

# Epoxide Ring Opening and Insertion into the M–X Bond of Niobium and Tantalum Pentahalides: a Route for the Synthesis of Halo / Alcoholate Complexes

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## Abstract

The Group 5 pentahalides  $\text{MX}_5$  ( $\text{M} = \text{Nb, Ta}$ ;  $\text{X} = \text{Cl, Br}$ ), **1**, react with a variety of epoxides (1,2-epoxybutane, styrene oxide, 2,3-dimethyl-2,3-epoxybutane, epoxycyclohexane, ethylene oxide), in 1:3 molar ratio, to afford the dinuclear dihalo-*tris*(2-haloalcoholate) complexes  $[\text{MX}_2(\text{OR})_2(\mu\text{-OR})]_2$  [ $\text{M} = \text{Nb}$ ,  $\text{X} = \text{Cl}$ ,  $\text{R} = -\text{CH}(\text{Et})\text{CH}_2\text{Cl}$ , **2a**;  $\text{M} = \text{Nb}$ ,  $\text{X} = \text{Cl}$ ,  $\text{R} = -\text{CH}_2\text{CH}(\text{Ph})\text{Cl}$ , **2b**;  $\text{M} = \text{Nb}$ ,  $\text{X} = \text{Cl}$ ,  $\text{R} = -\text{C}(\text{Me})_2\text{C}(\text{Me})_2\text{Cl}$ , **2c**;  $\text{M} = \text{Nb}$ ,  $\text{X} = \text{Br}$ ,  $\text{R} = -\text{CH}_2\text{CH}(\text{Ph})\text{Br}$ , **2d**;  $\text{M} = \text{Nb}$ ,  $\text{X} = \text{Br}$ ,  $\text{R} = -\text{C}(\text{Me})_2\text{C}(\text{Me})_2\text{Br}$ , **2e**;  $\text{M} = \text{Ta}$ ,  $\text{X} = \text{Cl}$ ,  $\text{R} = -\text{CH}(\text{Et})\text{CH}_2\text{Cl}$ , **2f**;  $\text{M} = \text{Ta}$ ,  $\text{X} = \text{Cl}$ ,  $\text{R} = -\overline{\text{CH}(\text{CH}_2)_4}\text{CHCl}$ , **2g**;  $\text{M} = \text{Ta}$ ,  $\text{X} = \text{Br}$ ,  $\text{R} = -\text{CH}_2\text{CH}_2\text{Br}$ , **2h**], in moderate to good yields. The products, **2a - h**, result from multiple epoxide insertion into metal-halide bonds, and the reactions involving 1,2-epoxybutane and styrene oxide proceed with high regioselectivity. The molecular structure of **2h** has been elucidated by X ray diffraction. Differently,  $\text{NbF}_5$  adds one equivalent of 2,3-dimethyl-2,3-epoxybutane to give the monomer  $\text{NbF}_5[\text{O}=\text{C}(\text{Me})(\text{Bu}^t)]$ , **3**, in high yield, as result of epoxide to ketone isomerization. The reactions of  $\text{MF}_5$  ( $\text{M} = \text{Nb, Ta}$ ) with other epoxides proceed non-selectively according to various pathways, including formation of C–O and C–F bonds and C–C and C–H cleavages.

*Keywords:* Niobium / Tantalum / Pentahalides / Epoxide insertion / Halo-alkoxides / Epoxide isomerisation

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## 1. Introduction

Epoxides have been employed as feasible materials for organic syntheses, and recent examples refer to the preparations of natural products [1], lactones [2] and amino-alcohols [3]. The reactions often proceed *via* epoxide ring-opening and, in a number of cases, they require mediation by metal species. Indeed, the aperture of epoxide rings promoted by transition metal and lanthanide derivatives is a widely described process [4].

In the recent past, we have been involved in studying the coordination chemistry of Group 5 pentahalides,  $\text{MX}_5$  (**1**; M = Nb, Ta; X = F, Cl, Br) [5], with potentially oxygen-donor ligands [6]. The strong acidic character of **1** is responsible for promoting C–O bond cleavages [6a] in mild conditions, and the ring-opening polymerization of tetrahydrofuran is a significant example [6b]. It is noteworthy that these C–O bond breaking processes may lead, in some cases, to interesting clean organic transformations [6c,d].

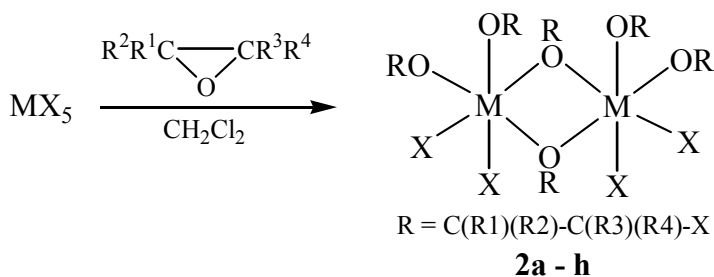
By contrast with the chemical behaviour exhibited by THF when contacted with **1**, different cyclic systems such as 1,4-dioxane and tetrahydropyran do not undergo C–O cleavage at room temperature in the presence of **1** [6b]. Thus, with the aim to extend the chemistry of **1** with cyclic oxygen-containing molecules, and in order to attain transformations on the organic substrate, we decided to study the reactivity of **1** with epoxides. We present herein the results of these studies, which have indicated an unprecedented route for the preparation of novel mixed halo-2-haloalcoholate complexes. Moreover, alternative reactions of epoxides mediated by  $\text{MF}_5$ , including epoxide to ketone isomerization, will be discussed.

## 2. Results and Discussion

**Reactivity of  $\text{MX}_5$  ( $\text{M} = \text{Nb, Ta}$ ,  $\text{X} = \text{Cl, Br}$ ) with epoxides: synthesis of novel mixed halo-haloalcoholate complexes.**

Dichloromethane suspensions of  $\text{MX}_5$  ( $\text{M} = \text{Nb, Ta}$ ;  $\text{X} = \text{Cl, Br}$ ) react vigorously with epoxides (1:3 molar ratio) to afford the dinuclear compounds  $[\text{MX}_2(\text{OR})_2(\mu\text{-OR})]_2$  [ $\text{M} = \text{Nb}$ ,  $\text{X} = \text{Cl}$ ,  $\text{R} = -\text{CH}(\text{Et})\text{CH}_2\text{Cl}$ , **2a**;  $\text{M} = \text{Nb}$ ,  $\text{X} = \text{Cl}$ ,  $\text{R} = -\text{CH}_2\text{CH}(\text{Ph})\text{Cl}$ , **2b**;  $\text{M} = \text{Nb}$ ,  $\text{X} = \text{Cl}$ ,  $\text{R} = -\text{C}(\text{Me})_2\text{C}(\text{Me})_2\text{Cl}$ , **2c**;  $\text{M} = \text{Nb}$ ,  $\text{X} = \text{Br}$ ,  $\text{R} = -\text{CH}_2\text{CH}(\text{Ph})\text{Br}$ , **2d**;  $\text{M} = \text{Nb}$ ,  $\text{X} = \text{Br}$ ,  $\text{R} = -\text{C}(\text{Me})_2\text{C}(\text{Me})_2\text{Br}$ , **2e**;  $\text{M} = \text{Ta}$ ,  $\text{X} = \text{Cl}$ ,  $\text{R} = -\text{CH}(\text{Et})\text{CH}_2\text{Cl}$ , **2f**;  $\text{M} = \text{Ta}$ ,  $\text{X} = \text{Cl}$ ,  $\text{R} = -\overline{\text{CH}(\text{CH}_2)_4\text{CHCl}}$ , **2g**;  $\text{M} = \text{Ta}$ ,  $\text{X} = \text{Br}$ ,  $\text{R} = -\text{CH}_2\text{CH}_2\text{Br}$ , **2h**], in 55 ÷ 70 % yield, Scheme 1. On the other hand, the reactions of  $\text{NbCl}_5$  with one, two, four and five equivalents of 1,2-epoxybutane, respectively, gave complicated mixtures of products containing mainly **2a**, suggesting that compounds **2** are the most stable species obtainable by reacting **1** with epoxides, independently on the stoichiometry. Similar conclusions were reached by studying the reactions of  $\text{NbCl}_5$  with styrene oxide and epoxycyclohexane (vide infra).

Scheme 1. The reactivity of  $\text{MX}_5$  ( $\text{M} = \text{Nb, Ta}$ ;  $\text{X} = \text{Cl, Br}$ ) with epoxides.



Scheme 1

The compounds **2a** - **h** have been characterized spectroscopically (IR and NMR), by elemental analyses, and by X ray diffraction in the case of **2h** (Figure 1 and Table 1).

Figure 1. Molecular structure of  $[\text{TaBr}_2(\text{OCH}_2\text{CH}_2\text{Br})_2(\mu\text{-OCH}_2\text{CH}_2\text{Br})_2]$ , **2h**. Thermal ellipsoids are drawn at 30% probability level. Only independent atoms are labelled.

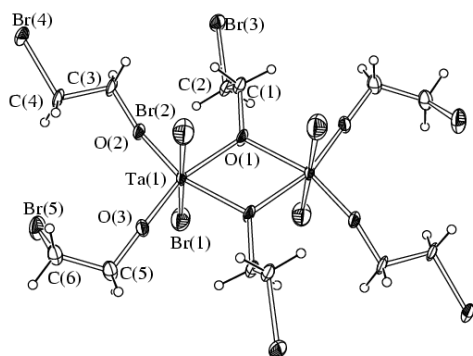


Figure 1 and Table 1 about here

The unit cell contains discrete dinuclear  $[\text{TaBr}_2(\text{OCH}_2\text{CH}_2\text{Br})_2(\mu\text{-OCH}_2\text{CH}_2\text{Br})_2]$  molecules, which reside on a crystallographic inversion centre. The dimeric species adopts an edge sharing bioctahedral geometry, with four terminal bromide ligands in the axial positions (*trans* geometry). Conversely, the equatorial plane is occupied by four terminal and two bridging haloalcoholate ligands. All bonding distances are comparable with those previously reported for Ta(V)–Br and Ta(V)–OR containing complexes [6]. The bridging ligand is almost symmetric [Ta(1)–O(1) 2.091(11) Å; Ta(1)–O(1)#1 2.107(10) Å], and these contacts are considerably elongated compared to the ones referring to the terminal haloalcoholate ligands [Ta(1)–O(2) 1.818(9) Å; Ta(1)–O(3) 1.822(10) Å].

Compounds **2** add to the rich family of transition metal alcoholate complexes [7], which have found various applications (film-deposition [8], nanotechnology [9], polymerization catalysis [10], preparation of materials of noticeable properties [11]); more in detail, cases of structurally

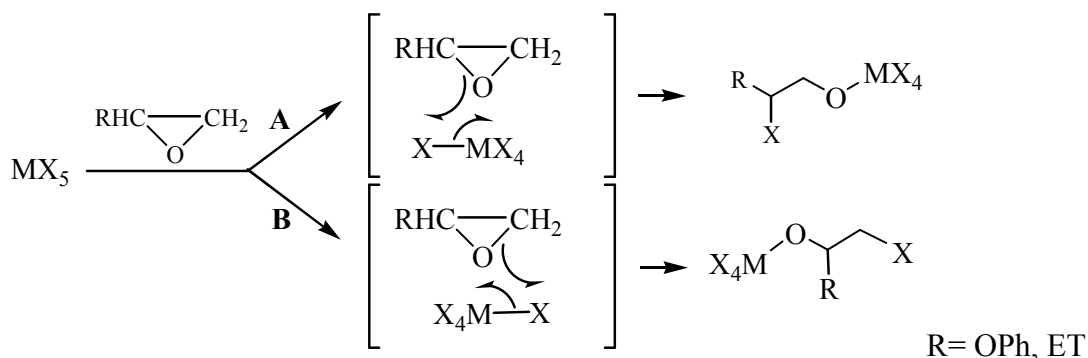
characterized metal complexes containing 2-haloalcoholate ligands are available in the literature, including both late [12] and early transition [13] metal species.

For what concerns niobium (V) and tantalum (V), although examples of pentaalcoholates are numerous [14], only few mixed halo-alcoholates have been crystallographically characterized so far [15]. Thus, complexes **2** come to belong to the rare class of halo-alcoholate derivatives of group 5 elements [16], moreover they represent the first case of structurally characterized group 5 coordination compounds containing halo-substituted alcoholate ligands.

The NMR spectra of **2a, c, e, f** exhibit slightly distinct resonances for terminal and bridging ligands respectively (see Experimental) [**Errore. Il segnalibro non è definito.**e], and agree with the dinuclear structure  $[\text{MX}_2(\text{OR})_2(\mu\text{-OR})]_2$ . For instance, the methyl units belonging to the  $\text{OC}(\text{Me})_2$  moieties, in **2c**, give rise to resonances at 1.70 (bridging ligands) and 1.58 (terminal) ppm in the  $^1\text{H}$  NMR spectrum, and at 29.1 (bridging) and 28.9 (terminal) in the  $^{13}\text{C}$  NMR spectrum. On the other hand, the  $^1\text{H}$  NMR spectra of **2b, d, g** display only broad resonances, for which the discrimination between terminal and bridging ligands has not been possible. In contrast to previous observations on some niobium or tantalum alkoxides, no dimer-monomer equilibria [**Errore. Il segnalibro non è definito.**e, 17] have been detected in solution at room temperature for compounds **2** [18].

It is worthy noting that the formal insertion of 1,2-epoxybutane into the metal-halide bond could in principle generate two isomeric forms, according to the site of attack of the halide, see Scheme 2.

Scheme 2. Possible routes of formation of the haloalcoholate fragment.



Scheme 2

A careful reading of the 1D and 2D NMR spectra of **2a, f** has evidenced the absence of resonances attributable to  $-\text{OCH}_2\text{CH}(\text{Et})\text{Cl}$  units [6c,d], suggesting that multiple 1,2-epoxybutane insertion into metal-chloride bonds of  $\text{MCl}_5$  ( $\text{M} = \text{Nb}, \text{Ta}$ ) occurs in highly regioselective mode (Scheme 2, path B), placing the halide on the less hindered carbon atom.

The NMR spectra of **2b, d**, obtained by reacting  $\text{NbX}_5$  ( $\text{X} = \text{Cl}, \text{Br}$ ) with styrene oxide, do not allow to rule out unambiguously the formation of any of the species obtainable by the two potential modes of insertion (see Scheme 2). Nevertheless, the hydrolysis of  $\text{CDCl}_3$  solutions of complexes **2b, d**, and subsequent GC-MS and NMR analyses on the organic phase, have pointed out that neither **2b** nor **2d** contain the  $[\text{OCH}(\text{Ph})\text{CH}_2\text{Cl}]$  fragment (entry 2, Table 2). In other words, the insertion of styrene oxide to give **2b, d** seems to proceed, differently from the insertion of 1,2-epoxybutane, according to the path A of Scheme 2, the halide going to the more impeded carbon atom. This feature may be attributable to the steric hindrance of the phenyl ring, which would force this latter to occupy the farthest position from the metal centre.

Table 2 about here

The identities of products **2a - h** have been corroborated by combined GC-MS / NMR analyses on concentrated  $\text{CDCl}_3$  solutions of these compounds after treatment with  $\text{H}_2\text{O}$ , see Experimental and Table 2. The addition of water causes quick precipitation of a white solid (probably metal oxides), and release of the organic material. The hydrolysis of **2c** (entry 4, Table 2) deserves more comments: beside 2,3-dimethyl-3-chloro-2-butanol, minor amounts of *t*-butylmethylketone have been observed by NMR and GC-MS analyses, suggesting that pathways alternative to the insertion (see Scheme 1) may be operating, at least for the reaction of 2,3-dimethyl-2,3-epoxybutane with  $\text{NbCl}_5$ .

With the purpose to extend the series of halo-2-haloalcoholate complexes of type **2**, we studied the reactivity of  $\text{NbBr}_5$  with 1,2-epoxybutane and with epoxycyclohexane, respectively. Unfortunately, these reactions afforded mixtures of compounds which could not be separated and characterized. Nonetheless, GC-MS and NMR analyses on the reaction mixtures treated with water led to the identification of 1,2-dibromobutane and 1-bromo-2-butene from  $\text{NbBr}_5$  and 1,2-epoxybutane, and of 2-bromocyclohexanol and 1,2-dibromocyclohexane from  $\text{NbBr}_5$  and epoxycyclohexane. These results indicate that the reactions of 1,2-epoxybutane and epoxycyclohexane with  $\text{NbBr}_5$  proceed *via* epoxide insertions, analogously to what discussed for **2a - h**.

**Reactivity of  $\text{MF}_5$  (M = Nb, Ta) with epoxides: isomerisation of 2,3-dimethyl-2,3-epoxybutane to 3,3-dimethyl-2-butanone.**



According to our recent reports, the reactivity of niobium and tantalum pentahalides with oxygen-donor ligands is strongly influenced by the metal-halide bond energy [6a,b], and the fluorides often show a chemistry quite different from that of the other halides. Therefore, we decided to investigate the reactivity of MF<sub>5</sub> (M = Nb, Ta) with epoxides, with the aim to see whether insertion reactions could take place despite the high value of the metal-fluoride bond energy [19] or not.

Thus, niobium pentafluoride and 2,3-dimethyl-2,3-epoxybutane react to afford the ketone complex NbF<sub>5</sub>[O=C(Me)(*t*Bu)], **3**, in *ca.* 90 % yield. This reaction is strictly stoichiometric: the same reaction, carried out by using variable epoxide to metal ratios greater than 1, resulted in formation of **3** in admixture with unreacted epoxide. Complex **3**, which belongs to the restricted family of carbonylic adducts of Group 5 pentahalides [6a], has been characterized spectroscopically (<sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR, IR) and by GC-MS analysis carried out on the organic material obtained by hydrolysis of **3** (entry 1, Table 3). Salient spectroscopic feature is given by a strong IR absorption at 1647 cm<sup>-1</sup>, ascribed to the carbon-oxygen double bond (uncoordinated *t*-butylmethylketone shows the C=O stretching vibration at 1708 cm<sup>-1</sup> - liquid film). The <sup>1</sup>H NMR spectrum displays one set of two resonances, attributed to the methyl unit (s, 2.84 ppm) and to the *t*-butyl group (s, 1.41 ppm), respectively. Major <sup>13</sup>C NMR aspect is given by the carbonylic resonance, seen at 245.6 ppm, *i.e.* significantly downfield-shifted with respect to the resonance of the uncoordinated ketone ( $\delta$  = 213.81 ppm). Furthermore, the <sup>19</sup>F NMR spectrum shows uniquely a broad resonance at 145.8 ppm, accounting for the five fluorines of the [NbF<sub>5</sub>] moiety, and indicating the monomeric, neutral nature of **3**.

Table 3 about here

In contrast with what discussed about the reaction of NbCl<sub>5</sub> with 2,3-dimethyl-2,3-epoxybutane, which affords some amounts of *t*-butylmethylketone as result of HCl releasing and subsequent hydrolysis (*vide infra*), the formation of *t*-butylmethylketone in the case of NbF<sub>5</sub> is probably the consequence of direct epoxide isomerisation promoted by niobium fluoride. This latter rearrangement has been reported to occur under the assistance of various metal species, including high valence vanadium [20], cobalt [21], erbium [22], bismuth [23] and lithium [24] compounds.

We tried to extend the chemistry of niobium and tantalum pentafluorides (MF<sub>5</sub>) to a series of epoxides, consisting of 1,2-epoxybutane, styrene oxide and epoxycyclohexane. At variance with what reported above about the synthesis of **3**, the reactions of MF<sub>5</sub> with epoxides different from 2,3-dimethyl-2,3-epoxybutane led to complicated mixtures of products. We did not succeed in the characterization of the inorganic species, but we were able to identify some of the organic compounds produced in the course of the reactions, and released from the metallic frames upon hydrolysis (see Table 3). Thus, ethylmethylketone has been recognized in the mixture obtained from NbF<sub>5</sub> and 1,2-epoxybutane (entry 2, Table 3): accordingly, this reaction proceeds with epoxide rearrangement, similar to that described for 2,3-dimethyl-2,3-epoxybutane (entry 2, Table 3). Analogous result has been achieved by using TaF<sub>5</sub> in the place of NbF<sub>5</sub> (entry 3, Table 3).

Conversely, no traces of acetophenone and cyclohexanone have been found in the hydrolyzed mixtures generated from the reactions of TaF<sub>5</sub> with styrene oxide and epoxycyclohexane, respectively. Therefore, alternative pathways are likely to be operating in these two cases. More precisely, benzene and ethoxybenzene have been recognized (GC-MS and NMR) as main products of the treatment of TaF<sub>5</sub> with styrene oxide followed by hydrolysis (entry 4,

Table 3). Furthermore, GC-MS and NMR analyses on a sample obtained by addition of epoxycyclohexane to TaF<sub>5</sub>, and successive hydrolysis, revealed the presence of little amounts of 2-fluorocyclohexanol (entry 5, Table 3). All these organics prove that C–C and C–H bonds activation, together with C–O and C–F bonds formation, are possible processes taking place in the course of the reactions of MF<sub>5</sub> (M = Nb, Ta) with epoxides.

### 3. Conclusions

The strong oxophilicity of niobium and tantalum pentahalides is tested in the room temperature reactions with epoxides, in 1:3 molar ratio, which proceed rapidly, exothermically and regioselectively. Multiple epoxide ring opening and insertion into metal–chloride (or bromide) bonds give novel stable dinuclear species containing both halide and 2-haloalcoholate ligands. Although MF<sub>5</sub> (M = Nb, Ta) are very reactive towards epoxides, the relatively high metal-fluoride bond energy inhibits insertion reactions. Several alternative pathways appear to be operative concurrently; among them, the epoxide to ketone isomerization prevails in some cases.

### 4. Experimental

#### 4.1. General procedures

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<sup>-2</sup> mmHg) and then filled with argon. All the reagents, including MX<sub>5</sub> (M = Nb, Ta, X = Cl; M = Nb, Ta, X = F), were commercial products

(Aldrich) of the highest purity available. NbBr<sub>5</sub> and TaBr<sub>5</sub> were prepared according to published procedures [25]. Epoxides were liquid commercial products stored under argon atmosphere as received. Solvents were distilled before use under argon atmosphere from appropriate drying agents: CH<sub>2</sub>Cl<sub>2</sub> and CDCl<sub>3</sub> from P<sub>4</sub>O<sub>10</sub>, pentane from LiAlH<sub>4</sub>.

Infrared spectra were recorded at 298 K on a FT IR-Perkin Elmer Spectrometer equipped with a UATR sampling accessory (solid samples). NMR measurements were performed at 298 K on Varian Gemini 200BB and Mercury Plus 400 instruments. The chemical shifts for <sup>1</sup>H-, <sup>13</sup>C-, and <sup>19</sup>F NMR spectra were referenced to TMS and to CFCl<sub>3</sub>, respectively. The chemical shifts were assigned *via* DEPT experiments and <sup>1</sup>H, <sup>13</sup>C correlation through gs-HSQC and gs-HMBC experiments [26]. NMR assignments related to terminal and bridging ligands have been specified only where a distinction has been possible. 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 sensitive compounds, which were weighed and directly introduced into the analyzer. The halide content refers to the metal-bound halides, and was determined by Volhardt method [27] after exhaustive hydrolysis of the sample. Metals were analyzed as M<sub>2</sub>O<sub>5</sub> obtained by hydrolysis of the sample followed by calcination in a platinum crucible. Every elemental analysis was repeated twice in order to get reproducible results.

4.2. Preparation of [MX<sub>2</sub>(OR)<sub>2</sub>(μ-OR)]<sub>2</sub> [M = Nb, X = Cl, R = -CH(Et)CH<sub>2</sub>Cl, **2a**; M = Nb, X = Cl, R = -CH<sub>2</sub>CH(Ph)Cl, **2b**; M = Nb, X = Cl, R = -C(Me)<sub>2</sub>C(Me)<sub>2</sub>Cl, **2c**; M = Nb, X = Br, R = -CH<sub>2</sub>CH(Ph)Br, **2d**; M = Nb, X = Br, R = -C(Me)<sub>2</sub>C(Me)<sub>2</sub>Br, **2e**; M = Ta, X = Cl, R = -

$CH(Et)CH_2Cl$ , **2f**;  $M = Ta$ ,  $X = Cl$ ,  $R = -\overline{CH(CH_2)_4}CHCl$ , **2g**;  $M = Ta$ ,  $X = Br$ ,  $R = -CH_2CH_2Br$ , **2h**].

*General procedure:* A suspension of  $MX_5$  ( $M = Nb, Ta$ ;  $X = Cl, Br$ ; 1.00 mmol), in  $CH_2Cl_2$  (15 mL) inside a Schlenk tube, was treated with the appropriate epoxide (3.00 mmol). In the case of the synthesis of **2h**, ethylene oxide was added as a  $CH_2Cl_2$  solution (50 mg/mL). Dissolution of the solid and colour change occurred rapidly and exothermically. The mixture was stirred for additional 30 minutes, then the final solution was concentrated (3 mL), layered with pentane (15 mL) and stored at  $-20^\circ C$ . The product was obtained as a solid after 48 ÷ 72 hours. In a different experiment,  $MX_5$  (0.50 mmol) was introduced into a NMR tube, hence  $CDCl_3$  (0.85 mL) and epoxide (1.50 mmol) were added in the order given. The  $^1H$  NMR analysis was performed once the solid dissolved: complete consumption of the epoxide occurred. Afterwards, the mixture was treated with a large excess of  $H_2O$  (ca. 20 mmol): precipitation of a white solid took place nearly instantaneously. The content of the resulting solution was determined by means of  $^1H$  and  $^{13}C$  NMR spectroscopies, and by GC-MS analysis.

**2a**: orange, from  $NbCl_5$  and 1,2-epoxybutane. Anal. Calc. for  $C_{24}H_{48}Cl_{10}Nb_2O_6$ : C 29.63, H 4.97, Nb 19.10, Cl 14.58. Found C 29.44, H 5.06, Nb 18.90, Cl 14.19 % [28]. Yield: 0.312 g, 64%.  $^1H$  NMR ( $CDCl_3$ )  $\delta = 5.05 \div 4.81$  (m-br, 6 H, CH);  $4.74 \div 3.82$  (m-br, 12 H,  $ClCH_2$ ); 1.95, 1.90, 1.63 (m-br, 12 H,  $CH_2CH_3$ ); 1.06 (m-br, 18 H,  $CH_3$ ) ppm.  $^{13}C$  NMR ( $CDCl_3$ )  $\delta = 63.4, 62.8$  [ $(CH)_{terminal}$  and  $(CH)_{bridging}$ ]; 46.3, 45.2 [ $(ClCH_2)_{terminal}$  and  $(ClCH_2)_{bridging}$ ]; 27.9, 26.9 [ $(CH_2CH_3)_{terminal}$  and  $(CH_2CH_3)_{bridging}$ ]; 10.9 ( $CH_3$ ) ppm. IR (solid state):  $\nu = 2975w-m, 1448m, 1378m, 1051s, 903s, 783vs\ cm^{-1}$ . Hydrolysis (entry 1, Table 2): 1-chloro-2-butanol, 1,2-dichlorobutane, 1-chloro-2-butene (NMR and GC-MS); ratio 4:2:1 ( $^1H$  NMR).

**2b**: orange, from NbCl<sub>5</sub> and styrene oxide. Anal. Calc. for C<sub>48</sub>H<sub>48</sub>Cl<sub>10</sub>Nb<sub>2</sub>O<sub>6</sub>: C 45.71, H 3.84, Nb 14.73, Cl 11.24. Found C 45.66, H 3.97, Nb 14.43, Cl 11.01 % [28]. Yield: 0.366 g, 58%. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ = 7.69÷6.89 (br, 30 H, *arom* CH); 5.18 (m-br, 6 H, CHCl); 4.16 (br, 12 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 137.9, 137.2 [(*ipso*-Ph)<sub>bridging and terminal</sub>]; 128.6, 127.4 (*arom* CH); 65.2 (CHCl); 60.7, 59.9 [(CH<sub>2</sub>)<sub>terminal</sub> and (CH<sub>2</sub>)<sub>bridging</sub>] ppm. Hydrolysis (entry 2, Table 2): 2-phenyl-2-chloroethanol (NMR and GC-MS).

**2c**: yellow, from NbCl<sub>5</sub> and 2,3-dimethyl-2,3-epoxybutane. Anal. Calc. for C<sub>36</sub>H<sub>72</sub>Cl<sub>10</sub>Nb<sub>2</sub>O<sub>6</sub>: C 37.89, H 6.36, Nb 16.28, Cl 12.42. Found C 37.77, H 6.19, Nb 16.10, Cl 12.23 % [28]. Yield: 0.337 g, 59%. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ = 1.70 [s, 12 H, (OCMe<sub>2</sub>)<sub>bridging</sub>]; 1.58 [s, 24 H, (OCMe<sub>2</sub>)<sub>terminal</sub>]; 1.27 (s, 36 H, CMe<sub>2</sub>Cl) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 80.7 (OCMe<sub>2</sub>); 75.8, 74.4 [(CMe<sub>2</sub>Cl)<sub>terminal</sub> and (CMe<sub>2</sub>Cl)<sub>bridging</sub>]; 29.1 [(OCMe<sub>2</sub>)<sub>bridging</sub>]; 28.9 [(OCMe<sub>2</sub>)<sub>terminal</sub>]; 25.2, 24.2 [(CMe<sub>2</sub>Cl)<sub>terminal</sub> and CMe<sub>2</sub>Cl]<sub>bridging</sub>] ppm. IR (solid state): ν = 2979w, 2936w, 2886w, 1447wm, 1384m, 1321wm, 1119m, 1097s, 1072s, 1043vs, 977m, 951s, 932vs, 831s, 811m, 674vs, 661s cm<sup>-1</sup>. Hydrolysis (entry 4, Table 2): 2,3-dimethyl-3-chloro-2-butanol, *t*-butylmethylketone (NMR and GC-MS); ratio 5:1 (<sup>1</sup>H NMR).

In a NMR tube, 2,3-dimethyl-2,3-epoxybutane (1.50 mmol) was added to NbCl<sub>5</sub> (0.50 mmol) in CDCl<sub>3</sub> (0.70 mL). An exothermic reaction took place accompanied by gas (HCl) evolution, and the solid quickly dissolved.

**2d**: light yellow, from NbBr<sub>5</sub> and styrene oxide. Anal. Calc. for C<sub>48</sub>H<sub>48</sub>Br<sub>10</sub>Nb<sub>2</sub>O<sub>6</sub>: C 33.80, H 2.84, Nb 10.89, Br 18.74. Found C 33.90, H 2.88, Nb 10.71, Br 18.55 % [28]. Yield: 0.512 g, 60%. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ = 7.69 ÷ 7.25 (br, 30 H, *arom* CH); 5.28 (m-br, 6 H, CHCl); 4.67 (br, 12 H, CH<sub>2</sub>) ppm. Hydrolysis (entry 2, Table 2): 2-phenyl-2-bromoethanol (NMR and GC-MS).

**2e**: yellow, from NbBr<sub>5</sub> and 2,3-dimethyl-2,3-epoxybutane. Anal. Calc. for C<sub>36</sub>H<sub>72</sub>Br<sub>10</sub>Nb<sub>2</sub>O<sub>6</sub>: C 27.27, H 4.58, Nb 11.71, Br 20.16. Found C 27.11, H 4.66, Nb 11.60, Br 19.95 % [28]. Yield: 0.484 g, 61%. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ = 1.84 [s, 12 H (OCMe<sub>2</sub>)<sub>bridging</sub>]; 1.75 [s, 24 H, (OCMe<sub>2</sub>)<sub>terminal</sub>]; 1.36, 1.32 [s, 36 H, (CMe<sub>2</sub>Br)<sub>terminal</sub> and (CMe<sub>2</sub>Br)<sub>bridging</sub>] ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 80.7 (OCMe<sub>2</sub>); 75.8, 74.4 [(CMe<sub>2</sub>Br)<sub>terminal</sub> and (CMe<sub>2</sub>Br)<sub>bridging</sub>]; 29.1 [(OCMe<sub>2</sub>)<sub>bridging</sub>]; 28.9 [(OCMe<sub>2</sub>)<sub>terminal</sub>]; 25.2, 24.2 [(CMe<sub>2</sub>Br)<sub>terminal</sub> and (CMe<sub>2</sub>Br)<sub>bridging</sub>] ppm. IR (solid state): ν = 2979w, 2936w, 2886w, 1447wm, 1384m, 1321wm, 1119m, 1097s, 1072s, 1043vs, 977m, 951s, 932vs, 831s, 811m, 674vs, 661s cm<sup>-1</sup>. Hydrolysis (entry 4, Table 2): 2,3-dimethyl-3-bromo-2-butanol (NMR and GC-MS).

**2f**: dark yellow, from TaCl<sub>5</sub> and 1,2-epoxybutane. Anal. Calc. for C<sub>24</sub>H<sub>48</sub>Cl<sub>10</sub>O<sub>6</sub>Ta<sub>2</sub>: C 25.09, H 4.21, Ta 31.50, Cl 12.34. Found C 25.21, H 4.07, Ta 31.29, Cl 12.12 % [28]. Yield: 0.368 g, 64%. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ = 5.26 ÷ 4.78 (m-br, 6 H, CH); 4.62 ÷ 3.53 (m-br, 12 H, ClCH<sub>2</sub>); 1.95, 1.82, 1.67, 1.54 (m-br, 12 H, CH<sub>2</sub>CH<sub>3</sub>); 1.02 [t, <sup>3</sup>J<sub>HH</sub> = 6.59 Hz, 12 H, (CH<sub>3</sub>)<sub>terminal</sub>]; 0.90 [t, <sup>3</sup>J<sub>HH</sub> = 8.05 Hz, 6 H, (CH<sub>3</sub>)<sub>bridging</sub>] ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 62.9, 62.4 [(CH)<sub>terminal</sub> and (CH)<sub>bridging</sub>]; 46.4, 45.3 [(ClCH<sub>2</sub>)<sub>terminal</sub> and (ClCH<sub>2</sub>)<sub>bridging</sub>]; 27.4, 27.3 [(CH<sub>2</sub>CH<sub>3</sub>)<sub>terminal</sub> and (CH<sub>2</sub>CH<sub>3</sub>)<sub>bridging</sub>]; 10.4 [(CH<sub>3</sub>)<sub>terminal</sub>]; 9.3 [(CH<sub>3</sub>)<sub>bridging</sub>] ppm. Hydrolysis (entry 1, Table 2): 1-chloro-2-butanol, 1,2-dichlorobutane, 1-chloro-2-butene (NMR and GC-MS); ratio 5:2:1 (<sup>1</sup>H NMR).

**2g**: orange, from TaCl<sub>5</sub> and epoxy cyclohexane. Anal. Calc. for C<sub>36</sub>H<sub>60</sub>Cl<sub>10</sub>O<sub>6</sub>Ta<sub>2</sub>: C 33.13, H 4.63, Ta 27.73, Cl 10.86. Found C 33.03, H 4.68, Ta 27.60, Cl 10.61 % [28]. Yield: 0.359 g, 55%. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ = 4.92 (m-br, 6 H, CHCl); 4.22 (m-br, 6 H, OCH); 2.32, 1.74, 1.31 (m-br, 48 H, CH<sub>2</sub>) ppm. IR (solid state): ν = 2944w, 2863w, 1595m, 1448m, 1362m, 1259s, 1205w, 1079s,

1050s, 1023s, 977ms, 794vs, 738s, 666s  $\text{cm}^{-1}$ . Hydrolysis (entry 3, Table 3): 2-chlorocyclohexanol (NMR and GC-MS).

**2h**: light yellow, from  $\text{TaBr}_5$  and ethylene oxide. Anal. Calc. for  $\text{C}_{12}\text{H}_{24}\text{Br}_{10}\text{O}_6\text{Ta}_2$ : C 10.11, H 1.70, Ta 25.39, Br 22.42. Found C 10.13, H 1.66, Ta 25.23, Br 22.19 % [28]. Yield: 0.499 g, 70%. IR (solid state):  $\nu = 2965\text{w}, 2906\text{w}, 1470\text{w-m}, 1434\text{m}, 1414\text{m}, 1368\text{w-m}, 1278\text{m}, 1214\text{w}, 1172\text{m-s}, 1122\text{s}, 1084\text{vs}, 1042\text{s}, 1014\text{vs}, 996\text{m-s}, 934\text{vs}, 861\text{s}, 763\text{m}, 737\text{m}, 697\text{s}, 678\text{vs} \text{ cm}^{-1}$ . Hydrolysis (entry 5, Table 2): 2-bromoethanol (NMR and GC-MS).

#### 4.3. Reactivity of $\text{NbBr}_5$ with 1,2-epoxybutane and epoxy cyclohexane.

*General procedure:* A suspension of  $\text{NbBr}_5$  (1.00 mmol), in  $\text{CDCl}_3$  (0.80 mL) inside a NMR tube, was treated with the appropriate epoxide (3.00 mmol). The tube was sealed, and left at room temperature overnight. Then,  $^1\text{H}$  NMR spectrum revealed that complete consumption of the epoxide had occurred, and formation of a complicated mixture of products had taken place. This mixture was treated with water (*ca.* 30 mmol), resulting in quick formation of a white precipitate. The precipitate was separated from the solution, which was analyzed by both GC-MS and  $^1\text{H}$  NMR. From  $\text{NbBr}_5$  and 1,2-epoxybutane: 1-bromo-2-butene, 1,2-dibromobutane (ratio 1:1). From  $\text{NbBr}_5$  and epoxy cyclohexane: 2-bromo-cyclohexanol, 1,2-dibromocyclohexane (ratio 3:1).

#### 4.4. Preparation of $\text{NbF}_5[\text{O}=\text{C}(\text{Me})(\text{Bu}^t)]$ , **3**.

A suspension of  $\text{NbF}_5$  (0.120 g, 0.639 mmol) in  $\text{CH}_2\text{Cl}_2$  was treated with 2,3-dimethyl-2,3-epoxybutane (0.082 mL, 0.64 mmol). The resulting mixture was stirred for 90 minutes, then the volatile materials were removed *under vacuum*. Compound **3** was obtained as a crystalline white



solid by storing a  $\text{CH}_2\text{Cl}_2$  solution (3 mL), layered with pentane (10 mL), at  $-20^\circ\text{C}$  for one week. Yield: 0.166 g, 90%. Anal. Calc. for  $\text{C}_6\text{H}_{12}\text{F}_5\text{NbO}$ : C 25.02, H 4.20, Nb 32.25. Found C 24.90, H 4.26, Nb 32.11%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 2.84 (s, 3 H, Me); 1.41 (s, 9 H,  $\text{Bu}^t$ ) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 245.6 (CO); 48.5 ( $\text{CMe}_3$ ); 26.7 (Me); 26.2 ( $\text{CMe}_3$ ) ppm.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 145.8 (br, 5 F) ppm. IR (solid state):  $\nu$  = 2979w-m, 2947w, 2881w, 1647s (C=O), 1482m, 1466m, 1404w-m, 1368m, 1293w, 1226w, 1146vs, 1054m, 994m, 923s, 797vs, 684vs  $\text{cm}^{-1}$ . In a different experiment,  $\text{NbF}_5$  (0.55 mmol),  $\text{CDCl}_3$  (0.85 mL) and 2,3-dimethyl-2,3-epoxybutane (0.50 mmol) were added in the order given in a NMR tube and the tube was sealed. The  $^1\text{H}$  NMR spectrum recorded when the solid dissolved (about 2 hours), evidenced the clean formation of **3**. The tube was opened, and an excess of water was introduced (*ca.* 30 mmol). Precipitation of a colourless solid occurred nearly instantaneously. 3,3-dimethyl-2-butanone was recognised in solution by both  $^1\text{H}$  NMR and GC-MS.

The reaction of  $\text{NbF}_5$  (0.05 mmol) with 2,3-dimethyl-2,3-epoxybutane (0.50 mmol), in  $\text{CDCl}_3$  inside a sealed NMR tube, resulted in clean formation of **3**, in admixture with a large quantity of unreacted epoxide (ratio: 1:80 *ca.*). The ratio did not change on heating the solution at  $120^\circ\text{C}$  for 30 minutes.

*4.5. Reactivity of  $\text{MF}_5$  ( $M = \text{Nb}, \text{Ta}$ ) with epoxides (1,2-epoxybutane, styrene oxide, cyclohexene oxide).*

*General procedure:* To a suspension of compound  $\text{MF}_5$  ( $M = \text{Nb}, \text{Ta}$ ; 0.50 mmol) in  $\text{CDCl}_3$  (0.80 mL) inside a NMR tube, the appropriate epoxide was added (0.50 mmol). The tube was sealed, and left at room temperature overnight. Hence,  $^1\text{H}$  NMR spectrum revealed the complete

consumption of the epoxide, and formation of a complicated mixture of unidentifiable products. The tube was opened, then the mixture was treated with a large excess of water (*ca.* 15 mmol), resulting in quick precipitation of a solid from a pale yellow solution. The latter was analyzed by both GC-MS and <sup>1</sup>H NMR. From NbF<sub>5</sub> or TaF<sub>5</sub> and 1,2-epoxybutane (entries 2, 3, Table 3): ethylmethylketone. From TaF<sub>5</sub> and cyclohexene oxide (entry 4, Table 3): 2-fluorocyclohexanol. From TaF<sub>5</sub> and styrene oxide (entry 5, Table 3): benzene, ethoxybenzene (ratio *ca.* 1:1).

#### 4.6. X-ray Crystallographic Study

Crystal data and collection details for [TaBr<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>Br)<sub>2</sub>(μ-OCH<sub>2</sub>CH<sub>2</sub>Br)]<sub>2</sub>, **2h**, are reported in Table 4. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector using *Mo-Kα* radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS) [29]. Structures were solved by direct methods and refined by full-matrix least-squares based on all data using *F*<sup>2</sup> [30]. The asymmetric unit contains only half of the molecule, whereas the second half is generated by an inversion centre. Hydrogen atoms bonded to C-atoms were fixed at calculated positions and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. The bridging –CH<sub>2</sub>CH<sub>2</sub>Br group and a terminal one are disordered. Disordered atomic positions were split and refined using one occupancy parameter per disordered group and restrained to have similar geometries (SAME line in SHELXTL). Similar *U* restraints were applied to the C, Br and O atoms (s.u. 0.003)

Table 4 about here

## 5. Supplementary Material

Crystallographic data of  $[\text{TaBr}_2(\text{OCH}_2\text{CH}_2\text{Br})_2(\mu\text{-OCH}_2\text{CH}_2\text{Br})]_2$ , **2h**, have been deposited with the Cambridge Crystallographic Data Centre, CCDC XXXX. Copies can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax 441223336033; email: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) or WWW: <http://www.ccdc.cam.ac.uk>).

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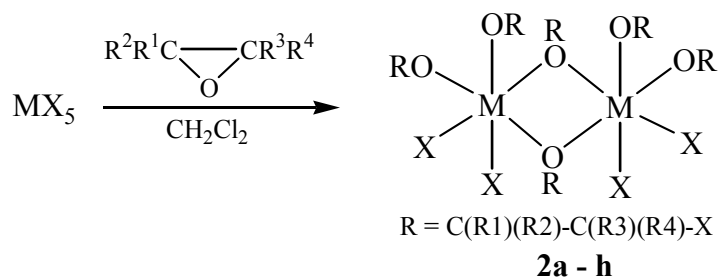
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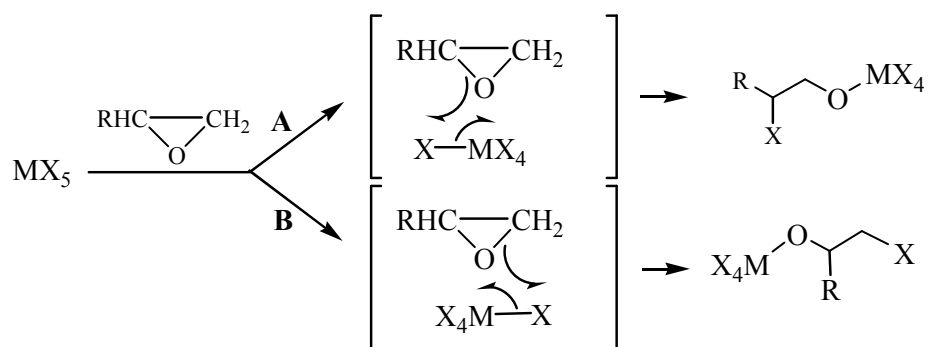
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- [29] G. M. Sheldrick, SADABS, University of Göttingen, Göttingen, Germany.
- [30] G. M. Sheldrick, SHELX97, University of Göttingen, Göttingen, Germany.

Scheme 1. The reactivity of  $\text{MX}_5$  ( $\text{M} = \text{Nb}, \text{Ta}; \text{X} = \text{Cl}, \text{Br}$ ) with epoxides.



Scheme 2. Possible routes of formation of the haloalcoholate fragment.



## Captions for Figures and Tables

- Figure 1. Molecular structure of  $[\text{TaBr}_2(\text{OCH}_2\text{CH}_2\text{Br})_2(\mu\text{-OCH}_2\text{CH}_2\text{Br})_2]$ , **2h**. Thermal ellipsoids are drawn at 30% probability level. Only independent atoms are labelled.
- Table 1. Selected bond distances (Å) and angles (deg) of  $[\text{TaBr}_2(\text{OCH}_2\text{CH}_2\text{Br})_2(\mu\text{-OCH}_2\text{CH}_2\text{Br})_2]$ , **2h**.
- Table 2. Products of hydrolysis of the haloalkoxo derivatives **2a-h**
- Table 3. Reactants and main products (after hydrolysis) of the reactions of  $\text{MF}_5$  with epoxides.
- Table 4. Crystal data and structure refinement for  $[\text{TaBr}_2(\text{OCH}_2\text{CH}_2\text{Br})_2(\mu\text{-OCH}_2\text{CH}_2\text{Br})_2]$ , **2h**.

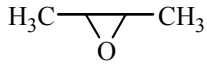
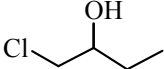
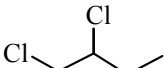
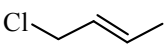
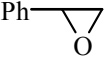
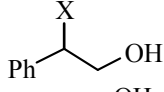
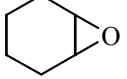
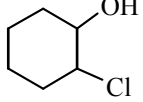
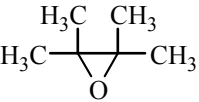
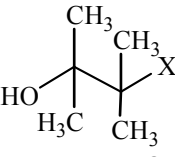

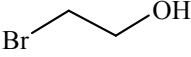


Table 1. Selected bond distances (Å) and angles (deg) of [TaBr<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>Br)<sub>2</sub>( $\mu$ -OCH<sub>2</sub>CH<sub>2</sub>Br)]<sub>2</sub>, **2h**.

Ta(1)–Br(1)	2.459(2)	C(2)–Br(3)	1.97(2)
Ta(1)–Br(2)	2.466(3)	O(2)–C(3)	1.43(2)
Ta(1)–O(1)	2.091(11)	C(3)–C(4)	1.52(3)
Ta(1)–O(1)#1	2.107(10)	C(4)–Br(4)	1.93(2)
Ta(1)–O(2)	1.818(9)	O(3)–C(5)	1.418(19)
Ta(1)–O(3)	1.822(10)	C(5)–C(6)	1.50(2)
O(1)–C(1)	1.50(2)	C(6)–Br(5)	1.950(16)
C(1)–C(2)	1.48(3)		
O(2)–Ta(1)–O(3)	105.8(5)	O(1)–Ta(1)–Br(1)	89.8(3)
O(2)–Ta(1)–O(1)	92.4(4)	O(1)#1–Ta(1)–Br(1)	90.0(3)
O(3)–Ta(1)–O(1)	161.8(4)	O(2)–Ta(1)–Br(2)	88.4(3)
O(2)–Ta(1)–O(1)#1	160.3(4)	O(3)–Ta(1)–Br(2)	91.4(3)
O(3)–Ta(1)–O(1)#1	93.8(4)	O(1)–Ta(1)–Br(2)	89.6(3)
O(1)–Ta(1)–O(1)#1	68.0(5)	O(1)#1–Ta(1)–Br(2)	89.6(3)
O(2)–Ta(1)–Br(1)	91.8(3)	Br(1)–Ta(1)–Br(2)	179.34(8)
O(3)–Ta(1)–Br(1)	89.2(3)	Ta(1)–O(1)–Ta(1)#1	112.0(5)

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

Table 2. Products of hydrolysis of the haloalkoxo derivatives **2a - h**

Entry	Epoxide	Haloalkoxo derivative	Hydrolysis product
1		<b>2a, f</b> <sup>a</sup>	  
2		<b>2b, d</b> <sup>b</sup>	
3		<b>2g</b>	
4		<b>2c, e</b> <sup>b</sup>	
5		<b>2h</b>	

<sup>a</sup> 1,2-dichlorobutane and 1-chloro-2-butene have been detected probably due to the action of HCl, product of the hydrolysis, on 1-chloro-2-butanol.

<sup>b</sup> X = Cl, Br

Table 3. Reactants and main products (after hydrolysis) of the reactions of MF<sub>5</sub> with epoxides.

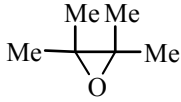
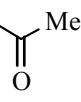
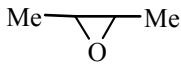

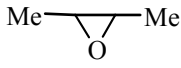

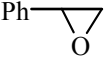
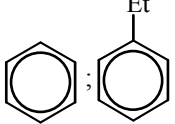
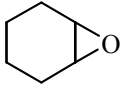
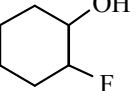
Entry	M	Epoxide	Hydrolysis product
1	Nb		<i>t</i> -But Me 
2	Nb		Et Me 
3	Ta		Et Me 
4	Ta		
5	Ta		

Table 4. Crystal data and experimental details for **2h**.

Complex	<b>2h</b>
Formula	C <sub>12</sub> H <sub>24</sub> Br <sub>10</sub> O <sub>6</sub> Ta <sub>2</sub>
<i>F</i> <sub>w</sub>	1425.31
T, K	100(2)
$\lambda$ , Å	0.71073
Crystal system	Monoclinic
Space group	C2/c
<i>a</i> , Å	12.2223(13)
<i>b</i> , Å	10.4276(12)
<i>c</i> , Å	23.080(3)
$\alpha$ , °	90
$\beta$ , °	95.602(2)
$\gamma$ , °	90
Cell Volume, Å <sup>3</sup>	2927.5(6)
<i>Z</i>	4
<i>D</i> <sub>c</sub> , g cm <sup>-3</sup>	3.234
$\mu$ , mm <sup>-1</sup>	21.144
F(000)	2560
Crystal size, mm	0.17×0.15×0.14
$\theta$ limits, °	2.57–25.03
Reflections collected	13415
Independent reflections	2595 [ <i>R</i> <sub>int</sub> = 0.0379]
Data / restraints / parameters	2595 / 100 / 192
Goodness on fit on F <sup>2</sup>	1.051
<i>R</i> <sub>1</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0561
<i>wR</i> <sub>2</sub> (all data)	0.1835
Largest diff. peak and hole, e Å <sup>-3</sup>	2.569 / -4.554