Polyhedron 28 (2009) 1235-1240

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Epoxide ring opening and insertion into the M–X bond of niobium and tantalum pentahalides: Synthesis of dihalide-*tris*(2-haloalcoholato) complexes

Fabio Marchetti^{a,1}, Guido Pampaloni^{a,*}, Stefano Zacchini^b

^a Università di Pisa, Dipartimento di Chimica e Chimica Industriale, Via Risorgimento 35, I-56126 Pisa, Italy ^b Dipartimento di Chimica Fisica e Inorganica, Università di Bologna, Viale Risorgimento 4, I-40136 Bologna, Italy

ARTICLE INFO

Article history: Received 27 November 2008 Accepted 13 February 2009 Available online 11 March 2009

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

ABSTRACT

The Group 5 pentahalides MX_5 (M = Nb, Ta; X = Cl, Br), **1**, react with a variety of epoxides (1,2-epoxybutane, styrene oxide, 2,3-dimethyl-2,3-epoxybutane, epoxycyclohexane, ethylene oxide) in a 1:3 molar ratio to afford the dinuclear dihalide-*tris*(2-haloalcoholato) complexes $[MX_2(OR)_2(\mu-OR)]_2$ [M = Nb, X = Cl, R = $-CH(Et)CH_2Cl$, **2a**; M = Nb, X = Cl, R = $-CH_2CH(Ph)Cl$, **2b**; M = Nb, X = Cl, R = $-C(Me)_2C(Me)_2Cl$, **2c**; M = Nb, X = Br, R = $-CH_2CH(Ph)Br$, **2d**; M = Nb, X = Br, R = $-C(Me)_2C(Me)_2Br$, **2e**; M = Ta, X = Cl, $-CH(Et)CH_2Cl$, **2f**; M = Ta, X = Cl, $-CH(CH)_2ACHCL$, **2g**; M = Ta, X = Br, R = $-CH_2CH_2Br$, **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, NbF₅ adds one equivalent of 2,3-dimethyl-2,3-epoxybutane to give the monomer NbF₅[O=C(Me)(Bu⁴)], **3**, in high yield, as a result of epoxide to ketone isomerization. The reactions of MF₅ (M = 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.

© 2009 Elsevier Ltd. All rights reserved.

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 opening 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, 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 cleavage [6a] under 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,6d].

In contrast to the chemical behaviour exhibited by THF when reacted 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 or-

der 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 dihalide-*tris*(2-haloalcoholato) complexes. Moreover, alternative reactions of epoxides mediated by MF_{5} , including epoxide to ketone isomerization, will be discussed.

2. Results and discussion

2.1. Reactivity of MX_5 (M = Nb, Ta, X = Cl, Br) with epoxides: synthesis of dihalide-**tris**(2-haloalcoholato) complexes

Dichloromethane suspensions of MX_5 (M = Nb, Ta; X = Cl, Br) react vigorously with epoxides (1:3 molar ratio) to afford the dinuclear compounds $[MX_2(OR)_2(\mu-OR)]_2$ [M = Nb, X = Cl, R = $-CH(Et)CH_2Cl$, **2a**; M = Nb, X = Cl, R = $-CH_2CH(Ph)Cl$, **2b**; M = Nb, X = Cl, R = $-C(Me)_2C(Me)_2Cl$, **2c**; M = Nb, X = Br, R = $-CH_2CH(Ph)Br$, **2d**; M = Nb, X = Br, R = $-C(Me)_2C(Me)_2Br$, **2e**; M = Ta, X = Cl, R = $-CH(Et)CH_2Cl$, **2f**; M = Ta, X = Cl, R = $-CH(CH_2)_4CHCl$, **2g**; M = Ta, X = Br, R = $-CH_2CH_2Br$, **2h**], in 55–70% yield, Scheme 1. On the other hand, the reactions of NbCl₅ with one, two, four and five equivalents of 1,2-epoxybutane, respectively, gave complicated mixtures of products containing mainly **2a**, suggesting that the compounds **2** are the most stable species obtainable by reacting **1** with epoxides, independent of the stoichiometry. Similar conclusions were reached





^{*} Corresponding author. Tel.: +39 50 2219 219; fax: +39 50 2219 246.

E-mail address: pampa@dcci.unipi.it (G. Pampaloni).

¹ Born in Bologna in 1974.

^{0277-5387/\$ -} see front matter \otimes 2009 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2009.02.037



Scheme 1. The reactivity of MX₅ (M = Nb, Ta; X = Cl, Br) with epoxides.

by studying the reactions of NbCl₅ with styrene oxide and epoxycyclohexane (vide infra).

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

The unit cell contains discrete dinuclear $[TaBr_2(OCH_2CH_2Br)_2(\mu-OCH_2CH_2Br)]_2$ 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 haloalcoholates. 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 haloalcoholates [Ta(1)–O(2) 1.818(9) Å; Ta(1)–O(3) 1.822(10) Å].



Fig. 1. Molecular structure of $[TaBr_2(OCH_2CH_2Br)_2(\mu-OCH_2CH_2Br)]_2$, **2h**. Thermal ellipsoids are drawn at the 30% probability level. Only independent atoms are labelled.

Table 1			
Selected bond distance	s (Å) and angles (°) of [TaBr ₂ (OCH ₂ CH ₂	Br)2(µ-OCH2CH2Br)]2,
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.



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

Compounds **2** add to the family of transition metal alcoholato complexes [7], which have found various applications (film-deposition [8], nanotechnology [9], polymerization catalysis [10] and the preparation of materials with notable properties [11]); and in more detail, cases of structurally characterized metal complexes containing 2-haloalcoholates are available in the literature, including both late [12] and early transition [13] metal species.

Regarding niobium(V) and tantalum(V), although examples of pentaalcoholates are numerous [14a-e], only a few mixed halidealcoholates $[MX_n(OR)_{5-n}]_2$ have been crystallographically characterized so far [14f-i]. Complexes **2** belong to this rather uncommon class of compounds [15], and represent the first case of structurally characterized coordination compounds of the heavier Group 5 elements containing halo-substituted alcoholates.

The NMR spectra of **2a**, **c**, **e** and **f** exhibit slightly distinct resonances for the terminal and bridging ligands (see Section 4) [13], and agree with the dinuclear structure $[MX_2(OR)_2(\mu-OR)]_2$. For instance, the methyl units belonging to the OC(Me)₂ moieties in **2c** give rise to resonances at 1.70 (bridging ligands) and 1.58 ppm (terminal) in the ¹H NMR spectrum, and at 29.1 (bridging) and 28.9 ppm (terminal) in the ¹³C NMR spectrum. On the other hand, the ¹H NMR spectra of **2b**, **d** and **g** display only broad resonances, for which discrimination between terminal and bridging ligands has not been possible. In contrast to the previous observations on some niobium or tantalum alkoxides, no dimer–monomer equilibria [13,16] have been detected in solution at room temperature for compounds **2**.²

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.

A careful reading of the 1D and 2D NMR spectra of **2a** and **f** has evidenced the absence of resonances attributable to $-OCH_2$ -CH(Et)Cl units [6c,6d], suggesting that multiple 1,2-epoxybutane insertion into the metal-chloride bonds of MCl₅ (M = Nb, Ta) occurs in a highly regioselective mode (Scheme 2, path B), placing the halide on the less hindered carbon atom.

The NMR spectra of **2b** and **d**, obtained by reacting NbX₅ (X = Cl, Br) with styrene oxide, do not allow, unambiguously, the formation of any of the species obtainable by the two potential modes of insertion to be ruled out (see Scheme 2). Nevertheless, the hydrolysis of CDCl₃ solutions of complexes **2b** and **d**, and subsequent GC–MS and NMR analyses on the organic phase, have pointed out that either **2b** or **2d** contain the [OCH₂CH(Cl)Ph] fragment (entry 2, Table 2). In other words, the insertion of styrene oxide to give **2b** and **d** seems to proceed, differently from the insertion of 1,2epoxybutane, according to path A of Scheme 2, the halide going to the more hindered carbon atom. This feature may be attributable to the steric hindrance of the phenyl ring, which would force this ligand to occupy the farthest position from the metal centre.

 $^{^2\,}$ NMR experiments could not be run on complex **2h**, because of its low solubility in suitable deuterated solvents (CDCl₃, CD₂Cl₂).

Table 2Products of hydrolysis of compounds 2a-h.



^a 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. ^b X = Cl. Br.

The identities of products **2a–h** have been corroborated by combined GC–MS and NMR analyses on concentrated CDCl₃ solutions of these compounds after treatment with H₂O, see Section 4 and Table 2. The addition of water causes the 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 comment: 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 NbCl₅.

With the purpose of extending the series of halo-2-haloalcoholato complexes of type **2**, we studied the reactivity of NbBr₅ with 1,2-epoxybutane and with epoxycyclohexane. 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 NbBr₅ and 1,2-epoxybutane, and of 2-bromocyclohexanol and 1,2-dibromocyclohexane from NbBr₅ and epoxycyclohexane. These results indicate that the reactions of 1,2-epoxybutane and epoxycyclohexane with NbBr₅ proceed *via* epoxide insertions, analogously to that discussed for **2a–h**.

2.2. Reactivity of MF_5 (M = Nb, Ta) with epoxides: isomerisation of 2,3dimethyl-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,6b], and the fluorides often show a chemistry quite different from that of the other halides. Therefore, we decided to investigate the reactivity of MF_5 (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 [17].

Niobium pentafluoride and 2,3-dimethyl-2,3-epoxybutane react to afford the ketone complex NbF₅[$O=C(Me)(^{t}Bu)$], **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 the formation of 3 in an admixture with the unreacted epoxide. Complex 3, which belongs to the restricted family of carbonylic adducts of Group 5 pentahalides [6a], has been characterized spectroscopically (¹H, ¹³C and ¹⁹F NMR, IR) and by GC-MS analysis carried out on the organic material obtained by hydrolysis of **3** (entry 1, Table 3). A salient spectroscopic feature is given by a strong IR absorption at 1647 cm⁻¹, ascribed to the carbon-oxygen double bond (uncoordinated t-butylmethylketone shows the C=O stretching vibration at 1708 cm⁻¹, recorded as a liquid film). The ¹H NMR spectrum displays one set of two resonances, attributed to the methyl unit (s, 2.84 ppm) and the tbutyl group (s, 1.41 ppm). The major ¹³C 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 (δ = 213.81 ppm). Furthermore, the ¹⁹F NMR spectrum shows uniquely a broad resonance at 145.8 ppm, accounting for the five fluorines of the [NbF₅] moiety, and indicating the monomeric, neutral nature of 3.

In contrast to that discussed about the reaction of NbCl₅ with 2,3-dimethyl-2,3-epoxybutane, which affords some *t*-butylmethylketone as result of HCl release and subsequent hydrolysis (vide infra), the formation of *t*-butylmethylketone in the case of NbF₅ 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 valent vanadium [18], cobalt [19], erbium [20], bismuth [21] and lithium [22] compounds.

We tried to extend the chemistry of niobium and tantalum pentafluorides to a series of epoxides (1,2-epoxybutane, styrene oxide and epoxycyclohexane). At variance with that reported

Table 3

Reactants and main products (after hydrolysis) of the reactions of MF_5 with epoxides.

Entry	М	Epoxide	Hydrolysis product
1	Nb	Me Me Me Me O	<i>t</i> -But \bigvee_{O} Me
2	Nb, Ta	Et — V	Et Me
3	Та	Ph-\O	OEt
4	Ta	0	OH F

above about the synthesis of **3**, the reactions of MF_5 with epoxides other than 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 NbF₅ or TaF₅ 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 1, Table 3).

Conversely, no traces of acetophenone and cyclohexanone have been found in the hydrolyzed mixtures generated from the reactions of TaF₅ 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 the main products from the treatment of TaF₅ with styrene oxide followed by hydrolysis (entry 3, Table 3). Furthermore, GC–MS and NMR analyses on a sample obtained by addition of epoxycyclohexane to TaF₅, and successive hydrolysis, revealed the presence of small amounts of 2-fluorocyclohexanol (entry 4, Table 3). All these organics prove that C–C and C–H bond activation, together with C–O and C–F bond formation, are possible processes taking place in the course of the reactions of MF₅ (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 a 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-haloalcoholato ligands. Although MF₅ (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, 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^{-2} mm Hg) and then filled with argon. All the reagents, including MX₅ (M = Nb, Ta, X = Cl; M = Nb, Ta, X = F), were commercial products (Aldrich) of the highest purity available. NbBr₅ and TaBr₅ were prepared according to published procedures [23]. Epoxides were liquid commercial products stored under an argon atmosphere as received. Solvents were distilled before use under an argon atmosphere from appropriate drying agents: CH₂Cl₂ and CDCl₃ from P₄O₁₀, pentane from LiAlH₄.

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 ¹H, ¹³C and ¹⁹F NMR spectra were referenced to TMS and to CFCl₃, respectively. The chemical shifts were assigned *via* DEPT experiments and ¹H, ¹³C correlation through gs-HSQC and gs-HMBC experiments [24]. 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 a 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 the Volhardt method [25] after exhaustive hydrolysis of the sample. Metals were analyzed as M₂O₅, 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 $[MX_2(OR)_2(\mu-OR)]_2$ $[M = Nb, X = Cl, R = -CH(Et)CH_2Cl,$ **2a** $; <math>M = Nb, X = Cl, R = -CH_2CH(Ph)Cl,$ **2b** $; <math>M = Nb, X = Cl, R = -C(Me)_2C(Me)_2Cl,$ **2c** $; <math>M = Nb, X = Br, R = -CH_2CH(Ph)Br,$ **2d**; $M = Nb, X = Br, R = -C(Me)_2C(Me)_2Br,$ **2e** $; <math>M = Ta, X = Cl, R = -CH(Et)CH_2Cl,$ **2f** $; <math>M = Ta, X = Cl, R = -CH(CH_2)_4CHCl,$ **2g** $; <math>M = Ta, X = Br, R = -CH_2CH_2Br,$ **2h**]

General procedure: A suspension of MX₅ (M = Nb, Ta; X = Cl, Br; 1.00 mmol), in CH₂Cl₂ (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 a colour change occurred rapidly and exothermically. The mixture was stirred for an additional 30 min, then the final solution was concentrated (3 mL), layered with pentane (15 mL) and stored at -20 °C. The product was obtained as a solid after 48–72 h. In a different experiment, MX₅ (0.50 mmol) was introduced into a NMR tube, then CDCl₃ (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 colourless solid took place nearly instantaneously. The content of the resulting solution was determined by means of ¹H and ¹³C NMR spectroscopies, and by GC-MS analysis.

2a: orange, from NbCl₅ and 1,2-epoxybutane. *Anal.* Calc. for $C_{24}H_{48}Cl_{10}Nb_2O_6^{-3}$: 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%. Yield: 0.312 g, 64%. ¹H NMR (CDCl₃) δ = 5.05–4.81 (m-br, 6H, CH); 4.74–3.82 (m-br, 12H, ClCH₂); 1.95, 1.90, 1.63 (m-br, 12H, CH₂CH₃); 1.06 (m-br, 18H, CH₃) ppm. ¹³C NMR (CDCl₃) δ = 63.4, 62.8 [(CH)_{terminal} and (CH)_{bridging}]; 46.3, 45.2 [(ClCH₂)_{terminal} and (ClCH₂)_{bridging}]; 27.9, 26.9 [(CH₂CH₃)_{terminal} and (CH₂CH₃)_{bridging}]; 10.9 (CH₃) ppm. IR (solid state): *v* = 2975w-m, 1448 m, 1378 m, 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 NbCl₅ and styrene oxide. *Anal.* Calc. for $C_{48}H_{48}Cl_{10}Nb_2O_6^{-3}$: 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%. Yield: 0.366 g, 58%. ¹H NMR (CDCl₃) δ = 7.69–6.89 (br, 30H, *arom* CH); 5.18 (m-br, 6H, CHCl); 4.16 (br, 12H, CH₂) ppm. ¹³C NMR (CDCl₃) δ = 137.9, 137.2 [(*ipso*-Ph)_{bridging and terminal}]; 128.6, 127.4 (*arom* CH); 65.2 (CHCl); 60.7, 59.9 [(CH₂)_{terminal} and (CH₂)_{bridging}] ppm. Hydrolysis (entry 2, Table 2): 2-phenyl-2-chloroethanol (NMR and GC–MS).

2c: yellow, from NbCl₅ and 2,3-dimethyl-2,3-epoxybutane. *Anal.* Calc. for $C_{36}H_{72}Cl_{10}Nb_2O_6^3$: 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%. Yield: 0.337 g, 59%. ¹H NMR (CDCl₃) δ = 1.70 [s, 12H, (OCMe₂)_{bridging}]; 1.58 [s, 24H, (OCMe₂)_{terminal}]; 1.27 (s, 36H, CMe₂Cl) ppm. ¹³C NMR (CDCl₃) δ = 80.7 (OCMe₂); 75.8, 74.4 [(CMe₂Cl)_{terminal} and (CMe₂Cl)_{bridging}]; 29.1 [(OCMe₂)_{bridging}]; 28.9 [(OCMe₂)_{terminal}]; 25.2, 24.2 [(CMe₂Cl)_{terminal} and CMe₂Cl)_{bridging}] ppm. IR (solid state):

 $^{^3}$ Due to the fact that the carbon-bonded halide does not precipitate with silver nitrate under the conditions used for the analysis, the halide content refers to the metal-bonded halide ion.

v = 2979w, 2936w, 2886w, 1447wm, 1384m, 1321wm, 1119m, 1097s, 1072s, 1043vs, 977m, 951s, 932vs, 831s, 811m, 674vs, 661s cm⁻¹. Hydrolysis (entry 4, Table 2): 2,3-dimethyl-3-chloro-2-butanol, *t*-butylmethylketone (NMR and GC–MS); ratio 5:1 (¹H NMR).

In a NMR tube, 2,3-dimethyl-2,3-epoxybutane (1.50 mmol) was added to NbCl₅ (0.50 mmol) in CDCl₃ (0.70 mL). An exothermic reaction took place accompanied by gas (HCl) evolution, and the solid quickly dissolved.

2d: light yellow, from NbBr₅ and styrene oxide. *Anal.* Calc. for $C_{48}H_{48}Br_{10}Nb_2O_6^{3}$: 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%. Yield: 0.512 g, 60%. ¹H NMR (CDCl₃) δ = 7.69–7.25 (br, 30H, *arom* CH); 5.28 (m-br, 6H, CHCl); 4.67 (br, 12H, CH₂) ppm. Hydrolysis (entry 2, Table 2): 2-phenyl-2-bromoethanol (NMR and GC–MS).

2e: yellow, from NbBr₅ and 2,3-dimethyl-2,3-epoxybutane. *Anal.* Calc. for $C_{36}H_{72}Br_{10}Nb_2O_6^{3:}$ 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%. Yield: 0.484 g, 61%. ¹H NMR (CDCl₃) δ = 1.84 [s, 12H (OCMe₂)_{bridging}]; 1.75 [s, 24H, (OCMe₂)_{terminal}]; 1.36, 1.32 [s, 36H, (CMe₂Br)_{terminal} and (CMe₂Br)_{bridging}] ppm. ¹³C NMR (CDCl₃) δ = 80.7 (OCMe₂); 75.8, 74.4 [(CMe₂Br)_{terminal} and (CMe₂Br)_{bridging}]; 28.9 [(OCMe₂)_{terminal}]; 25.2, 24.2 [(CMe₂Br)_{terminal} and CMe₂Br)_{bridging}] ppm. IR (solid state): v = 2979w, 2936w, 2886w, 1447wm, 1384m, 1321wm, 1119m, 1097s, 1072s, 1043vs, 977m, 951s, 932vs, 831s, 811m, 674vs, 661s cm⁻¹. Hydrolysis (entry 4, Table 2): 2,3-dimethyl-3-bromo-2-butanol (NMR and GC–MS).

2f: dark yellow, from TaCl₅ and 1,2-epoxybutane. *Anal.* Calc. for $C_{24}H_{48}Cl_{10}O_6Ta_2^{-3}$: 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%. Yield: 0.368 g, 64%. ¹H NMR (CDCl₃) δ = 5.26–4.78 (m-br, 6H, CH); 4.62–3.53 (m-br, 12H, ClCH₂); 1.95, 1.82, 1.67, 1.54 (m-br, 12H, CH₂CH₃); 1.02 [t, ³J_{HH} = 6.59 Hz, 12 H, (CH₃)_{terminal}]; 0.90 [t, ³J_{HH} = 8.05 Hz, 6 H, (CH₃)_{bridging}] ppm. ¹³C NMR (CDCl₃) δ = 62.9, 62.4 [(CH)_{terminal} and (CH)_{bridging}]; 46.4, 45.3 [(ClCH₂)_{terminal} and (CH₂)_{bridging}]; 27.4, 27.3 [(CH₂CH₃)_{terminal} and (CH₂CH₃)_{bridging}] 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 (¹H NMR).

2g: orange, from TaCl₅ and epoxycyclohexane. *Anal.* Calc. for $C_{36}H_{60}Cl_{10}O_6Ta_2^{-3}$: 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%. Yield: 0.359 g, 55%. ¹H NMR (CDCl₃) δ = 4.92 (m-br, 6H, CHCl); 4.22 (m-br, 6H, OCH); 2.32, 1.74, 1.31 (m-br, 48H, CH₂) ppm. IR (solid state): *v* = 2944w, 2863w, 1595m, 1448m, 1362m, 1259s, 1205w, 1079s, 1050s, 1023s, 977ms, 794vs, 738s, 666s cm⁻¹. Hydrolysis (entry 3, Table 3): 2-chlorocyclohexanol (NMR and GC–MS).

2h: light yellow, from TaBr₅ and ethylene oxide. *Anal.* Calc. for $C_{12}H_{24}Br_{10}O_6Ta_2^{3}$: 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%. Yield: 0.499 g, 70%. IR (solid state): v = 2965w, 2906w, 1470w-m, 1434m, 1414m, 1368w-m, 1278m, 1214w, 1172m-s, 1122s, 1084vs, 1042s, 1014vs, 996m-s, 934vs, 861s, 763m, 737m, 697s, 678vs cm⁻¹. Hydrolysis (entry 5, Table 2): 2-bromoethanol (NMR and GC–MS).

4.3. Reactivity of NbBr₅ with 1,2-epoxybutane and epoxycyclohexane

General procedure: A suspension of NbBr₅ (1.00 mmol), in CDCl₃ (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, a ¹H 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 solu-

tion, which was analyzed by both GC–MS and ¹H NMR. From NbBr₅ and 1,2-epoxybutane: 1-bromo-2-butene, 1,2-dibromobutane (ratio 1:1). From NbBr₅ and epoxycyclohexane: 2-bromocyclohexanol, 1,2-dibromocyclohexane (ratio 3:1).

4.4. Preparation of $NbF_5[O=C(Me)(Bu^t)]$, 3

A suspension of NbF₅ (0.120 g, 0.639 mmol) in CH₂Cl₂ was treated with 2,3-dimethyl-2,3-epoxybutane (0.082 mL, 0.64 mmol). The resulting mixture was stirred for 90 min, then the volatile materials were removed under vacuum. Compound 3 was obtained as a crystalline colourless solid by storing a CH₂Cl₂ solution (3 mL), layered with pentane (10 mL), at $-20 \degree$ C for one week. Yield: 0.166 g, 90%. Anal. Calc. for C₆H₁₂F₅NbO: C, 25.02; H, 4.20; Nb, 32.25. Found: C, 24.90; H, 4.26; Nb, 32.11%. ¹H NMR (CDCl₃) $\delta = 2.84$ (s, 3H, Me); 1.41 (s, 9H, Bu^t) ppm. ¹³C NMR (CDCl₃) δ = 245.6 (CO); 48.5 (CMe₃); 26.7 (Me); 26.2 (CMe₃) ppm. ¹⁹F NMR (CDCl₃) δ = 145.8 (br, 5F) ppm. IR (solid state): v = 2979wm, 2947w, 2881w, 1647s (C=O), 1482m, 1466m, 1404w-m, 1368m, 1293w, 1226w, 1146vs, 1054m, 994m, 923s, 797vs, 684vs cm⁻¹. In a different experiment, NbF₅ (0.55 mmol), CDCl₃ (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 ¹H NMR spectrum, recorded when the solid dissolved (about 2 h), 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 recognized in solution by both ¹H NMR and GC-MS.

The reaction of NbF₅ (0.05 mmol) with 2,3-dimethyl-2,3-epoxybutane (0.50 mmol), in CDCl₃ inside a sealed NMR tube, resulted in the clean formation of **3**, in an admixture with a large quantity of unreacted epoxide (ratio: 1:80 *ca*.). The ratio did not change on heating the solution at 120 °C for 30 min.

4.5. Reactivity of MF_5 (M = Nb, Ta) with epoxides (1,2-epoxybutane, styrene oxide, cyclohexene oxide)

General procedure: To a suspension of compound MF_5 (M = Nb, Ta; 0.50 mmol) in CDCl₃ (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. A ¹H NMR spectrum revealed the complete consumption of the epoxide and the 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 the quick precipitation of a solid from the pale yellow solution. The latter was analyzed by both GC–MS and ¹H NMR. From NbF₅ or TaF₅ and 1,2-epoxybutane (entry 2, Table 3): ethylmethylketone. From TaF₅ and cyclohexene oxide (entry 3, Table 3): 2-fluorocyclohexanol. From TaF₅ and styrene oxide (entry 4, Table 3): benzene, ethoxybenzene (ratio *ca.* 1:1).

4.6. X-ray crystallographic study

Crystal data and collection details for $[TaBr_2(OCH_2CH_2Br)_2(\mu-OCH_2CH_2Br)]_2$, **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 K α radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS) [26]. The structure was solved by direct methods and refined by full-matrix least-squares based on all data using F^2 [27]. 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.

Та	ble	4
	~~~	-

Crystal data and experimental details for 2h.

Complex	2h
Formula	
	1425 21
	1425.31
I (K)	100(2)
λ(A)	0.71073
Crystal system	monoclinic
Space group	C2/c
a (Å)	12.2223(13)
b (Å)	10.4276(12)
<i>c</i> (Å)	23.080(3)
α (°)	90
$\beta$ (°)	95.602(2)
γ (°)	90
Cell volume (Å ³ )	2927.5(6)
Ζ	4
$D_{\text{calc}}$ , g cm ⁻³	3.234
$\mu (\mathrm{mm}^{-1})$	21.144
F(000)	2560
Crystal size (mm)	$0.17 \times 0.15 \times 0.14$
$\theta$ limits (°)	2.57-25.03
Reflections collected	13415
Independent reflections [R _{int} ]	2595 [0.0379]
Data/restraints/parameters	2595/100/192
Goodness on fit on $F^2$	1.051
$R_1 (I > 2\sigma(I))$	0.0561
$wR_2$ (all data)	0.1835
Largest difference in peak and hole (e $Å^{-3}$ )	2.569/-4.554

The bridging –CH₂CH₂Br 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.

#### Supplementary data

CCDC 710805 contains the supplementary crystallographic data for  $[TaBr_2(OCH_2CH_2Br)_2(\mu-OCH_2CH_2Br)]_2$ , **2h**. 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.

#### Acknowledgments

The authors wish to thank the Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR, Roma), Programmi di Ricerca Scientifica di Notevole Interesse Nazionale, Cofinanziamento 2004–2005, and the Consiglio Nazionale delle Ricerche (C.N.R.) Progetto CNR-MIUR "Sviluppo di microcelle a combustibile", for financial support.

#### References

- [1] (a) Y. Shichijo, A. Migita, H. Oguri, M. Watanabe, T. Tokiwano, K. Watanabe, H. Oikawa, J. Am. Chem. Soc. 130 (2008) 12230;
- (b) J. Justicia, A.G. Campaña, B. Bazdi, R. Robles, J.M. Cuerva, J.E. Oltra, Adv. Synth. Catal. 350 (2008) 571.
- [2] H.S. Park, D.W. Kwon, K. Lee, Y.H. Kim, Tetrahedron Lett. 49 (2008) 1616.
- [3] (a) T. Ollevier, E. Nadeau, Tetrahedron Lett. 49 (2008) 1546;
- (b) M. Curini, F. Epifano, M.C. Marcotullio, O. Rosati, Eur. J. Org. Chem. 21 (2001) 4149.
- [4] (a) A. Gansäuer, A. Barchuk, F. Keller, M. Schmitt, S. Grimme, M. Gerenkamp, C. Mück-Lichtenfeld, K. Daasbjerg, H. Svith, J. Am. Chem. Soc. 129 (2007) 1359; (b) A.W. Eppley, N.I. Totah, Tetrahedron 53 (1997) 16545;
  - (c) K. Fujiwara, T. Tokiwano, A. Murai, Tetrahedron Lett. 36 (1995) 8063;
  - (d) M. Emziane, P. Lhoste, D. Sinou, J. Mol. Catal. 49 (1988) L23;
  - (e) A.E. Vougioukas, H.B. Kagan, Tetrahedron Lett. 28 (1987) 6065.
- [5] The fluorides of niobium(V) and tantalum(V) have tetranuclear structures in
- the solid state, while the corresponding heavier halides are dinuclear in the solid state and mononuclear in the vapour phase A.F. Wells, Structural

Inorganic Chemistry, 5th Ed., Clarendon Press, Oxford, 1993. For the sake of simplicity, in this paper the general formula MX₅, when dealing with the niobium(V) and tantalum(V) halides, will be used.

- [6] (a) F. Marchetti, G. Pampaloni, S. Zacchini, Dalton Trans. (2007) 4343;
  - (b) F. Marchetti, G. Pampaloni, S. Zacchini, Inorg. Chem. 47 (2008) 365; (c) F. Marchetti, G. Pampaloni, S. Zacchini, Chem. Commun. (2008) 3651;
  - (d) F. Marchetti, G. Pampaloni, S. Zacchini, Dalton Trans. (2008) 7026;
  - (e) F. Marchetti, G. Pampaloni, S. Zacchini, Polyhedron 27 (2008) 1969;
  - (f) F. Marchetti, G. Pampaloni, S. Zacchini, Eur. J. Inorg. Chem. (2008) 453;
  - (g) F. Marchetti, G. Pampaloni, T. Repo, Eur. J. Inorg. Chem. (2008) 2107.
- [7] (a) As general references see: J.A. McCleverty, T.J. Meyer (Eds.), Comprehensive Coordination Chemistry II, Elsevier Pergamon, London, 2005; (b) A. Singh, R.C. Mehrotra, Coord. Chem. Rev. 248 (2004) 101.
- (a) N. Huesing, B. Launay, G. Kickelbick, S. Gross, L. Armelao, G. Bottaro, M.P. [8] Feth, H. Bertagnolli, G. Kothleitner, Appl. Catal. A 254 (2003) 297 (b) T.J. Boyle, T.M. Alam, D. Dimos, G.J. Moore, C.D. Buchheit, H.N. Al-Shareef, E.R. Mechenbier, B.R. Bear, J.W. Ziller, Chem. Mater. 9 (1997) 3187; (c) P.A. Shcheglov, D.V. Drobot, G.A. Seisenbaeva, S. Gohil, V.G. Kessler, Chem. Mater. 14 (2002) 2378.
- [9] (a) J.H. Jung, T. Shimizu, S. Shinkai, J. Mater. Chem. 15 (2005) 3979; (b) M. Niederberger, N. Pinna, J. Polleux, M. Antonietti, Angew. Chem., Int. Ed.
- 43 (2004) 2270. [10] (a) Some recent references are: E.C.E. Rosenthal, H. Cui, J. Koch, ACS Symp. Ser.
  - 974 (2007) 70; (b) T. Gueta-Neyroud, B. Tumanskii, M. Kapon, M.S. Eisen, Macromolecules 40
    - (2007) 5261; (c) J. Yamada, K. Nomura, Organometallics 24 (2005) 3621;
    - (d) E.C.E. Rosenthal, H. Cui, J. Koch, P. Escarpa Gaede, M. Hummert, S. Dechert,
    - J. Chem. Soc., Dalton Trans. (2005) 3108;
    - (e) A.V. Grafov, C.L. Firme, I.A. Grafova, F. Benetollo, M.L. Dias, M.J.M. Abadie, Polymer 46 (2005) 9626;
  - (f) B. Lian, Y. Qian, W. Zhou, J. Huang, Appl. Organomet. Chem. 19 (2005) 621; (g) E.C.E. Rosenthal, H. Cui, K.C.H. Lange, S. Dechert, Eur. J. Inorg. Chem. (2004) 4681
  - (h) Z. Janas, L.B. Jerzykiewicz, K. Przybylak, P. Sobota, K. Szczegot, Eur. J. Inorg. Chem. (2004) 1639.
- [11] (a) U. Schubert, Acc. Chem. Res. 40 (2007) 730;
- (b) G.J.deA.A. Soler-Illia, C. Sanchez, New J. Chem. 24 (2000) 493; (c) J.H. Thurston, K.H. Whitmire, Inorg. Chem. 41 (2002) 4194.
- [12] R.M. Trend, B.M. Stoltz, J. Am. Chem. Soc. 126 (2004) 4482.
- (a) A. Decken, G.B. Nikiforov, J. Passmore, Dalton Trans. (2006) 4328; (b) F. Wolff, R. Choukroun, C. Lorber, B. Donnadieu, Eur. J. Inorg. Chem. (2003) 628;
  - (c) Y. Li, A. Turnas, J.T. Ciszewski, A.L. Odom, Inorg. Chem. 41 (2002) 6298;
  - (d) T. Carofiglio, P.G. Cozzi, C. Floriani, A. Chiesi-Villa, C. Rizzoli, Organometallics 12 (1993) 2726;
  - (e) D.C. Bradley, H. Chudzynska, M.E. Hammond, M.B. Hursthouse, M. Motevalli, W. Rouwen, Polyhedron 11 (1992) 375;
  - (f) C.H. Winter, P.H. Sheridan, M.J. Heeg, Inorg. Chem. 30 (1991) 1962.
- [14] (a) A.A. Pinkerton, D. Schwarzenbach, L.G. Hubert-Pfalzgraf, J.G. Riess, Inorg.
  - Chem. 15 (1976) 1196;
  - (b) L.N. Lewis, M.F. Garbauskas, Inorg. Chem. 24 (1985) 363;
  - (c) R.N. Kapoor, F. Cervantes-Lee, C.F. Campana, C. Haltiwanger, K. Abney, K.H. Pannell, Inorg. Chem. 45 (2006) 2203:
  - (d) S.C. Goel, J.A. Hollingsworth, A.M. Beatty, K.D. Robinson, W.E. Buhro, Polyhedron 17 (1998) 781;
  - (e) R. Wang, K. Folting, J.C. Huffman, L.R. Chamberlain, I.P. Rotwell, Inorg. Chim. Acta 120 (1986) 81;
  - (f) J.R. Clark, A.L. Pulvirenti, P.E. Fanwick, M. Sigalas, O. Eisenstein, I.P. Rothwell, Inorg. Chem. 36 (1997) 3623;
  - (g) T. Matsuo, H. Kawaguchi, Inorg. Chem. 41 (2002) 6090;
  - (h) H. Kawaguchi, T. Matsuo, J. Organomet. Chem. 690 (2005) 5333;
  - (i) C. Redshaw, D.M. Homden, M.A. Rowan, M.R.J. Elsegood, Inorg. Chim. Acta 358 (2005) 4067.
- [15] Niobium(V) fluoroalkoxides have been reported as being obtained from the reaction of NbOCl3 and the corresponding fluoroalcohols L.G. Hubert-Pfalzgraf, I.G. Riess, Inorg. Chim. Acta 41 (1980) 111.
- [16] D.C. Bradley, C.E. Holloway, J. Chem. Soc. (A) (1968) 219.
  [17] J.E. Huheey, E.A. Keiter, R.L. Keiter, Inorganic Chemistry, 4th Ed., Principles of Structure and Reactivity, Harper and Collins College Publisher, New York, 1993.
- [18] F. Martinez, C. del Campo, E.F. Llama, J. Chem. Soc., Perkin 1 (2000) 1749.
- [19] J.-Y. Kim, T. Kwan, Chem. Pharm. Bull. 18 (1970) 1040.
- [20] A. Procopio, R. Dalpozzo, A. De Nino, M. Nardi, G. Sindona, A. Tagarelli, Synlett 14 (2004) 2633
- [21] A.M. Anderson, J.M. Blazek, P. Garg, B.J. Payne, R.S. Mohan, Tetrahedron Lett. 41 (2000) 1527.
- [22] B. Rickborn, R.M. Gerkin, J. Am. Chem. Soc. 93 (1971) 1693.
- [23] F. Calderazzo, P. Pallavicini, G. Pampaloni, P.F. Zanazzi, J. Chem. Soc., Dalton Trans. (1990) 2743.
- [24] W. Wilker, D. Leibfritz, R. Kerssebaum, W. Bermel, Magn. Reson. Chem. 31 (1993) 287.
- [25] D.A. Skoog, D.M. West, Fundamentals of Analytical Chemistry, 2nd Ed., Holt, Rinehart and Winston, Chatham, UK, 1974. p. 233.
- [26] G.M. Sheldrick, SADABS, University of Göttingen, Göttingen, Germany.
- [27] G.M. Sheldrick, SHELX97, University of Gottingen, Göttingen, Germany.