4-dioxane but, under in these conditions, several fragmentation routes turn to be operative. The halide $MeOCH_2CH_2Br$ plausibly generates from **2a** by reaction of the $[OCH_2CH_2OMe]$ ligand with H_2O/HBr, HBr being produced during the hydrolysis. Actually the formation of 1,2-dibromoethane and methanol

appears to be the consequence of the scission of internal C–O bonds. Methanol may be produced upon hydrolysis of niobium-methoxide species [Nb–OMe].

Scheme 5 about here

The different reactions of NbX_5 (X = Cl, **1b**; X = Br, **1c**) with a two-fold excess of dme (eqn. (1)) might be explained on the basis of steric factors. We can suggest that the interaction of **1b,c** with one equivalent of dme produces the intermediate species $[NbX_4(dme)_2][NbX_6]$ (X = Cl, **3a**; X = Br, **3b**), and that only compound **3a** is able to react efficiently with a second equivalent of dme, providing $NbOCl_3(dme)$, **4a** (Scheme 3, pathway b). Compound **3b** is substantially inert towards addition of further dme, hence the formation of $NbOBr_3(dme)$, **4b**, is inhibited (Scheme 4). The observed inertness of **3b** could be the consequence of the steric hindrance of the bromide ligands, which may favour a rearrangement with distribution of the two dme fragments between the two metal centers, rather than the addition of further dme required for the formation of **4b**.

The hypothesis that steric factors play a crucial role in the reactivity of **1** with 1,2-dialkoxyalkanes finds support in the fact that the 1:2 molar reactions of niobium pentachloride with 1,2-dialkoxyalkanes more encumbered than dme (*O–O*) do afford alkoxide complexes analogous to **2h** and not $NbOCl_3$(*O–O*) [5e].

The 1:2 molar reactions of MX_5 (M = Nb, Ta; X = Br, I) with 1,2-dialkoxyalkanes.

In the present Section, we deal with the 1:2 molar reactions of Nb(V) bromides and iodides with 1,2-dialkoxyalkanes (see Table 3). They have been performed in NMR tubes in $CDCl_3$ solution, using CH_2Cl_2 as NMR standard.

The 1:2 reactions of $NbBr_5$, **1c**, with $ROCH_2CH(R')OR$ (R = Et, R′ = H; R = R′ = Me) give the alkoxyether compounds **2c,d**, in admixture with *ca.* one equivalent of RBr per metal atom. After treatment with water, CH_2Cl_2, unreacted diether [$EtOCH_2CH_2OEt$ and $MeOCH_2CH(Me)OMe$], RBr and $BrOCH_2CH(R')OR$ have been detected in comparable amounts in the respective mixtures. The bromide $BrOCH_2CH(R')OR$ reasonably origins from hydrolysis of the alkoxyether ligand; in fact, treatment of $NbBr_4[OCH_2CH(R')OR]$ with water in excess should generate niobium oxides, HBr and $HOCH_2CH(R')OR$, which in turn may react with HBr to give $BrOCH_2CH(R')OR$. The experimental evidences indicate that the two reactions basically proceed with the cleavage of one terminal C–O bond per molecule to give the adducts **2**, thus leaving one equivalent of diether unreacted. Traces of 1,4-dioxane have been recognized in the reaction mixture of **1c** with 1,2-diethoxyethane.

The mixtures obtained by addition of a two-fold excess of diether to NbI_5, **1d**, in $CDCl_3$, could be analyzed after hydrolysis. Thus, the outcomes of the reactions with 1,2-dimethoxyethane or 1,2-dimethoxypropane resemble what discussed above for $NbBr_5$: one equivalent of RI (R = Et, Me) generates per metal atom, indicating the occurrence of a single C–O breaking process. Besides, one equivalent of diether comes unreacted. Interestingly, minor amounts of CH_2ICH_2I, MeOH and 1,4-dioxane have been found as products of the treatment of NbI_5 with dme/H_2O. This indicates that advanced fragmentation of the ligand may be operative although to a low extent.

In agreement with the higher reactivity usually exhibited by $MeO(CH_2)_2OCH_2Cl$ when reacting with M(V) pentahalides [5e], the room temperature interaction between NbI_5 and $MeO(CH_2)_2OCH_2Cl$ leads to quantitative and non-selective degradation of the organic material. Hence, MeI, CH_2ICH_2I, CH_2ClI, $ClCH_2OCH_2OCH_2Cl$, dme and Me_2O have been clearly detected after hydrolysis. The presence of $ClCH_2OCH_2OCH_2Cl$, dme and Me_2O is remarkable, since it

indicates that C–O bond formation somehow takes place in the course of the reaction. Moreover, the prevalence of MeI with respect to CH_2ClI points that the less hindered terminal C–O bond may be broken preferentially, analogously to what shown above for the 1:1 reaction of $NbBr_5$ with $MeO(CH_2)_2OCH_2Cl$.

3. Conclusions

In this paper, we have presented some new aspects concerning the chemistry of niobium and tantalum pentahalides with 1,2-dialkoxyalkanes. The 1:1 molar reactions of MX_5 (X = Br, I) with $ROCH_2CH(R')OR''$ proceed with single C–O bond cleavage and lead to selective formation of uncommon monoalkoxo-tetrahalo compounds, whose nuclearity appears to be determined by the dimension of the halide. This novel synthetic procedure may give further impulse to the use of Nb(V) and Ta(V) derivatives in metal-directed synthesis.

The 1:2 reactivity of MX_5 (X = Cl, Br, I) with $ROCH_2CH(R')OR''$ is mainly regulated by kinetic factors, associated with the steric demand of X, R and R′. In the case of low impediment, advanced activation of the organic material may occur affording oxo-niobium compounds and 1,4-dioxane in high yield. This is the case of the 1:2 reaction of $NbCl_5$ with dme. On the other hand, increased steric encumbrance, due to either the halide ligand or the organic reactant, inhibits the pathway leading to 1,4-dioxane. In such case, monoalkoxo-tetrahalo compounds are obtained prevalently, with nearly one equivalent of organic material remaining unreacted. For instance, the generation of $NbOBr_3$(dme)/1,4-dioxane is not observed from $NbBr_5$/excess dme, although computer calculations suggest that this process is highly exoergonic.

4. Experimental

4.1. General procedures

All manipulations of air and/or moisture sensitive compounds were performed under 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. Compounds MX_5 (M = Nb, X = Cl, **1b**; M = Nb, X = I, **1d**) were purchased from Aldrich and stored under argon atmosphere as received. Compounds MBr_5 (M = Nb, **1c**; M = Ta, **1g**) were prepared according to literature procedures and stored under argon atmosphere [15], CH_2Cl_2, $CHCl_3$, CD_2Cl_2, $CDCl_3$ and $MeO(CH_2)_2OMe$ (dme) were distilled before use under argon atmosphere from P_4O_{10}, while pentane was distilled from $LiAlH_4$. The commercial $MeOCH_2CH(Me)OMe$, $EtO(CH_2)_2OEt$ and $MeO(CH_2)_2OCH_2Cl$ were distilled before use under argon atmosphere from appropriate drying agents. Infrared spectra were recorded at 293 K on a FT IR-Perkin Elmer Spectrometer, equipped with a UATR sampling accessory. NMR measurements were recorded on Mercury Plus 400 instrument at 293 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. Conductivity measurements were carried out with Eutech Con 700 Instrument (cell constant = 1.0 cm^{-1}) [16]. Carbon and hydrogen analyses were performed on Carlo Erba mod. 1106 instrument. The halide content was determined by the Volhardt method [17] after exhaustive hydrolysis of the sample. The metal was analyzed as M_2O_5 (M = Nb, Ta), 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 check for reproducibility.

4.2. Preparation of $MX_4[OCH_2CH(R')OR'']$ (M = Nb, X = Br, R′ = H, R′′ = Me, ***2a****; M = Ta, X = Br, R′ = H, R′′ = Me,* ***2b****; M = Nb, X = Br, R′ = H, R′′ = Et,* ***2c****; M = Nb, X = Br, R′ = R′′ = Me,* ***2d****; M = Nb, X = I, R′ = H, R′′ = Me,* ***2e****; M = Nb, X = I, R′ = H, R′′ = Et,* ***2f****; M = Nb, X = I, R′ = H, R′′ = CH_2Cl,* ***2g****).*

The preparation of $NbBr_4[OCH_2CH_2OMe]_2$, **2a**, is described in detail; compounds **2b**-**g** were obtained by analogous procedure.

$NbBr_4[OCH_2CH_2OMe]$, **2a**. A suspension of $NbBr_5$ (0.180 g, 0.366 mmol) in CH_2Cl_2 (10 mL) was treated with dme (0.038 mL, 0.37 mmol), and the resulting mixture was stirred for 30 minutes at room temperature. Progressive dissolution of the solid was observed. Compound **2a** was obtained as a red microcrystalline precipitate upon addition of pentane. Yield: 0.161 g (90%). Anal. Calcd for $C_3H_7Br_4NbO_2$: C, 7.39; H, 1.45; Nb, 19.05; Br, 65.55. Found: C, 7.26; H, 1.37; Nb, 18.46; Br, 65.09. ^{1}H NMR ($CDCl_3$): δ = 5.31 (t, 2 H, $^3J_{HH}$ = 5.86 Hz, CH_2ONb), 4.36 (t, 2 H, $^3J_{HH}$ = 5.86 Hz, CH_2OMe), 3.97 ppm (s, 3 H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 79.6 (*C*H_2ONb), 78.6 (*C*H_2OMe), 65.9 ppm (Me). Λ_M = 0.080 S·cm^2·mol^{-1}.

$TaBr_4[OCH_2CH_2OMe]$, **2b**. Yellow solid, 82% yield from **1g** (0.210 g, 0.362 mmol) and dme (0.038 mL, 0.37 mmol). Time: 1 hour. Anal. Calcd for $C_3H_7Br_4O_2Ta$: C, 6.26; H, 1.23; Ta, 31.43; Br, 55.52. Found: C, 6.32; H, 1.28; Ta, 31.20; Br, 54.77. ^{1}H NMR ($CDCl_3$): δ = 5.40 (t, 2 H, $^3J_{HH}$ = 5.86 Hz, CH_2OTa), 4.45 (t, 2 H, $^3J_{HH}$ = 5.86 Hz, CH_2OMe), 4.16 ppm (s, 3 H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 81.0 (*C*H_2OTa), 74.9 (*C*H_2OMe), 66.8 ppm (Me).

$NbBr_4[OCH_2CH_2OEt]$, **2c**. Red solid, 77% yield from **1c** (0.190 g, 0.39 mmol) and 1,2-diethoxyethane (0.055 mL, 0.39 mmol). Time: 1 hour. Anal. Calcd for $C_4H_9Br_4NbO_2$: C, 9.58; H, 1.81; Nb, 18.52; Br, 63.71. Found: C, 9.50; H, 1.72; Ta, 18.36; Br, 63.21. ^{1}H NMR ($CDCl_3$): δ = 5.29 (t, 2 H, $^3J_{HH}$ = 5.86 Hz, CH_2ONb), 4.21 (m, 2 H, CH_2OEt), 3.67 (q, 2 H, $^3J_{HH}$ = 8 Hz, CH_2CH$_3$), 1.45 ppm (t, 3 H, $^3J_{HH}$ = 8 Hz, CH$_2$CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 81.2 (*C*H$_2$ONb), 76.1 (*C*H$_2$OEt), 72.8 (*C*H$_2$CH$_3$), 18.6 ppm (CH$_2$*C*H$_3$).

$NbBr_4[OCH_2CH(Me)OMe]$, **2d**. Red microcrystalline solid, 86% yield from **1c** (0.165 g, 0.335 mmol) and 1,2-dimethoxypropane (0.042 mL, 0.34 mmol). Time: 6 hours. Anal. Calcd for $C_4H_9Br_4NbO_2$: C, 9.58; H, 1.81; Nb, 18.52; Br, 63.71. Found: C, 9.50; H, 1.74; Nb, 18.63; Br, 63.21. ^{1}H NMR ($CDCl_3$): δ (major isomer) = 5.24÷5.11 (m, 2 H, NbOCH_2), 4.61 (m, 1 H, C*H*), 3.96 (s, 3 H, O*Me*), 1.59 ppm (d, 3 H, $^3J_{HH}$ = 6.23 Hz, CH*Me*); δ (minor isomer) = 5.30÷5.07 (m, NbOCH_2), 4.45 (m, C*H*), 3.93 (s, O*Me*), 1.62 ppm (d, $^3J_{HH}$ = 5.86 Hz, CH*Me*). Isomer ratio 2:1. ^{13}C{^{1}H} NMR ($CDCl_3$): δ (major isomer) = 86.4 (NbO*C*H$_2$), 84.6 (*C*H), 62.5 (O*Me*), 13.5 ppm (CH*Me*); δ (minor isomer) = 87.2 (NbO*C*H$_2$), 84.2 (*C*H), 62.5 (O*Me*), 14.9 ppm (CH*Me*).

$NbI_4[OCH_2CH_2OMe]$, **2e**. Red solid, 58% yield from **1d** (0.195 g, 0.268 mmol) and dme (0.030 mL, 0.29 mmol). Time: 170 hours. Anal. Calcd for $C_3H_7I_4NbO_2$: C, 5.33; H, 1.04; Nb, 13.75; I, 75.13. Found: C, 5.26; H, 1.10; Nb, 13.61; I, 74.22. ^{1}H NMR ($CDCl_3$): δ = 5.03 (t, 2 H, $^3J_{HH}$ = 5.13 Hz, CH_2ONb), 3.88 (t, 2 H, $^3J_{HH}$ = 5.13 Hz, CH_2OMe), 3.60 ppm (s, 3 H, Me).

$NbI_4[OCH_2CH_2OEt]$, **2f**. Red solid, 61% yield from **1d** (0.240 g, 0.330 mmol) and 1,2-diethoxyethane (0.055 mL, 0.39 mmol). Time: 120 hours. Anal. Calcd for $C_4H_9I_4NbO_2$: C, 6.97; H, 1.32; Nb, 13.47; I, 73.61. Found: C, 7.04; H, 1.24; Nb, 13.31; I, 73.30. ^{1}H NMR ($CDCl_3$): δ =

4.92 (t, 2 H, $^{3}J_{HH}$ = 5.86 Hz, CH_2ONb), 4.32 (m, 2 H, CH_2OEt), 3.65 (q, 2 H, $^{3}J_{HH}$ = 8 Hz, CH_2CH$_3$), 1.41 ppm (t, 3 H, $^{3}J_{HH}$ = 8 Hz, CH$_2$CH_3).

$NbI_4[OCH_2CH_2OCH_2Cl]$, **2g**. Orange solid, 62% yield from **1c** (0.265 g, 0.364 mmol) and $MeO(CH_2)_2OCH_2Cl$ (0.042 mL, 0.37 mmol). Time: 48 hours. Anal. Calcd for $C_3H_6ClI_4NbO_2$: C, 5.07; H, 0.85; Nb, 13.08; I, 71.49. Found: C, 5.13; H, 0.74; Nb, 13.00; I, 70.56. ^{1}H NMR ($CDCl_3$): δ = 5.80 (s, 2 H, CH_2Cl), 4.99 (t, 2 H, $^{3}J_{HH}$ = 5.8 Hz, CH_2ONb), 4.46 ppm (t, 2 H, $^{3}J_{HH}$ = 5.8 Hz, CH_2OCH$_2$Cl). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 83.0 (*C*H$_2$Cl), 75.4 (*C*H$_2$OCH$_2$Cl), 74.9 ppm (*C*H$_2$ONb).

The reactions of MX_5 (0.30 mmol) with 1,2-dialkoxyalkanes (0.30 mmol) were also performed in NMR tubes ($CDCl_3$ solutions, 0.65 mL *ca.*). Compounds **2a-g** formed cleanly together with MeBr (**2a,b,d**), EtBr (**2c**), MeI (**2e,g**), or EtI (**2f**) respectively, in about 1:1 ratio (^{1}H NMR).

*4.3. NMR studies on the reactivity of $NbCl_5$, **1b**, with dme.*

a) Formation of 1,4-dioxane in the 1:1 reaction of $NbCl_5$ with dme. To a suspension of $NbCl_5$ (0.250 mmol) in $CDCl_3$ (0.75 mL) in a NMR tube, CH_2Cl_2 (0.250 mmol) and dme (0.250 mmol) were added in the order. The tube was sealed, shaken in order to homogenize the mixture, and stored at variable temperature for variable time. Subsequent ^{1}H NMR spectrum did not give useful information. Then the tube was opened and the yellow solution inside was treated with water (*ca.* 5 mmol). A light-yellow solution was separated from a colourless precipitate, thus the former was analyzed by NMR/GC-MS.

From sample stored at 20°C for 24 h: CH_2Cl_2, 1,4-dioxane, MeCl and $MeO(CH_2)_2Cl$ (ratio 20:2:18:18 *ca.*).

From sample stored at 90°C (temperature of the external oil-bath) for 3 h: CH_2Cl_2, 1,4-dioxane, MeCl and $MeO(CH_2)_2Cl$ (ratio 12:1:8:8 ratio).

From sample stored at 120°C (temperature of the external oil-bath) for 5 h: CH_2Cl_2, MeOH, $ClCH_2CH_2OMe$, CH_2ClCH_2Cl, 1,4-dioxane and MeCl (ratio 7:2:2:2:1:4).

b) Reaction of $NbCl_4(OCH_2CH_2OMe)$, **2h**, with dme. A solution of compound $NbCl_4(OCH_2CH_2OMe)$ (2h, 0.60 mmol) in $CDCl_3$ (0.80 mL) was treated with CH_2Cl_2 (0.60 mmol) and then with dme (0.90 mmol). The tube was sealed, shaken in order to homogenize the mixture, and stored at variable temperature for variable time. Subsequent ^1H NMR spectrum did not indicate clearly formation of **4a**. Then the tube was opened and the yellow solution inside was treated with water (*ca.* 5 mmol). A solution was separated from a colourless precipitate, thus the former was analyzed by NMR/GC-MS.

From sample stored at 20°C for 24 h: CH_2Cl_2, $MeO(CH_2)_2Cl$, MeCl, dme and 1,4-dioxane (ratio 10:8:8:15:1).

From sample stored at 90°C (temperature of the external oil-bath) for 12 h: CH_2Cl_2, $MeO(CH_2)_2Cl$, MeCl, dme and 1,4-dioxane (ratio 10:7:10:13:3).

From sample stored at 120°C (temperature of the external oil-bath) for 5 h: $MeO(CH_2)_2Cl$, MeCl, dme, 1,4-dioxane, MeOH and CH_2ClCH_2Cl (ratio 2:4:2:3:2:1).

4.4. NMR studies on the reactivity of $NbBr_5$ with dme.

a) Characterization of $[NbBr_4(\kappa^1\text{-dme})(\kappa^2\text{-dme})][NbBr_6]$, **3b.** A mixture of $NbBr_5$ (0.450 mmol), $CDCl_3$ (0.75 mL) and CH_2Cl_2 (0.450 mmol) was introduced into a NMR tube, then dme (0.350 mmol) was added. The tube was sealed, shaken in order to homogenize the content, and stored at –10°C for 10 minutes. Subsequent NMR spectrum at –60°C evidenced the absence of

uncoordinated dme and the clean formation of **3b**. ^{1}H NMR ($CDCl_3$, 213 K): δ = 4.61 [m-br, 2 H, $NbOCH_2$ (κ^1-dme)], 4.24 [s, 3 H, $MeONb(\kappa^1$-dme)], 4.00 [s, 4 H, CH_2 (κ^2-dme)], 3.90 [m-br, 2 H, CH_2 (κ^1-dme)], 3.68 [s, 6 H, CH_3 (κ^2-dme)], 3.41 ppm [s, 3 H, Me (κ^1-dme)]. Similar NMR pattern was obtained upon reaction of **1c** (0.450 mmol) with dme (0.950 mmol).

In a different experiment, a suspension of **1c** (0.900 mmol) in CH_2Cl_2 (25 mL) was cooled at –10°C and treated with dme (0.910 mmol). An orange solution formed upon stirring the mixture for 10 minutes at –10°C. Λ_M (CH_2Cl_2, 263 K) = 8.1 $S \cdot cm^2 \cdot mol^{-1}$ The solution was allowed to warm up to room temperature and stirred for additional 30 minutes. Subsequent conductivity measurement resulted in agreement with the formation of $NbBr_4[OCH_2CH_2OMe]$, **2a** (Λ_M = 0.25 $S \cdot cm^2 \cdot mol^{-1}$).

b) Reactions of $NbBr_5$ with dme in 2:1 molar ratio. To a suspension of $NbBr_5$ (0.250 mmol) in $CDCl_3$ (0.75 mL) in a NMR tube, CH_2Cl_2 (0.250 mmol) and dme (0.500 mmol) were added in the order. The tube was sealed, shaken and maintained at room temperature for 15 days. Subsequent ^{1}H NMR analysis evidenced the presence of CH_2Cl_2, complex **2a** and MeBr in *ca.* 1:1:1 ratio. Then, the tube was opened and water was added inside (*ca.* 4 mmol). Immediate precipitation of a colourless solid from a pale-yellow solution occurred. NMR/GC-MS analyses on the solution revealed the presence of CH_2Cl_2, $MeOCH_2CH_2Br$, MeBr and 1,4-dioxane (ratio *ca.* 10:9:9:1).

In a different experiment, a NMR tube was charged with $NbBr_5$ (0.200 g, 0.406 mmol), $CDCl_3$ (0.85 mL), CH_2Cl_2 (0.410 mmol) and dme (0.83 mmol), in the order given. Then the tube was sealed, and the mixture was heated at 80°C (temperature of the external oil-bath) for 12 hours. Hence, the tube was cooled to –20°C and opened. A large excess of water (*ca.* 5 mmol) was added, thus the solution obtained was analyzed by GC/MS and NMR spectroscopy: CH_2Cl_2, dme,

$MeOCH_2CH_2Br$, MeBr, CH_2BrCH_2Br, MeOH and 1,4-dioxane were finally recognized in 25:8:5:16:7:6:3 ratio.

4.5. Isolation of the complex $NbOBr_3(dme)NbBr_5$ (Nb–O–Nb), ***5b****.*

A mixture of $NbBr_5$, **1c** (0.700 g, 1.42 mmol), and dme (2.10 mmol), in CH_2Cl_2 (9 mL) in a Schlenk tube, was stirred at room temperature for 4 hours. The resulting red solution was layered with pentane and stored at room temperature. Hence, dark-red crystals of compound $NbOBr_3(dme)NbBr_5$, **5b**, formed in 12 hours. Yield: 0.038 g (6% yield). Anal. Calcd for $C_4H_{10}Br_8Nb_2O_3$: C, 5.16; H, 1.08; Br, 68.65. Found: C, 5.06; H, 1.13; Br, 67.86. IR (solid state): 2962w, 2896w, 2825vw, 1467w, 1443m, 1403w, 1259m, 1067s, 1015s, 857m-s ($\nu_{Nb=O}$), 792vs cm^{-1}. ^1H NMR ($CDCl_3$): δ = 4.30 (s, 4 H, CH_2), 3.93 ppm (s, 6 H, CH_3).

4.6. Reactions of MX_5 (X = Br, I, M = Nb, Ta) with 1,2-dialkoxyalkanes in 1:2 molar ratio.

General procedure**:** A suspension of MX_5 (0.200 mmol) in $CDCl_3$ (0.70 mL) in a NMR tube, was treated with CH_2Cl_2 (0.200 mmol) and with the appropriate diether (0.400 mmol). The tube was sealed, shaken in order to homogenise the content, and stored at room temperature for 48 hours. Then ^1H NMR spectrum was recorded. Afterwards, the tube was opened and water (*ca.* 3 mmol) was added to the mixture, giving the precipitation of a colourless solid from a solution. The latter was analyzed by ^1H NMR/GC-MS.

From $NbBr_5$ and $MeOCH_2CH(Me)OMe$: CH_2Cl_2, **2d**, MeBr and $MeOCH_2CH(Me)OMe$ (ratio *ca.* 1:1:1:1). After hydrolysis: CH_2Cl_2, $BrCH_2CH(Me)OMe$, MeBr and $MeOCH_2CH(Me)OMe$ (ratio 1:1:1:1).

From $NbBr_5$ and $EtO(CH_2)_2OEt$: CH_2Cl_2, **2c**, EtBr and $EtO(CH_2)_2OEt$ (ratio *ca.* 1:1:1:1). After hydrolysis: CH_2Cl_2, $Br(CH_2)_2OEt$, EtBr, $EtO(CH_2)_2OEt$ and 1,4-dioxane (ratio 20:15:20:16:1).

From NbI_5 and $MeO(CH_2)_2OMe$ (dme)/H_2O: CH_2Cl_2, CH_2ICH_2I, MeOH, MeI, dme, $MeO(CH_2)_2OH$ and 1,4-dioxane (ratio 20:3:2:15:13:12:3).

From NbI_5 and $EtO(CH_2)_2OEt/H_2O$: CH_2Cl_2, EtI, $EtO(CH_2)_2OEt$ and $EtOCH_2CH_2OH$ (ratio 10:8:10:7).

From NbI_5 and $MeOCH_2CH(Me)OMe/H_2O$: CH_2Cl_2, MeI, $MeOCH_2CH(Me)OMe$ and $ICH_2CH(Me)OMe$ (ratio *ca.* 1:1:1:1).

From NbI_5 and $MeO(CH_2)_2OCH_2Cl/H_2O$: CH_2Cl_2, MeI, CH_2ICH_2I, CH_2ClI, $ClCH_2OCH_2OCH_2Cl$, dme and Me_2O (ratio *ca.* 16:12:4:2:4:11:1).

4.7. X-ray Crystallographic Study

Crystal data and collection details for $NbOBr_3(dme)NbBr_5$, **5b**, are listed in Table 4. The diffraction experiment was 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) [18]. The structure was solved by direct methods and refined by full-matrix least-squares based on all data using F^2 [18]. All non-hydrogen atoms were refined with anisotropic displacement parameters. H-atoms 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.

Table 4 about here

4.8. Computational studies.

Geometry optimizations were carried out with the Gaussian 03 program package [19] in the framework of the density functional theory (DFT), employing the Becke's three-parameter hybrid exchange functional combined with the Lee, Yang, and Parr correlation functional (B3LYP method [20]), in conjugation with the LANL2DZ effective core potential and basis set [21]. Hence, the B3LYP calculations are denoted as B3LYP/LANL2DZ. No symmetry constraints were adopted. Vibrational frequencies were calculated at stationary points at the B3LYP/LANL2DZ level of theory, by identifying the points as minima. A Table reporting the thermodynamic results from B3LYP/LANL2DZ optimization and vibrational analysis is given as Supplementary Data (Table S1). Thermodynamic results refer to 298.15 K and 101300 Pa.

Appendix A. Supplementary Data

CCDC 771999 contains the supplementary crystallographic data for $NbOBr_3(dme)NbBr_5$, **5b**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Table S1 reports the thermodynamic results from B3LYP/LANL2DZ optimization and vibrational analysis.

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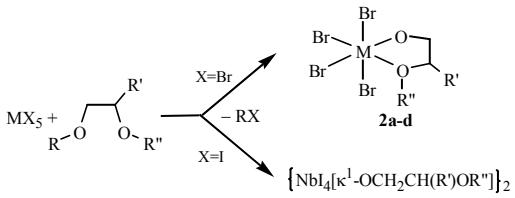
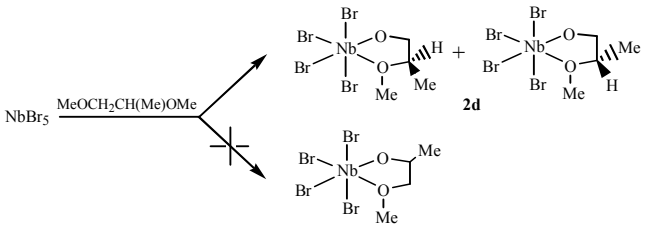
Scheme 1. Preparation of mixed halo-alkoxides of niobium and tantalum.

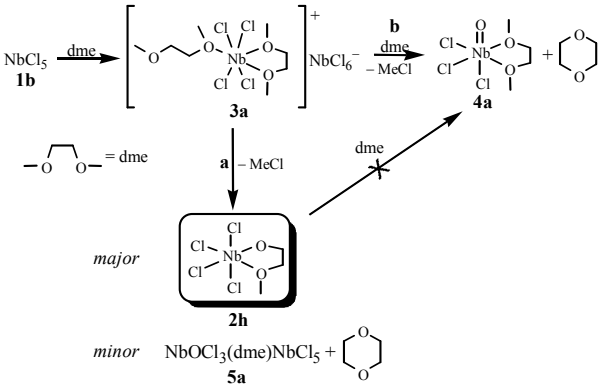


Halide	Dialkoxyalkane	Compound
$NbBr_5$	$MeOCH_2CH_2OMe$	**2a**
$TaBr_5$	$MeOCH_2CH_2OMe$	**2b**
$NbBr_5$	$EtOCH_2CH_2OEt$	**2c**
$NbBr_5$	$MeOCH_2CH(Me)OMe$	**2d**
NbI_5	$MeOCH_2CH_2OMe$	**2e**
NbI_5	$EtOCH_2CH_2OEt$	**2f**
NbI_5	$MeOCH_2CH_2OCH_2Cl$	**2g**

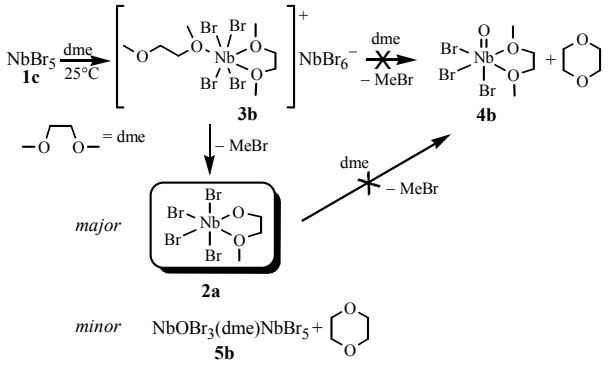
Scheme 2. The reaction of $NbBr_5$ with 1,2-dimethoxypropane.



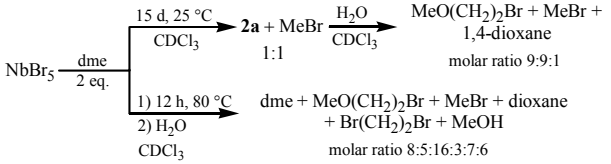
Scheme 3. Reactions of $NbCl_5$ with dme.



Scheme 4. Room temperature reactions of $NbBr_5$ with dme.



Scheme 5. Reactions of $NbBr_5$ with two equivalents of dme.



Captions for Figures and Tables

Figure 1. B3LYP/LANL2DZ-optimized structure of $[NbBr_4(\kappa^1\text{-dme})(\kappa^2\text{-dme})][NbBr_6]$, **3b**, in the gas phase.

Figure 2. View of the molecular structure of $NbOBr_3(dme)NbBr_5$, **5b**. Displacement ellipsoids are at the 30% probability level. Only one of the two independent molecules present in the unit cell is represented.

Figure 3. B3LYP/LANL2DZ-optimized structure of $NbOBr_3(dme)NbBr_5$, **5b**, in the gas phase.

Table 1. Selected computed bond distances (Å) and angles (deg) for $[NbBr_4(\kappa^1\text{-dme})(\kappa^2\text{-dme})][NbBr_6]$, **3b.**

Table 2. Selected experimental and calculated bond distances (Å) and angles (deg) for $NbOBr_3(dme)NbBr_5$, **5b**.

Table 3. Products of the 1:2 reactions of **1c,d** with $ROCH_2CH(R')OR''$, detected after hydrolysis (CH_2Cl_2 used as standard, in 1:1 ratio with the metal compound).

Table 4. Crystal data and structure refinement for $NbOBr_3(dme)NbBr_5$, **5b**.

Table 1 Selected computed bond distances (Å) and angles (deg) for $[NbBr_4(\kappa^1\text{-dme})(\kappa^2\text{-dme})][NbBr_6]$, **3b.**

Nb(2)–Br(21)	2.653	O(4)–C(10)	1.457
Nb(2)–Br(22)	2.597	O(5)–C(11)	1.494
Nb(2)–Br(23)	2.529	O(5)–C(12)	1.488
Nb(2)–Br(24)	2.677	C(12)–C(13)	1.538
Nb(2)–O(3)	2.292	O(6)–C(13)	1.490
Nb(2)–O(4)	4.350	O(6)–C(14)	1.503
Nb(2)–O(5)	2.213	O(3)–Nb(2)–Br(21)	71.73
Nb(2)–O(6)	2.199	O(5)–Nb(2)–O(6)	66.72
O(3)–C(7)	1.489	Br(24)–Nb(2)–Br(21)	141.87
O(3)–C(8)	1.497	Br(24)–Nb(2)–Br(22)	87.13
C(8)–C(9)	1.522	Br(21)–Nb(2)–O(5)	75.56
O(4)–C(9)	1.447		

Table 2. Selected experimental and calculated bond distances (Å) and angles (deg) for $NbOBr_3(dme)NbBr_5$, **5b**.

	Experimental		Calculated
	Molecule 1	**Molecule 2**	
Nb(1)–O(1)	2.137(5)	2.120(6)	2.184
Nb(2)–O(1)	1.747(5)	1.755(6)	1.783
Nb(2)–O(2)	2.199(6)	2.202(6)	2.239
Nb(2)–O(3)	2.307(6)	2.283(6)	2.363
Nb(2)–Br(6)	2.4274(12)	2.4076(13)	2.525
Nb(2)–Br(7)	2.4863(12)	2.4833(14)	2.598
Nb(2)–Br(8)	2.4998(12)	2.5098(13)	2.600
C(2)–O(2)	1.440(10)	1.440(11)	1.475
C(2)–C(3)	1.488(12)	1.455(14)	1.519
C(3)–O(3)	1.412(10)	1.410(11)	1.472
Nb(1)–Br(1)	2.4147(11)	2.4169(12)	2.511
Nb(1)–Br(2)	2.4752(12)	2.4812(12)	2.599
Nb(1)–Br(3)	2.4825(11)	2.4832(12)	2.609
Nb(1)–Br(4)	2.4829(12)	2.4868(12)	2.560
Nb(1)–Br(5)	2.4807(12)	2.4724(13)	2.559
Nb(1)–O(1)–Nb(2)	170.2(3)	170.6(3)	172.95
O(1)–Nb(2)–O(3)	164.2(2)	164.6(2)	167.24
O(1)–Nb(2)–O(2)	93.4(2)	92.6(2)	96.39
O(1)–Nb(1)–Br(1)	179.75(17)	179.67(17)	179.06

Table 3. Products of the 1:2 reactions of **1c,d** with $ROCH_2CH(R')OR''$, detected after hydrolysis (CH_2Cl_2 used as standard, in 1:1 ratio with the metal compound).

$NbBr_5$	
Diether	**Products (relative molar ratio)**
$MeOCH_2CH(Me)OMe$	CH_2Cl_2 (1), $BrCH_2CH(Me)OMe$ (1), MeBr (1), $MeOCH_2CH(Me)OMe$ (1),
$EtO(CH_2)_2OEt$	CH_2Cl_2 (20), $Br(CH_2)_2OEt$ (15), EtBr (20), $EtO(CH_2)_2OEt$ (16), 1,4-dioxane (1)
NbI_5	
Diether	**Products (relative molar ratio)**
$MeO(CH_2)_2OMe$	CH_2Cl_2 (20), CH_2ICH_2I (3), MeOH (2), MeI (15), dme (13), $MeO(CH_2)_2OH$ (12), 1,4-dioxane (3)
$EtO(CH_2)_2OEt$	CH_2Cl_2 (10), EtI (8), $EtO(CH_2)_2OEt$ (10), $EtOCH_2CH_2OH$ (7)
$MeOCH_2CH(Me)OMe$	CH_2Cl_2 (1), MeI (1), $MeOCH_2CH(Me)OMe$ (1), $ICH_2CH(Me)OMe$ (1)
$MeO(CH_2)_2OCH_2Cl$	CH_2Cl_2 (16), MeI (12), CH_2ICH_2I (4), CH_2ClI (2), $ClCH_2OCH_2OCH_2Cl$ (4), $MeO(CH_2)_2OMe$ (11), Me_2O (1)

Table 4. Crystal data and experimental details for $NbOBr_3(dme)NbBr_5$, **5b**.

Formula	$C_4H_{10}Br_8Nb_2O_3$
Fw	931.22
λ, Å	0.71073
Temperature, K	100(2)
Crystal system	Orthorhombic
Space group	$Pna2_1$
a, Å	36.552(6)
b, Å	10.1067(15)
c, Å	10.0757(15)
β,°	90
Cell volume, Å^3	3719.1(10)
Z	8
D_c, g cm^{-3}	3.326
μ, mm^{-1}	18.415
F(000)	3360
θ limits, °	1.12-28.00
Reflections collected	30406
Independent reflections	8706 (R_{int} = 0.0647)
Data/restraints/parameters	8706 / 2 / 311
Goodness on fit on F^2	1.022
R1 ($I > 2\sigma(I)$)	0.0393
wR2 (all data)	0.0850
Largest diff. peak and hole, e.Å^{-3}	1.460 and –1.476