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Structures and Unusual Rearrangements of Coordination Adducts of MX_5 (M = Nb, Ta; X = F, Cl) with Simple Diethers. A Crystallographic, Spectroscopic, and Computational Study

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High-yield reactions of the pentafluoride complexes MF_5 (M=Nb, Ta) with a variety of diethers, $ROCH_2CH(R')OR''$, afford the ionic derivatives $[MF_4\{\kappa^2\text{-}ROCH_2CH(R')OR''\}_2][MF_6]$ (**2a**−**2e**) or $[MF_4\{ROCH_2CH(R')OR''\}_2][M_2F_{11}]$ (**3a**−**3f**) according to the metal/diether ratio employed. The structures of $[MF_4(\kappa^2\text{-dme})_2][MF_6]$ [M=Nb (**2a**), Ta (**2b**); dme=$MeOCH_2CH_2OMe$] have been determined by X-ray diffraction. Moreover, the structure of the cationic part of **2a** in the gas phase has been optimized by density functional theory calculations (the B3LYP/LANL2DZ method). An analogous computational study has allowed one to predict the existence of a heptacoordinated niobium cation within the species $[NbCl_4(dme)_2][NbCl_6]$. This prediction has been confirmed by NMR identification at −60 °C of the complexes $[MCl_4(\kappa^2\text{-dme})(\kappa^1\text{-dme})][MCl_6]$ [M=Nb (**4a**), Ta (**4b**)], obtained by the addition of dme to MCl_5 in $CDCl_3$. Activation of the coordinated diether in **2** and **3** takes place in solution at high temperature and generally proceeds via cleavage of C−O bonds and coupling of the fragments produced. Thus, OR_2 (R=Me, Et) and 1,4-dioxane have been obtained selectively upon thermal reaction of MF_5 with dme, diglyme, or 1,2-diethoxyethane, followed by treatment with water. In analogous conditions, 1,2-dimethoxypropane converts mainly into acetone and dimethyl ether. The formation of dioxane from dme occurs in high yield also by using a catalytic amount of NbF_5. The activation of dme by NbF_5 follows a pathway different from that previously reported for $NbCl_5$, and an explanation based on the thermodynamic parameters calculated at the B3LYP/LANL2DZ level is given: the formation of Me_2O and dioxane is the most favored reaction between NbF_5 and dme ($\Delta G_r° = -15.16\ \text{kcal}\cdot\text{mol}_{Nb}^{-1}$), while the formation of MeCl and dioxane is the most favored reaction in the case of $NbCl_5$/dme ($\Delta G_r° = -53.13\ \text{kcal}\cdot\text{mol}_{Nb}^{-1}$).

Introduction

The use of early-transition-metal halides for synthetic purposes has been the object of extraordinary interest, and the alkene polymerization reactions promoted by derivatives of group 4 metal halides have definitely become a fundamental issue of modern organometallic chemistry.[1] Recent and relevant examples of metal-mediated organic syntheses include the use of Lewis acids[2] such as the homoleptic halides of titanium,[3] zirconium,[4] hafnium,[5] and group 6[6] metals. In this context, the use of the pentahalides of the heavier group

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5 metals, MX_5 [M = Nb, X = F (**1a**); M = Ta, X = F (**1b**); M = Nb, X = Cl (**1c**); M = Ta, X = Cl (**1d**)],[7] appears more circumscribed, even though niobium and tantalum are essentially disposable[8] and are considered biocompatible elements.[9] However, an increasing interest in the employment of **1c** and **1d** in synthetic chemistry[6e,10] has grown up in the past decade because of the fact that these compounds show in some cases unusual and striking behavior, compared to other early-transition-metal halides.[6e,11] Otherwise, a restricted number of reactions mediated by the pentafluorides **1a** and **1b** have been reported in the literature,[12] and the group 5 pentabromides and pentaiodides have been even less studied[13] probably because of their reduced availability due to difficulties concerning the preparation and storage.[14]

The relatively limited exploitation of **1** in catalysis reflects the scarce information available on the coordination chemistry of these oxophilic compounds, especially with respect to oxygen-containing substrates.[15] In this framework, we have spent the very last years on investigating the reactivity of **1** with potential O-donor ligands. Thus, we have found that the reactions of **1** with limited amounts of O donors lead to simple coordination adducts, which, under appropriate conditions, may evolve as result of C−Y bond activation (Y = H, O).[15,16] The outcomes of these reactions are strictly related to the nature of the halide, while the metal (niobium or tantalum) does not seem to play a crucial role. More remarkably, we have reported that the reactions of MCl_5 (M = Nb, Ta) with simple bifunctional O donors (i.e., esters,[17] acetals and ketals,[18] and 1,2-dialkoxyalkanes[16c,19]) may proceed unusually, giving noticeable transformations. As a pertinent example, the room temperature reaction of **1c** and **1d** with a 2-fold excess of 1,2-dimethoxyethane (dme) leads to selective conversion into 1,4-dioxane.[16c,19] Such a result is interesting from the point of view that dioxane formation requires the establishment of new C−O bonds, other than C−O cleavages. This is not trivial because the activation of dme by means of oxophilic metal derivatives, including group 4 tetrahalides, generally consists of breaking down into smaller fragments, and no C−O bond formation is observed.[19]

Considering the interesting features shown by the reactions of simple diethers with MCl_5 (M = Nb, Ta), we moved to explore the analogous chemistry of the pentafluorides **1a** and **1b**, which were expected to exhibit different behavior (see above). The study has focused on diethers of the type $ROCH_2CH(R')OR''$ and intends to expand the knowledge on the role possibly played by MF_5 (M = Nb, Ta) in organic reactions, with the aim of contributing to the development of the use of these oxygen-affine materials in metal-directed syntheses. The experimental investigations, driven by density functional theory (DFT) calculations, have been extended to some aspects of the chemistry of the metal chlorides **1c** and **1d** with dme. The results of these studies will be presented in the following.

Experimental Section

General Considerations. All manipulations of air- and/or moisture-sensitive compounds were performed under an atmosphere of prepurified 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. Commercial (Aldrich) MX_5 [M = Nb, X = F (**1a**); M = Ta, X = F (**1b**); M = Nb, X = Cl (**1c**); M = Ta, X = Cl (**1d**)] compounds were transferred into vials and sealed under an argon atmosphere as received. CH_2Cl_2, $CHCl_3$, CD_2Cl_2, $CDCl_3$, and $MeOCH_2CH_2OCH_2Cl$ were distilled from P_4O_{10} under an argon atmosphere before use, $MeO(CH_2)_2OMe$ (dme), $MeOCH_2CH(Me)OMe$, and $EtO(CH_2)_2OEt$ were distilled from sodium, while pentane was distilled from $LiAlH_4$. $MeO(CH_2)_2O(CH_2)_2OMe$ (diglyme) was distilled from sodium at reduced pressure. IR spectra were recorded at 298 K on a Fourier transform IR Perkin-Elmer spectrometer, equipped with a UATR sampling accessory. Unless otherwise specified, ^1H and ^{13}C NMR measurements were recorded on a Mercury Plus 400 instrument at 298 K, while ^{19}F NMR measurements were recorded on a Varian Gemini 200BB at 298 K. The chemical shifts for ^1H and ^{13}C NMR spectra were referenced to the nondeuterated aliquot of the solvent, while the chemical shifts for ^{19}F NMR spectra were referenced to $CFCl_3$. Line widths ($\Delta\nu_{1/2}$) of ^{19}F NMR resonances were measured at half-height. gas chromatography/mass spectrometry (GC/MS) analyses were performed on a HP6890 instrument, interfaced with a MSD-HP5973 detector and equipped with a Phenonex Zebron column. Molar conductivities (Λ_M) were calculated per 1 mol of metal atoms, on the basis of resistance measurements performed by a Metrohm AG Konduktometer E382 instrument (cell constant = 0.815 cm^{-1}) on dichloromethane solutions of ca. 0.010 M.[20] Carbon and hydrogen analyses were performed by paying particular attention to the more sensitive compounds that were weighed and directly introduced into the analyzer. The metal was analyzed as M_2O_5 (M = Nb, Ta), obtained by hydrolysis of the sample followed by calcination in a platinum

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(7) The pentafluorides of niobium(V) and tantalum(V) have tetranuclear structures in the solid state, while the corresponding chlorides are dinuclear in the solid state and mononuclear in the vapor phase [Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, U.K., 1993]. For the sake of simplicity, these compounds may be mentioned in this paper by the empirical formula MX_5.

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crucible. The metal analyses were repeated twice in order to check for reproducibility.

1. Synthesis of $[\mathrm{MF_4\{\kappa^2\text{-}ROCH_2CH(R')OR''\}_2][MF_6]}$ [M = Nb, R = R″ = Me, R′ = H (2a); M = Ta, R = R″ = Me, R′ = H (2b); M = Nb, R = R″ = Et, R′ = H (2c); M = Nb, R = R′ = R″ = Me (2d); M = Ta, R = R′ = R″ = Me (2e)]. The synthesis of $[\mathrm{NbF_4(\kappa^2\text{-}dme)_2][NbF_6]}$ (**2a**) is described in detail, with compounds **2b**−**2e** being obtained by analogous procedures.

1A. $[\mathrm{NbF_4(\kappa^2\text{-}dme)_2][NbF_6]}$ (2a). A suspension of $\mathrm{NbF_5}$ (**1a**; 0.110 g, 0.585 mmol), in $\mathrm{CH_2Cl_2}$ (13 mL), was treated with dme (0.082 mL, 0.800 mmol), and the resulting mixture was stirred at room temperature for 2 h. Progressive dissolution of the solid was observed. Then the volatile materials were removed in vacuo, and the residue was crystallized from $\mathrm{CH_2Cl_2}$/pentane at room temperature. Colorless crystals of **2a** suitable for X-ray analysis were obtained after 24 h. Yield: 0.130 g (80%). Anal. Calcd for $\mathrm{C_8H_{20}F_{10}Nb_2O_4}$: C, 17.28; H, 3.63; Nb, 33.42. Found: C, 17.38; H, 3.51; Nb, 33.25. IR (solid state): 2966 w, 1474 m, 1460 m s, 1446 m s, 1294 m, 1258 m, 1191 m, 1118 m, 1061 s, 1002 vs, 969 s, 854 s, 806 w m $\mathrm{cm^{-1}}$. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 3.76 (s, 8 H, $\mathrm{C}H_2$), 3.56 (s, 12 H, $\mathrm{C}H_3$). ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 188 K): δ 3.81 (s, 8 H, $\mathrm{C}H_2$), 3.57 (s, 12 H, $\mathrm{C}H_3$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 73.2 ($C\mathrm{H_2}$), 60.2 ($C\mathrm{H_3}$). ^{19}F NMR ($\mathrm{CD_2Cl_2}$): δ 182.0 (s, 4 F, $\Delta\nu_{1/2} =$ 70 Hz, $\mathrm{Nb}F_4$), 103.8 (br, 6 F, $\mathrm{Nb}F_6$). ^{19}F NMR ($\mathrm{CD_2Cl_2}$, 188 K): δ 178.6 (s, 4 F, $\Delta\nu_{1/2} = 40$ Hz, $\mathrm{Nb}F_4$), 103.8 (dec, $^1J_{\mathrm{Nb-F}} = 330$ Hz, 6 F, $\mathrm{Nb}F_6$). Λ_{M} (298 K) = 2.4 $\mathrm{S\cdot cm^2\cdot mol^{-1}}$.

1B. $[\mathrm{TaF_4(\kappa^2\text{-}dme)_2][TaF_6]}$ (2b). A colorless crystalline solid was obtained in 75% yield from **1b** (0.125 g, 0.453 mmol) and dme (0.068 mL, 0.650 mmol). Crystals suitable for X-ray analysis were collected by layering of a dichloromethane solution of **2b** with pentane, at 243 K. Anal. Calcd for $\mathrm{C_8H_{20}F_{10}O_4Ta_2}$: C, 13.12, H, 2.75, Ta, 49.43. Found: C, 13.25, H, 2.66, Ta, 49.28. IR (solid state): 2981 m, 2889 w, 1462 m, 1447 m, 1382 w m, 1295 m, 1192 m, 1062 s, 1000 vs, 978 s, 858 s, 806 m $\mathrm{cm^{-1}}$. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 3.87 (s, 8 H, $\mathrm{C}H_2$), 3.62 (s, 12 H, $\mathrm{C}H_3$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 72.9 ($C\mathrm{H_2}$), 60.1 ($C\mathrm{H_3}$). ^{19}F NMR ($\mathrm{CD_2Cl_2}$): δ 93.2 (s, 4 F, $\Delta\nu_{1/2} = 44$ Hz, $\mathrm{Ta}F_4$), 39.7 (s, 6 F, $\Delta\nu_{1/2} =$ 160 Hz, $\mathrm{Ta}F_6$). ^{19}F NMR ($\mathrm{CD_2Cl_2}$, 188 K): δ 92.9 (s, 4 F, $\Delta\nu_{1/2} =$ 42 Hz, $\mathrm{Ta}F_4$), 38.0 (s, 6 F, $\Delta\nu_{1/2} = 28$ Hz, $\mathrm{Ta}F_6$).

1C. $[\mathrm{NbF_4\{\kappa^2\text{-}EtO(CH_2)_2OEt\}_2][NbF_6]}$ (2c). A light-brown microcrystalline solid was obtained in 77% yield from **1a** (0.085 g, 0.450 mmol) and 1,2-diethoxyethane (0.089 mL, 0.63 mmol). Anal. Calcd for $\mathrm{C_{12}H_{28}F_{10}Nb_2O_4}$: C, 23.54; H, 4.61; Nb, 30.35. Found: C, 23.26; H, 4.79; Nb, 29.90. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 3.90 (m, 8 H, $\mathrm{C}H_2\mathrm{CH_3}$), 3.80 (s br, 8 H, $\mathrm{C}H_2\mathrm{C}H_2$), 1.28 (t, 12 H, $^3J_{\mathrm{H-H}} = 6.0$ Hz, $\mathrm{C}H_3$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): δ 71.0, 70.1 ($C\mathrm{H_2}$), 14.8 ($C\mathrm{H_3}$). ^{19}F NMR ($\mathrm{CDCl_3}$): δ 180.0 (s, 4 F, $\Delta\nu_{1/2} = 72$ Hz, $\mathrm{Nb}F_4$), 103.0 (m br, 6 F, $\mathrm{Nb}F_6$). ^{19}F NMR ($\mathrm{CDCl_3}$, 218 K): δ 173.5 (s, 4 F, $\Delta\nu_{1/2} = 62$ Hz, $\mathrm{Nb}F_4$), 102.9 (dec, $^1J_{\mathrm{Nb-F}} = 335$ Hz, 6 F, $\mathrm{Nb}F_6$). Λ_{M} (298 K) = 6.3 $\mathrm{S\cdot cm^2\cdot mol^{-1}}$.

1D. $[\mathrm{NbF_4\{\kappa^2\text{-}MeOCH_2CH(Me)OMe\}_2][NbF_6]}$ (2d). An orange solid was obtained in 84% yield from **1a** (0.105 g, 0.559 mmol) and 1,2-dimethoxypropane (0.102 mL, 0.837 mmol). Anal. Calcd for $\mathrm{C_{10}H_{24}F_{10}Nb_2O_4}$: C, 20.56; H, 4.14, Nb; 31.81. Found: C, 20.32; H, 4.03; Nb; 30.65. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 183 K): δ 4.45 (m br, 4 H, $\mathrm{C}H_2$), 4.34 (m, 2 H, $\mathrm{C}H$), 3.95 (s, 6 H, $\mathrm{O}Me$), 3.73 (s, 6 H, $\mathrm{O}Me$), 1.31 (m, 6 H, $\mathrm{C}Me$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 183 K): δ 78.9 ($C\mathrm{H}$), 76.3 ($C\mathrm{H_2}$), 65.2, 60.0 ($\mathrm{O}Me$), 14.8 ($\mathrm{C}Me$). ^{19}F NMR ($\mathrm{CD_2Cl_2}$): δ 189.1 (s, 2 F, $\Delta\nu_{1/2} = 240$ Hz, $\mathrm{Nb}F_4$), 174.3 (s, 2 F, $\Delta\nu_{1/2} = 310$ Hz, $\mathrm{Nb}F_4$), 104.1 (m br, 6 F, $\Delta\nu_{1/2} = 2.50$ kHz, $\mathrm{Nb}F_6$). ^{19}F NMR ($\mathrm{CD_2Cl_2}$, 183 K): δ 183.9 (m, 2 F, $\Delta\nu_{1/2} = 320$ Hz, $\mathrm{Nb}F_4$), 164.0 (m, 2 F, $\Delta\nu_{1/2} = 880$ Hz, $\mathrm{Nb}F_4$), 104.1 (dec, $^1J_{\mathrm{Nb-F}} = 340$ Hz, 6 F, $\mathrm{Nb}F_6$). Λ_{M} (298 K) = 2.4 $\mathrm{S\cdot cm^2\cdot mol^{-1}}$.

1E. $[\mathrm{TaF_4\{\kappa^2\text{-}MeOCH_2CH(Me)OMe\}_2][TaF_6]}$ (2e). An orange solid was obtained in 81% yield from **1b** (0.180 g, 0.652 mmol) and 1,2-dimethoxypropane (0.113 mL, 0.930 mmol). Anal. Calcd for $\mathrm{C_{10}H_{24}F_{10}O_4Ta_2}$: C, 15.80; H, 3.18; Ta, 47.61. Found: C, 15.44; H, 3.03; Ta, 47.11. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 183 K): δ 4.45 (m br, 4 H, $\mathrm{C}H_2$), 4.26 (m, 2 H, $\mathrm{C}H$), 3.90 (s, 6 H, $\mathrm{O}Me$), 3.68 (s, 6 H, $\mathrm{O}Me$), 1.21 (m, 6 H, $\mathrm{C}Me$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 183 K): δ 79.0 ($C\mathrm{H}$), 76.1 ($C\mathrm{H_2}$), 65.2, 60.3 ($\mathrm{O}Me$), 15.1 ($\mathrm{C}Me$). ^{19}F NMR ($\mathrm{CD_2Cl_2}$): δ 99.8 (s, 2 F, $\Delta\nu_{1/2} = 260$ Hz, $\mathrm{Ta}F_4$), 87.3 (s, 2 F, $\Delta\nu_{1/2} = 580$ Hz, $\mathrm{Ta}F_4$), 38.9 (s, 6 F, $\Delta\nu_{1/2} = 118$ Hz, $\mathrm{Ta}F_6$). ^{19}F NMR ($\mathrm{CD_2Cl_2}$, 183 K): δ 96.9 (m, 2 F, $\Delta\nu_{1/2} = 320$ Hz, $\mathrm{Ta}F_4$), 81.0 (m, 2 F, $\Delta\nu_{1/2} = 1.20$ kHz, $\mathrm{Ta}F_4$), 38.9 (s, 6 F, $\Delta\nu_{1/2} =$ 80 Hz, $\mathrm{Ta}F_6$).

2. Synthesis of $[\mathrm{MF_4\{\kappa^2\text{-}ROCH_2CH(R')OR''\}_2][M_2F_{11}]}$ [M = Nb, R = R″ = Me, R′ = H (3a); M = Ta, R = R″ = Me, R′ = H (3b); M = Ta, R = R″ = Et, R′ = H (3c); M = Nb, R = R′ = R″ = Me (3d); M = Ta, R = R′ = R″ = Me (3e)]. The synthesis of **3a** is described in detail; compounds **3b**−**3e** were obtained by analogous procedures.

2A. $[\mathrm{NbF_4(\kappa^2\text{-}dme)_2][Nb_2F_{11}]}$ (3a). A suspension of $\mathrm{NbF_5}$ (0.110 g, 0.585 mmol), in $\mathrm{CH_2Cl_2}$ (12 mL), was treated with dme (0.299 mL, 0.280 mmol), and the resulting mixture was stirred at room temperature. Partial dissolution of the solid was observed. After 2 h, the mixture was filtered in order to remove the unreacted $\mathrm{NbF_5}$, and the resulting solution was dried in vacuo. Crystallization of the residue from $\mathrm{CH_2Cl_2}$/heptane at room temperature gave **3a** as a light-yellow solid. Yield: 0.087 g (84%). Anal. Calcd for $\mathrm{C_8H_{20}F_{15}Nb_3O_4}$: C, 12.9; H, 2.7; Nb, 37.47. Found: C, 13.02; H, 2.57; Nb, 36.99. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 4.34 (s, 8 H, $\mathrm{C}H_2$), 4.01 (s, 12 H, $\mathrm{C}H_3$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 75.0 ($C\mathrm{H_2}$), 66.5 ($C\mathrm{H_3}$). ^{19}F NMR ($\mathrm{CD_2Cl_2}$): δ 183.7 (s, 4 F, $\Delta\nu_{1/2} = 560$ Hz, $\mathrm{Nb}F_4$), 153.3 (s, 11 F, $\Delta\nu_{1/2} = 580$ Hz, $\mathrm{Nb_2}F_{11}$). Λ_{M} (293 K) = 4.0 $\mathrm{S\cdot cm^2\cdot mol^{-1}}$.

2B. $[\mathrm{TaF_4(\kappa^2\text{-}dme)_2][Ta_2F_{11}]}$ (3b). A colorless solid was obtained in 77% yield from **1b** (0.125 g, 0.453 mmol) and dme (0.230 mmol). Anal. Calcd for $\mathrm{C_8H_{20}F_{15}O_4Ta_3}$: C, 9.53; H, 2.00; Ta, 53.85. Found: C, 9.36; H, 2.08; Ta, 53.41. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 4.35 (s, 8 H, $\mathrm{C}H_2$), 3.98 (s, 12 H, $\mathrm{C}H_3$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 74.8 ($C\mathrm{H_2}$), 66.4 ($C\mathrm{H_3}$). ^{19}F NMR ($\mathrm{CD_2Cl_2}$): δ 94.7 (s, 4 F, $\Delta\nu_{1/2} = 740$ Hz, $\mathrm{Ta}F_4$), 72.2 (s, 11 F, $\Delta\nu_{1/2} = 710$ Hz, $\mathrm{Ta_2}F_{11}$). ^{19}F NMR ($\mathrm{CD_2Cl_2}$, 183 K): δ 120.0 (s, 2 F, $\Delta\nu_{1/2} = 910$ Hz, $\mathrm{Ta_2}F_{11}$), 89.6 (s, 4 F, $\Delta\nu_{1/2} = 62$ Hz, $\mathrm{Ta}F_4$), 71.2 (s, 8 F, $\Delta\nu_{1/2} = 1.5$ kHz, $\mathrm{Ta_2}F_{11}$), −80.0 (s, 1 F, $\Delta\nu_{1/2} = 780$ Hz, $\mathrm{Ta_2}F_{11}$).

2C. $[\mathrm{TaF_4\{\kappa^2\text{-}EtO(CH_2)_2OEt\}_2][Ta_2F_{11}]}$ (3c). A light-yellow solid was obtained in 78% yield from **1b** (0.135 g, 0.489 mmol) and 1,2-diethoxyethane (0.046 mL, 0.33 mmol). Anal. Calcd for $\mathrm{C_{12}H_{28}F_{15}O_4Ta_3}$: C, 13.54; H, 2.65; Ta, 51.01. Found: C, 13.46; H, 2.69; Ta, 50.90. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 4.33 (q, 8 H, $^3J_{\mathrm{H-H}} =$ 7.33 Hz, $\mathrm{C}H_2\mathrm{CH_3}$), 4.29 (s, 8 H, $\mathrm{C}H_2\mathrm{C}H_2$), 1.43 (t, 12 H, $^3J_{\mathrm{H-H}} = 7.33$ Hz, $\mathrm{C}H_3$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 73.9, 70.1 ($C\mathrm{H_2}$), 13.6 ($C\mathrm{H_3}$). ^{19}F NMR ($\mathrm{CD_2Cl_2}$): δ 93.1 (s, 4 F, $\Delta\nu_{1/2} = 160$ Hz, $\mathrm{Ta}F_4$), 68.0 (s, 11 F, $\Delta\nu_{1/2} = 2.0$ kHz, $\mathrm{Ta_2}F_{11}$).

2D. $[\mathrm{NbF_4\{\kappa^2\text{-}MeOCH_2CH(Me)OMe\}_2][Nb_2F_{11}]}$ (3d). A yellow solid was obtained in 77% yield from **1a** (0.100 g, 0.532 mmol) and 1,2-dimethoxypropane (0.043 mL, 0.350 mmol). Anal. Calcd for $\mathrm{C_{10}H_{24}F_{15}Nb_3O_4}$: C, 15.56; H, 3.13; Nb, 36.10. Found: C, 15.36; H, 3.00; Nb, 35.56. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 183 K): δ 4.79−4.51 (m br, 4 H, $\mathrm{C}H_2$), 4.28 (m, 2 H, $\mathrm{C}H$), 3.95 (s, 6 H, $\mathrm{O}Me$), 3.75 (s, 6 H, $\mathrm{O}Me$), 1.33 (m, 6 H, $\mathrm{C}Me$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 183 K): δ 79.0 ($C\mathrm{H}$), 78.1 ($C\mathrm{H_2}$), 64.9, 60.3 ($\mathrm{O}Me$), 13.9 ($\mathrm{C}Me$). ^{19}F NMR ($\mathrm{CD_2Cl_2}$): δ 190.7 (m, 2 F, $\Delta\nu_{1/2} = 2.10$ kHz, $\mathrm{Nb}F_4$), 168.1 (m, 2 F, $\Delta\nu_{1/2} = 2$ kHz, $\mathrm{Nb}F_4$), 143.8 (m, 11 F, $\Delta\nu_{1/2} = 1.05$ kHz, $\mathrm{Nb_2}F_{11}$). ^{19}F NMR ($\mathrm{CD_2Cl_2}$, 183 K): δ 193.2 (m, 2 F, $\Delta\nu_{1/2} = 340$ Hz, $\mathrm{Nb_2}F_{11}$), 185.5 (m, 2 F, $\Delta\nu_{1/2} = 420$ Hz, $\mathrm{Nb}F_4$), 164.0 (m, 2 F, $\Delta\nu_{1/2} = 800$ Hz, $\mathrm{Nb}F_4$), 144.2 (s, 8 F, $\Delta\nu_{1/2} = 145$ Hz, $\mathrm{Nb_2}F_{11}$), −57.6 (m, 1 F, $\Delta\nu_{1/2} = 322$ Hz, $\mathrm{Nb_2}F_{11}$). Λ_{M} (298 K) = 3.7 $\mathrm{S\cdot cm^2\cdot mol^{-1}}$.

2E. $[\mathrm{TaF_4\{\kappa^2\text{-}MeOCH_2CH(Me)OMe\}_2][Ta_2F_{11}]}$ (3e). A yellow solid was obtained in 80% yield from **1b** (0.175 g, 0.634 mmol) and 1,2-dimethoxypropane (0.051 mL, 0.420 mmol). Anal. Calcd for $\mathrm{C_{10}H_{24}F_{15}O_4Ta_3}$: C, 11.59; H, 2.33; Ta, 52.39. Found: C, 11.62; H, 2.20; Ta, 50.79. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 183 K): δ 4.54, 4.23 (m br, 4 H, $\mathrm{C}H_2$), 4.30 (m, 2 H, $\mathrm{C}H$), 4.00 (s, 6 H, $\mathrm{O}Me$), 3.79 (s, 6 H, $\mathrm{O}Me$), 1.32 (s br, 6 H, $\mathrm{C}Me$). ^{13}C{^{1}H} NMR

(CD_2Cl_2, 183 K): δ 78.8 (*C*H), 77.9 (*C*H_2), 65.0, 60.4 (O*Me*), 13.9 (C*Me*). ^{19}F NMR (CD_2Cl_2): δ 101.7 (s, 2 F, $\Delta\nu_{1/2}$ = 1.6 kHz, TaF_4), 90.0 (s, 2 F, $\Delta\nu_{1/2}$ = 1.4 kHz, TaF_4), 70.2 (s br, 11 F, $\Delta\nu_{1/2}$ = 2.4 kHz, Ta_2F_{11}). ^{19}F NMR (CD_2Cl_2, 183 K): δ 117.9 (m br, 2 F, $\Delta\nu_{1/2}$ = 185 Hz, Ta_2F_{11}), 97.0 (m, 2 F, $\Delta\nu_{1/2}$ = 440 Hz, TaF_4), 80.2 (m, 2 F, $\Delta\nu_{1/2}$ = 440 Hz, TaF_4), 70.3 (s, 8 F, $\Delta\nu_{1/2}$ = 380 Hz, Ta_2F_{11}), −80.7 (s, 1 F, $\Delta\nu_{1/2}$ = 420 Hz, Ta_2F_{11}).

3. Reactivity of MF_5 (M = Nb, Ta) with $MeO(CH_2)_2OCH_2Cl$. Detection in Solution of $[NbF_4\{\kappa^1\text{-}MeO(CH_2)_2O(CH_2Cl)\}\{\kappa^2\text{-}MeO(CH_2)_2O(CH_2Cl)\}][Nb_2F_{11}]$ (3f). Compound NbF_5 (0.500 mmol) was treated with $MeO(CH_2)_2OCH_2Cl$ (0.250 mmol) in CD_2Cl_2 (0.60 mL) inside a sealed NMR tube. Fast darkening of the mixture was noticed. After 30 min, a dark-red oily precipitate and a light-yellow solution were present. The latter was analyzed by NMR spectroscopy. NMR data at room temperature have not been useful to the characterization and are omitted. NMR spectra collected at low temperature allowed one to detect the presumable species **3f**, which was found in the admixture with additional compounds that we have not been able to identify.

$[NbF_4\{\kappa^1\text{-}MeO(CH_2)_2O(CH_2Cl)\}\{\kappa^2\text{-}MeO(CH_2)_2O(CH_2Cl)\}][Nb_2F_{11}]$ (3f). ^{1}H NMR (CD_2Cl_2, 183 K): δ 5.70 [s, 2 H, CH_2Cl (κ^2-ligand)], 5.62 [s, 2 H, CH_2Cl (κ^1-ligand)], 5.13 [t, 2 H, $^3J_{H-H}$ = 5.13 Hz, CH_2 (κ^2-ligand)], 4.78 [t, 2 H, $^3J_{H-H}$ = 5.86 Hz, CH_2 (κ^1-ligand)], 4.65 [t, 2 H, $^3J_{H-H}$ = 5.13 Hz, CH_2 (κ^2-ligand)], 4.40 [t, 2 H, $^3J_{H-H}$ = 5.86 Hz, CH_2 (κ^1-ligand)], 4.29 (s, 6 H, O*Me*). ^{13}C{^{1}H} NMR (CD_2Cl_2, 203 K): δ 81.6 [CH_2Cl, (κ^2-ligand)], 77.3 [CH_2Cl (κ^1-ligand)], 74.0, 69.9, 69.4 (CH_2), 65.7 (O*Me*). ^{19}F NMR (CD_2Cl_2, 183 K): δ 201.9 (s br, $\Delta\nu_{1/2}$ = 205 Hz, NbF_4), 181.6 (s, 2 F, $\Delta\nu_{1/2}$ = 690 Hz, Nb_2F_{11}), 151.9 (s, 8 F, $\Delta\nu_{1/2}$ = 1.30 kHz, Nb_2F_{11}), −43.9 (s, 1 F, $\Delta\nu_{1/2}$ = 1.90 kHz, Nb_2F_{11}).

The reaction of TaF_5 (0.500 mmol) with $MeO(CH_2)_2OCH_2Cl$ (0.250 mmol) was carried out analogously. ^{1}H and ^{13}C NMR spectra of the resulting mixture were not interpretable. The ^{19}F NMR spectrum appeared as follows. ^{19}F NMR (CD_2Cl_2, 183 K): δ 123.5 (s, 2 F, $\Delta\nu_{1/2}$ = 250 Hz, Ta_2F_{11}), 111.9 (s, 1 F, $\Delta\nu_{1/2}$ = 205 Hz, TaF_4), 102.3 (s, 1 F, $\Delta\nu_{1/2}$ = 130 Hz, TaF_4), 83.4 (m, 2 F, $\Delta\nu_{1/2}$ = 200 Hz, TaF_4), 69.5 (s, 8 F, $\Delta\nu_{1/2}$ = 180 Hz, Ta_2F_{11}), −79.3 (s, 1 F, $\Delta\nu_{1/2}$ = 390 Hz, Ta_2F_{11}).

The addition of further $MeO(CH_2)_2OCH_2Cl$ (0.450 mmol) to the reaction mixtures obtained from MF_5 (M = Nb, Ta; 0.500 mmol) and $MeO(CH_2)_2OCH_2Cl$ (0.250 mmol) resulted in further darkening. The ^{1}H NMR spectra recorded at 183 K indicated the formation of complicated mixtures of products. Otherwise, ^{19}F NMR analyses at 183 K pointed out the presence of the $[MF_6]^-$ anions [M = Nb, δ 103.7 (decet, $^1J_{Nb-F}$ = 330 Hz); M = Ta, δ 39.5 (s)]. An attempt to obtain pure compound **3f** was made by crystallization of a dichloromethane reaction mixture (from NbF_5, 0.720 mmol, and $MeOCH_2CH_2OCH_2Cl$, 0.910 mmol), layered with heptane. A light-brown powder was obtained after storing the mixture at −30 °C for 3 days, but NMR characterization of this powder was not possible because of low solubility.

4. Reactions of MF_5 with Diethers at High Temperature. The reaction of NbF_5 with dme is described in detail. The other reactions were performed by analogous procedures, unless otherwise specified.

4A. NbF_5 + dme. An NMR tube was charged with NbF_5 (0.080 g, 0.430 mmol), $CDCl_3$ (0.70 mL), CH_2Cl_2 (0.430 mmol), and dme (0.050 mL, 0.480 mmol) and sealed. After 12 h, ^{1}H NMR spectroscopy indicated the absence of uncoordinated dme. The tube was heated for 30 min at ca. 90 °C (temperature of the external oil bath), during which the solution turned orange. A precipitate formed upon cooling of the tube to room temperature: the ^{1}H NMR spectrum of the solution revealed the presence of CH_2Cl_2, NbF_5(1,4-dioxane),[17] $NbF_5(Me_2O)$,[17] uncoordinated 1,4-dioxane, and uncoordinated Me_2O in ca. 20:1:1:6:12 ratio. The tube was cooled at ca. −20 °C, and water (ca. 10 mmol) was added to the mixture. The immediate formation of a colorless solid was noticed, from which a yellow solution was separated. ^{1}H and ^{13}C NMR and GC/MS analyses on the organic layer pointed out the presence of CH_2Cl_2, 1,4-dioxane, and dimethyl ether, in ca. 2:1:2 ratio (^{1}H NMR).

4B. TaF_5 (0.30 mmol) + dme (0.33 mmol). Reaction time (90 °C): 30 min. A red mixture was obtained. Hydrolysis of the mixture gave a colorless solid and a pale-yellow solution, which was analyzed by GC/MS and ^{1}H and ^{13}C NMR: CH_2Cl_2, 1,4-dioxane, and Me_2O were detected in ca. 2:1:2 ratio (^{1}H NMR).

4C. TaF_5 (0.25 mmol) + $EtO(CH_2)_2OEt$ (0.26 mmol). Reaction time (90 °C): 1 h. A red mixture containing unidentifiable products was obtained. Hydrolysis of the mixture gave a colorless solid and a light-pink solution. The latter was analyzed by GC/MS and ^{1}H and ^{13}C NMR: CH_2Cl_2, 1,4-dioxane, Et_2O, and EtOH were detected in ca. 6:2:4:1 ratio (^{1}H NMR).

4D. NbF_5 (0.30 mmol) + $MeOCH_2CH(Me)OMe$ (0.32 mmol). Reaction time (110 °C): 4 h. A red solution was obtained and treated with excess water. Hydrolysis of the mixture gave a yellow solution over a white precipitate. The solution was analyzed by GC/MS and ^{1}H and ^{13}C NMR: CH_2Cl_2, Me_2O, MeOH, $Me_2C{=}O$, and $MeOCH_2CH(Me)OH$ were detected in ca. 6:4:2:3:1 ratio (^{1}H NMR).

4E. TaF_5 (0.30 mmol) + $MeOCH_2CH(Me)OMe$ (0.31 mmol). Reaction time (110 °C): 2 h. A red solution containing a complicated mixture of products was obtained. Hydrolysis of the mixture gave a dark-yellow solution over a white precipitate. The solution was analyzed by GC/MS and ^{1}H and ^{13}C NMR: CH_2Cl_2, Me_2O, MeOH, and $Me_2C{=}O$ were detected in ca. 5:3:1:2 ratio (^{1}H NMR).

4F. NbF_5 (0.30 mmol) + $MeO(CH_2)_2OCH_2Cl$ (0.32 mmol). Reaction time (70 °C): 1 h. A dark-yellow solution over a brown precipitate oil containing CH_2Cl_2, NbF_5(1,4-dioxane),[17] $NbF_5(Me_2O)$,[17] $NbF_5(HCO_2Me)$,[17] uncoordinated dioxane, and MeCl was obtained in ca. 75:2:2:1:1:25 ratio. Hydrolysis of the mixture gave a colorless solid and a colorless solution, which was analyzed by GC/MS and ^{1}H and ^{13}C NMR: CH_2Cl_2, 1,4-dioxane, Me_2O, MeCl, dme, $MeOCH_2Cl$, CH_2Cl-CH_2Cl, MeOH, and HCO_2Me were detected in ca. 18:6:12:5:3:1:1:1:1 ratio (^{1}H NMR). In a different experiment, the mixture obtained from mixing of NbF_5 (0.50 mmol) with $MeO(CH_2)_2OCH_2Cl$ (0.75 mmol), in CD_2Cl_2 (0.60 mL), was stored in a sealed NMR tube for ca. 70 h. Then the tube was cooled to −20 °C and opened. Water (ca. 5 mmol) was added; thus, the overall mixture was homogenized by brief stirring. The resulting yellow solution, separated from a dark precipitate, was analyzed by NMR, by which compounds $MeO(CH_2)_2OCH_2Cl$, Me_2O, 1,4-dioxane, and MeCl were recognized in ca. 2:3:2:0.6 ratio.

4G. NbF_5 (0.25 mmol) + diglyme (0.26 mmol). Reaction time (80 °C): 1.5 h. A light-yellow solution was obtained. The final mixture was allowed to cool to −20 °C and treated with water (ca. 5 mmol): a colorless solution over a colorless precipitate formed. The ^{1}H NMR spectrum of the solution evidenced the presence of CH_2Cl_2, Me_2O, and 1,4-dioxane in ca. 1:1:1 ratio.

5. Catalytic Formation of 1,4-Dioxane from NbF_5 and dme. An NMR tube was charged with NbF_5 (0.040 g, 0.21 mmol), CH_2Cl_2 (0.210 mmol), $CDCl_3$ (0.45 mL), and dme (0.327 mL, 3.15 mmol), sealed, and heated at 363 K (temperature of the external oil bath) for 1 h, during which the solution darkened. After cooling to −20 °C, the tube was opened and water (ca. 5 mmol) was added. ^{1}H NMR spectrum carried out on an aliquot of the resulting solution revealed the presence of CH_2Cl_2, dme, 1,4-dioxane, and dimethyl ether in ca. 1:1:6:12 ratio, corresponding to a 93% conversion of dme and to an approximate yield in dioxane of 80%.

6. Reactivity of MCl_5 (M = Nb, Ta) with dme: Characterization of $[MCl_4(\kappa^2\text{-dme})(\kappa^1\text{-dme})][MCl_6]$ [M = Nb (4a), Ta (4b)]. In

Table 1. Crystal Data and Details of the Structure Refinement for **2a** and **2b**

formula	$C_8H_{20}F_{10}Nb_2O_4$	$C_8H_{20}F_{10}O_4Ta_2$
fw	556.06	732.14
λ, Å	0.710 73	0.710 73
temp, K	100(2)	100(2)
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a, Å	12.569(7)	12.650(5)
b, Å	12.764(7)	12.719(5)
c, Å	12.731(7	12.671(5)
β, deg	118.753(7)	118.920(5)
cell volume, Å^3	1790.6(16)	1784.4(12)
Z	4	4
D_c, g·cm^{-3}	2.063	2.725
μ, mm^{-1}	1.387	12.363
F(000)	1088	1344
θ limits, deg	1.60−26.37	1.60−25.03
reflns collected	13613	14812
indep reflns	3636 (R_{int} = 0.0891)	3146 (R_{int} = 0.1586)
data/restraints /param	3636/24/218	3146/113/222
GOF on F^2	1.408	1.068
R1 [$I > 2\sigma(I)$]	0.1136	0.0848
wR2 (all data)	0.3622	0.1927
largest diff peak and hole, e·Å^{-3}	3.580 and −2.866	4.190 and −5.917

an NMR tube, a suspension of $NbCl_5$ and **1c** (0.085 g, 0.315 mmol) in $CDCl_3$ (0.80 mL) was treated with CH_2Cl_2 (0.315 mmol) and dme (0.31 mmol). The tube was sealed, cooled to ca. 263 K, and stirred for 10 min. The resulting yellow solution was analyzed by NMR. In a different experiment, a solution of **4a** in CH_2Cl_2 (28 mL), in a Schlenk tube at 253 K, was prepared from **1c** (0.265 g, 0.981 mmol) and dme (1.10 mmol). Conductivity measurement was performed on the solution at 253 K. Similar experiments were carried out for the characterization of **4b**.

Compound 4a. ^{1}H NMR ($CDCl_3$, 273 K): δ 4.05 (s, 4 H, C*H*$_2$), 3.74 (s, 6 H, C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 273 K): δ 74.5 (*C*H$_2$), 63.6 (*C*H3). ^{1}H NMR ($CDCl_3$, 213 K): δ 4.65 [m br, 2 H, NbOC*H*$_2$ (κ^1-dme)], 4.32 [s, 3 H, *Me*ONb (κ^1-dme)], 3.98 [s, 4 H, C*H*$_2$ (κ^2-dme)], 3.88 [m br, 2 H, C*H*$_2$ (κ^1-dme)], 3.67 [s, 6 H, C*H*$_3$ (κ^2-dme)], 3.41 [s, 3 H, *Me* (κ^1-dme)]. ^{13}C{^{1}H} NMR ($CDCl_3$, 213 K): δ 82.1 [NbO*C*H$_2$ (κ^1-dme)], 72.5, 71.6, 71.2 [*C*H$_2$ (κ^1-dme) + *C*H$_2$ (κ^2-dme) + *Me*ONb (κ^1-dme)], 60.5, 59.6 [*Me* (κ^2-dme) + *Me* (κ^1-dme)]. Λ_M (253 K) = 3.6 S·cm^2·mol^{-1}.

Compound 4b. ^{1}H NMR ($CDCl_3$, 273 K): δ 4.01 (s, 4 H, C*H*$_2$), 3.70 (s, 6 H, C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 273 K): δ 74.5 (*C*H$_2$), 63.6 (*C*H3). ^{1}H NMR ($CDCl_3$, 213 K): δ 4.80 [m br, 2 H, NbOC*H*$_2$ (κ^1-dme)], 4.48 [s, 3 H, *Me*ONb (κ^1-dme)], 3.97 [s, 4 H, C*H*$_2$ (κ^2-dme)], 3.90 [m br, 2 H, C*H*$_2$ (κ^1-dme)], 3.67 [s, 6 H, C*H*$_3$ (κ^2-dme)], 3.41 [s, 3 H, *Me* (κ^1-dme)]. ^{13}C{^{1}H} NMR ($CDCl_3$, 213 K): δ 83.2 [NbO*C*H$_2$ (κ^1-dme)], 72.3, 71.5, 71.0 [*C*H$_2$ (κ^1-dme) + *C*H$_2$ (κ^2-dme) + *Me*ONb (κ^1-dme)], 60.5, 59.7 [*Me* (κ^2-dme) + *Me* (κ^1-dme)]. Λ_M (253 K) = 2.2 S·cm^2·mol^{-1}.

7. X-ray Crystallography. Crystal data and collection details for **2a** and **2b** are listed in Table 1. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector and using Mo Kα radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).[21] Structures were solved by direct methods and refined by full-matrix least squares based on all data using F^2.[21] Hydrogen 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 carbon atom. The crystals of **2a** and **2b** are isomorphous, and both are pseudo-merohedrally twinned with twin matrix [0 0 −1 0 −1 0 −1 0 0]. Thus, refinement was performed using the instructions TWIN with the appropriate twin law in *SHELXL* and one BASF parameter, which refined as 0.120 70 and 0.489 57 for **2a** and **2b**, respectively. Similar *U* restraints were applied to fluorine (s.u. 0.01 for **2a** and 0.005 for **2b**), oxygen (s.u. 0.04 for **2a** and 0.005 for **2b**), carbon (s.u. 0.01 for **2a** and 0.002 for **2b**), and tantalum (s.u. 0.01 for **2b**).

8. Computational Studies. Geometry optimizations were carried out with the *Gaussian 03* program package,[22] in the framework of DFT, employing Becke's three-parameter hybrid-exchange functional combined with the Lee, Yang, and Parr correlation functional (the B3LYP method[23]), in conjugation with the LANL2DZ effective core potential and basis set.[24] 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. Thermodynamic results refer to 298.15 K and 101 300 Pa. The basis sets used for the natural bond order (NBO) analysis[25] were LANL2DZ for niobium and 6-31 g(d, p) for the remaining atoms, in order to describe atomic orbitals in more detail.

Results and Discussion

Coordination Compounds of Niobium and Tantalum Pentafluorides with Diethers. The ionic adducts **2a**−**2e** are obtained in high yield by reacting suspensions of MF_5 [M = Nb (**1a**), Ta (**1b**)] in CH_2Cl_2 with a slight molar excess of the appropriate diether (see Scheme 1). Compounds **2a**−**2e** are, in fact, the result of the coordination of 1 equiv of a bidentate O donor per metal, accompanied by self-ionization of MF_5 into $[MF_4]^+$ and $[MF_6]^-$. When an approximate 2-fold excess of the pentafluoride is used, the species **3a**−**3e** are obtained cleanly (see Scheme 1). In contrast, the reactions of **1a** and **1b** with MeO-$(CH_2)_2OCH_2Cl$ proceed with low selectivity: among the products, compounds $[MF_4\{\kappa^1\text{-MeO(CH}_2)_2\text{OCH}_2\text{Cl}\}\{\kappa^2\text{-MeO(CH}_2)_2\text{OCH}_2\text{Cl}\}][M_2F_{11}]$ [M = Nb (**3f**), Ta (**3g**)], containing presumably a bidentate MeO-$(CH_2)_2OCH_2Cl$ ligand and a monodentate one, could be identified in a CD_2Cl_2 solution by low-temperature NMR experiments, upon reaction of **1a** and **1b** with 2-methoxyethoxymethyl chloride in about a 2:1 ratio.

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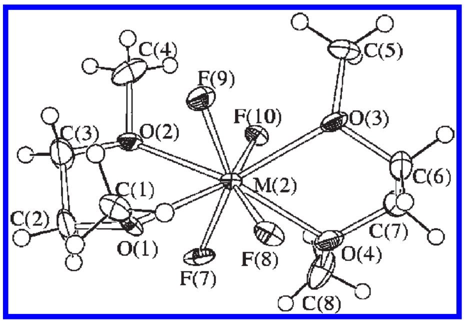
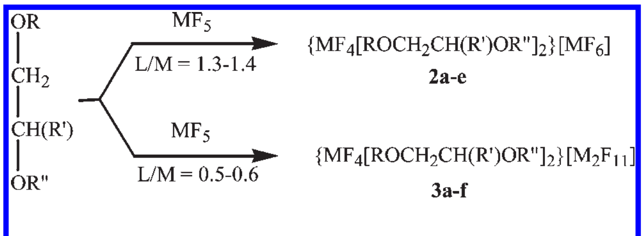


Figure 1. View of the structure of the $[MF_4(\kappa^2\text{-}MeOCH_2CH_2OMe)_2]^+$ cation in $[MF_4(\kappa^2\text{-}MeOCH_2CH_2OMe)_2][MF_6]$ [M = Nb (**2a**), Ta (**2b**)]. Displacement ellipsoids are at the 50% probability level.

Scheme 1. Reaction of Niobium and Tantalum Pentafluorides with Diethers



M	R	R'	R"	
Nb	Me	H	Me	**2a**
Ta	Me	H	Me	**2b**
Nb	Et	H	Et	**2c**
Nb	Me	Me	Me	**2d**
Ta	Me	Me	Me	**2e**
Nb	Me	H	Me	**3a**
Ta	Me	H	Me	**3b**
Ta	Et	H	Et	**3c**
Nb	Me	Me	Me	**3d**
Ta	Me	Me	Me	**3e**
Nb	Me	H	CH_2Cl	**3f**

Complexes **2** and **3a**−**3e** have been isolated in good yields and characterized by spectroscopical and analytical techniques and by X-ray structural studies in the cases of **2a** and **2b**. Figure 1 reports a view of the $[MF_4(\kappa^2\text{-}MeOCH_2CH_2OMe)_2]^+$ cation in **2a** and **2b**, whereas selected bond lengths and angles are reported in Table 2.

Compounds **2a** and **2b** are ionic derivatives made of distorted square-antiprismatic $[MF_4\{\kappa^2\text{-}O(Me)CH_2CH_2O(Me)\}_2]^+$ cations and octahedral $[MF_6]^-$ anions. Although examples of coordination compounds of octa-coordinated niobium and tantalum are known,[26] structurally characterized coordination adducts of a group 5 metal fluoride with a neutral ligand are really rare, with the only well-defined examples being adducts of vanadium trifluoride[26a,27] and the polynuclear derivative $[\{NbF_4(\mu\text{-}o\text{-}C_6H_4(CH_2SMe)_2)_2\}_n][(NbF_5)_xF]_n$.[28]

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2a** and **2b**

	2a	**2b**
M(2)−F(7)	1.863(9)	1.878(12)
M(2)−F(8)	1.865(10)	1.865(13)
M(2)−F(9)	1.873(9)	1.889(13)
M(2)−F(10)	1.868(9)	1.889(14)
M(2)−O(1)	2.269(10)	2.236(16)
M(2)−O(2)	2.339(12)	2.303(14)
M(2)−O(3)	2.265(12)	2.232(13)
M(2)−O(4)	2.358(11)	2.351(15)
F(7)−M(2)−F(8)	97.3(4)	98.6(6)
F(7)−M(2)−F(10)	92.6(4)	92.6(6)
F(8)−M(2)−F(10)	143.0(4)	142.9(5)
F(7)−M(2)−F(9)	143.7(4)	141.5(5)
F(8)−M(2)−F(9)	95.5(4)	95.2(5)
F(10)−M(2)−F(9)	97.3(4)	97.7(6)
F(7)−M(2)−O(3)	142.6(4)	144.1(6)
F(8)−M(2)−O(3)	74.4(4)	74.1(6)
F(10)−M(2)−O(3)	76.2(4)	76.1(6)
F(9)−M(2)−O(3)	73.7(4)	74.3(5)
F(7)−M(2)−O(1)	73.7(4)	72.6(6)
F(8)−M(2)−O(1)	73.5(4)	73.6(6)
F(10)−M(2)−O(1)	143.3(4)	143.3(6)
F(9)−M(2)−O(1)	77.7(4)	77.2(6)
O(3)−M(2)−O(1)	134.1(4)	134.2(6)
F(7)−M(2)−O(2)	76.1(4)	74.8(5)
F(8)−M(2)−O(2)	143.6(4)	143.3(6)
F(10)−M(2)−O(2)	73.4(4)	143.3(6)
F(9)−M(2)−O(2)	73.6(4)	72.7(6)
O(3)−M(2)−O(2)	131.3(4)	131.2(6)
O(1)−M(2)−O(2)	70.3(4)	70.0(5)
F(7)−M(2)−O(4)	72.6(4)	73.5(5)
F(8)−M(2)−O(4)	74.8(4)	75.4(6)
F(10)−M(2)−O(4)	74.4(4)	74.2(6)
F(9)−M(2)−O(4)	143.7(4)	145.0(5)
O(3)−M(2)−O(4)	70.0(4)	70.7(5)
O(1)−M(2)−O(4)	129.6(4)	129.2(6)
O(2)−M(2)−O(4)	133.3(4)	133.2(6)

The M(2)−O interactions with the two dme ligands [2.265(12)−2.358(11) Å for **2a**; 2.232(13)−2.351(15) Å for **2b**] are sensibly longer than those in other niobium(V) and tantalum(V) complexes containing the same ligand, e.g., 2.1661(15)−2.2898(14) and 2.158(3)−2.232(3) Å for the previously reported $MOCl_3(dme)MCl_5$ (M = Nb, Ta) derivatives.[16c] This is probably due to the fact that the coordination number (cn = 8) of the metals in **2a** and **2b**$^+$ is higher than that in $MOCl_3(dme)MCl_5$ (cn = 6). Nonetheless, the difference in the coordination number does not affect the M(2)−F interactions [1.863(9)−1.873(9) Å for **2a**; 1.865(13)−1.889(13) Å for **2b**], which are comparable to the M(1)−F distances present within the $[MF_6]^-$ counteranion in the same salts [1.868(14)−1.901(10) Å for **2a**; 1.813(15)−1.887(12) Å for **2b**] or in previously reported ones.[15] On the other hand, examples of elongation of the M−F (M = Nb, Ta) interactions due to expanded coordination have been described for $[TaF\{OC(Me)C(Me)C(Me)O\}_3][TaF_6]$ [cn = 7; Ta−F = 1.909(5) Å],[15] $NBu_4(TaF_4pc)$ [pc = phthalocyaninato dianion; cn = 8; Ta−F = 1.919(7)−1.966(11) Å],[26a] and Na_3TaF_8 [cn = 8; Ta−F = 1.98 Å].[29] In the present cases, the cationic nature of **2a**+ and **2b**$^+$ probably reinforces the interactions of the metal with the fluoride ligands, thus shortening the M−F distances; instead, elongation is detected in the interactions with the neutral dme ligands.

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The ^{1}H and ^{13}C NMR spectra of complexes **2a**−**2e** and **3a**−**3e** (in a CD_2Cl_2 or $CDCl_3$ solution) exhibit resonances due to two equivalent diether ligands, high-frequency shifted with respect to the uncoordinated molecules. For instance, the dme units in **2a** give two singlets at 3.76 (CH_2) and 3.56 (CH_3) ppm, to be compared with the corresponding values for uncoordinated dme observed at 3.55 and 3.39 ppm. It is noteworthy that the ^{1}H NMR spectra of **2a**−**2e** and **3a**−**3e**, recorded between 188 and 218 K, exhibit the same patterns as the respective spectra recorded at room temperature: this fact rules out the possibility of the occurrence of some exchange process and indicates that both of the diether units act as bidentate ligands in solution (see below), coherent with what was found in the solid state for **2a** and **2b**.

^{19}F NMR spectroscopy has been demonstrated to be a powerful tool for the characterization of MF_5 derivatives (M = Nb, Ta):[30] actually complexes of types **2** and **3**, which differ mostly for the nature of the anion (i.e., $[MF_6]^-$ in the former and $[M_2F_{11}]^-$ in the latter) could be discriminated by reading the ^{19}F NMR spectra. More precisely, the ^{19}F NMR spectra of **2a**−**2e** exhibit the resonance related to the $[MF_6]^-$ anion, at chemical shifts close to those reported for the salts [Y][MF_6] [Y = NBu_4,[31] $S(NMe_2)_3$;[30] M = Nb, Ta]. The decet structure of the $[NbF_6]^-$ resonance[32] in **2a**, **2c**, and **2d** becomes discernible at 183−188 K (see the Experimental Section), while the $[TaF_6]^-$ resonance in **2b** and **2e** appears as a singlet[30] even at low temperature. On the other hand, the $[M_2F_{11}]^-$ unit in **3a**−**3e** gives rise to one broad resonance at room temperature, at ca. 150 ppm for the niobium-containing species **3a** and **3d** and at ca. 70 ppm for the tantalum derivatives **3b**, **3c**, and **3e**. Splitting of this resonance has been observed by low-temperature NMR experiments performed on **3b**,**3d**, and **3e**, in agreement with what was described previously for the salts [NBu_4][M_2F_{11}][31] and [$S(NMe_2)_3$][M_2F_{11}][30] (M = Nb, Ta) (see the Experimental Section for details).

The fluorine nuclei within the $[MF_4]^+$ frame of the cations **2a**$^+$−**2c**$^+$ and **3a**$^+$−**3c**$^+$ resonate as unique narrow singlets at room temperature in the ranges 183.7−180.0 (niobium complexes) and 94.7−93.1 (tantalum complexes). In these cases, the $[MF_4]^+$ resonance looks basically unchanged at low temperature, apart from slight shifting to lower frequencies. Differently, the unsymmetrical $[MF_4]^+$ unit of **2d**, **2e**, **3d**, and **3e** gives rise to two broad peaks at room temperature, accounting for two nonequivalent couples of fluorines (e.g., at 189.1 and 174.3 ppm in the case of **2d**). Some multiplicity is observable at low temperature; however, this appears rather complicated, and we have not been able to solve undoubtedly the maps of the couplings.

Furthermore, NMR spectroscopy has been revealed to be useful in the understanding of the main aspects of the reactions of **1a** and **1b** with $MeO(CH_2)_2OCH_2Cl$ in a 2:1 ratio, although these proceed with low selectivity, giving mixtures of products. The reactions afford mainly ionic derivatives, coherent with the observation of the [$M_2F_{11}^-$] anions (see the Experimental Section for the ^{19}F NMR data recorded at 183 K). The ^{1}H and ^{13}C NMR spectra (CD_2Cl_2, 183 K) of the main product (**3f**) of the reaction involving **1a** show two sets of resonances, attributed tentatively to bidentate and monodentate MeO(CH_2)$_2$OCH_2Cl ligands, respectively. The chemical shifts related to the methoxy groups in the two sets are coincident [δ(^{1}H) 4.29; δ(^{13}C) 65.7] and fall high-frequency-shifted with respect to that seen in uncoordinated 2-methoxyethoxymethyl chloride, suggesting that both molecules use the [OMe] moiety to bind the metal. Conversely, the two ^{13}C NMR resonances due to the OCH_2Cl groups differ significantly from each other (δ 81.6 and 77.3), reinforcing the hypothesis that the monodentate diether coordinates the niobium center through the more basic OMe oxygen rather than through the OCH_2Cl one. Unambiguous ^{1}H and ^{13}C NMR characterization of the mixture obtained from TaF_5 and $MeO(CH_2)_2OCH_2Cl$ has not been possible; however, evidence for a heptacoordinated metal center has been collected by low-temperature ^{19}F NMR investigations. The ^{19}F NMR spectrum (in CD_2Cl_2) at 183 K clearly displays three resonances (δ 111.9, 102.3, and 83.4, accounting for 1:1:2 relative ratios) for the $[TaF_4]^+$ frame, as is expected for a cation of type $[TaF_4\{\kappa^1\text{-RO(CH}_2)_2\text{OR}'\}\{\kappa^2\text{-RO(CH}_2)_2\text{OR}'\}]^+$.

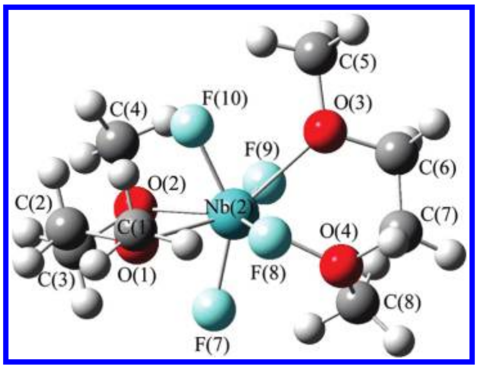

Figure 2. B3LYP/LANL2DZ-optimized structure of $[NbF_4(\kappa^2\text{-dme})_2]^+$ (**2a**$^+$) in the gas phase.

On the other hand, the reactions of **1a** and **1b** with an excess of $MeO(CH_2)_2OCH_2Cl$ afforded mixtures of unidentified products comprising the $[MF_6]^-$ anion (^{19}F NMR spectra; see the Experimental Section).

Finally, the ionic nature of compounds **2a**, **2c**, **2d**, **3a**, and **3d** has been confirmed by solution conductivity analyses, for which the molar conductivities [Λ_M = 2.4 (**2a** and **2d**) to 6.3 (**2c**)] fall at values indicative of ionic compounds;[17] in fact, the Λ_M values related to simple neutral derivatives of **1** are generally lower than 1.0 $S \cdot cm^2 \cdot mol^{-1}$.

The structure of **2a**$^+$ in the gas phase could be optimized by the B3LYP/LANL2DZ method (see Figure 2), showing acceptable agreement with the solid-state features determined by X-ray diffraction. A selection of bond lengths (Å) and angles (deg) is presented in Table 3 and compared to the corresponding X-ray data.

NBO population analysis for **2a**$^+$ has revealed that the main contribution (95%) to the Nb−O σ bonds is given by the oxygen orbitals (the oxygen atoms are approximately sp$^{2.5}$-hybridized), whereas niobium hybrid orbitals, holding mainly d character (70%), are scarcely

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Table 3. Selected Experimental and Calculated Bond Distances (Å) and Angles (deg) for **2a**$^+$

	experimental[a]	calculated
	Bond Distances (Å)	
Nb(2)−F(7)	1.863(9)	1.930
Nb(2)−F(8)	1.865(10)	1.923
Nb(2)−F(9)	1.873(9)	1.908
Nb(2)−F(10)	1.868(9)	1.944
Nb(2)−O(1)	2.269(10)	2.317
Nb(2)−O(2)	2.339(12)	2.272
Nb(2)−O(3)	2.265(12)	2.379
Nb(2)−O(4)	2.358(11)	2.302
	Bond Angles (deg)	
F(7)−Nb(2)−F(8)	97.3(4)	95.8
F(8)−Nb(2)−F(10)	143.0(4)	141.2
F(7)−Nb(2)−F(9)	143.7(4)	144.3
F(8)−Nb(2)−F(9)	95.5(4)	98.0
O(1)−Nb(2)−O(2)	70.3(4)	71.2
O(3)−Nb(2)−O(4)	70.0(4)	69.8

[a] From Table 2.

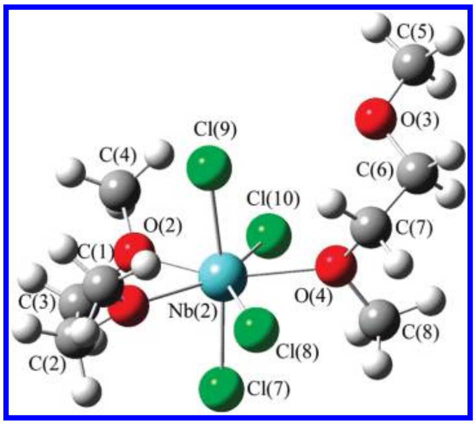


Figure 3. B3LYP/LANL2DZ-optimized structure of **4a**$^+$ in the gas phase.

Table 4. Selected Computed Bond Distances (Å) and Angles (deg) for **4a**$^+$

	Bond Distances (Å)		
Nb(2)−Cl(7)	2.417	Nb(2)−O(1)	2.185
Nb(2)−Cl(8)	2.482	Nb(2)−O(2)	2.191
Nb(2)−Cl(9)	2.371	Nb(2)−O(3)	4.362
Nb(2)−Cl(10)	2.458	Nb(2)−O(4)	2.271
	Bond Angles (deg)		
Cl(7)−Nb(2)−Cl(8)	87.6	Cl(8)−Nb(2)−Cl(9)	93.5
Cl(8)−Nb(2)−Cl(10)	142.2	O(1)−Nb(2)−O(2)	67.2
Cl(7)−Nb(2)−Cl(9)	172.8	O(3)−Nb(2)−O(4)	40.4

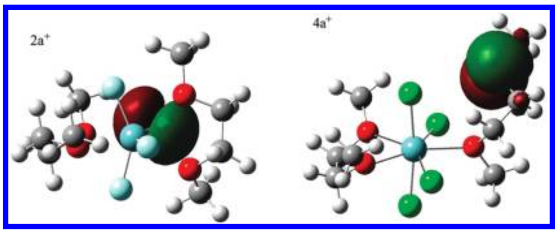


Figure 4. Representation of the HOMO orbitals (isovalue = 0.02) for the cations **2a**$^+$ and **4a**$^+$ [from NBO analysis, calculated with the B3LYP functional using the LANL2DZ basis set and core potential for niobium and the 6-31g(d,p) basis set for the remaining atoms].

involved. In other terms, the Nb−O bonds are strongly polarized on the oxygen atoms, giving poor charge distribution on bond formation. Likewise, the Nb−F bonds are strongly polarized on the fluorine atoms (93%).

Because of the satisfactory accordance between the gas-phase theoretical data and the X-ray parameters collected for **2a**$^+$ (Table 2), we moved to optimize the structure of the analogous chloro-containing cation, i.e., $[NbCl_4(dme)_2]^+$ (**4a**$^+$). With reference to Figure 3, a selection of bond lengths (Å) and angles (deg) is reported in Table 4.

After several attempts (NBO analysis), including changes of the basis set, the best structure that has been achieved for the cation **4a**$^+$ comprises covalent Nb−Cl bonds polarized on the chlorine atoms (79% on average) and highly polarized Nb−O bonds, so that "Coulomblike" interactions may be more properly outlined between the niobium center and the lone pairs on the dme oxygen atoms.

The main difference between **2a**$^+$ and **4a**$^+$ regards the coordination modes of the dme ligands: only one dme ligand has to be considered as coordinated to the metal center via the two oxygen atoms in **4a**$^+$, with the second dme moiety being bound to niobium through one oxygen atom only. As a matter of fact, three calculated Nb−O distances are comparable for the two cations [Nb(2)−O(1) = 2.317 Å, Nb(2)−O(2) = 2.272 Å, and Nb(2)−O(4) = 2.302 Å for **2a**$^+$; Nb(2)−O(1) = 2.185 Å, Nb(2)−O(2) = 2.191 Å, and Nb(2)−O(4) = 2.271 Å for **4a**$^+$]. The remaining Nb−O distance is typical for a Nb−O bond in **2a**$^+$ [Nb(2)−O(3) = 2.379 Å], while a rather longer separation [Nb(2)···O(3) = 4.362 Å] is present in the chloride **4a**$^+$. This feature is probably an effect of the repulsions of the electronic clouds of the chlorine atoms, leading to enlargement of the X(7)−Nb(2)−X(9) angle [172.80° for X = Cl (**4a**$^+$); 144.28° for X = F (**2a**$^+$)].

Evaluation of the atomic coefficients of the highest occupied molecular orbital (HOMO) in **2a**$^+$ has evidenced that the major contribution comes from a p orbital belonging to a fluorine atom. Otherwise, similar analysis on **4a**$^+$ points to the fact that the HOMO is mainly composed by the p orbital bearing the lone pair on the uncoordinated oxygen atom (see Figure 4). In other words, the uncoordinated oxygen, within the κ^1-dme unit in **4a**$^+$, could, in principle, act as an electron donor, although this possibility seems to be inhibited by the steric hindrance exerted by the adjacent chlorine atoms.

Differences in the reactivity of **2a**$^+$ and **4a**$^+$ could be predicted by analyzing the atomic orbital coefficients of the lowest unoccupied molecular orbitals (LUMOs), which should give an idea of the Lewis acidic behavior. Thus, taking into account the dme ligands only, the LUMO is approximately delocalized over all ligands in **2a**$^+$, while in **4a**$^+$, it prevalently originates from empty p orbitals (nonvalence orbitals) centered on the uncoordinated oxygen atom and from empty p orbitals of appropriate symmetry centered on the adjacent methyl carbon atom (see Figure 5). The latter antibonding π*-orbital construction may render the κ^1-dme unit in a **4a**$^+$ suitable site of attack by an incoming nucleophile agent, leading to the breaking of the C−O bond.

We have previously reported[19] that the complex **4a**, analogous to **2a**, forms initially when $NbCl_5$ reacts with

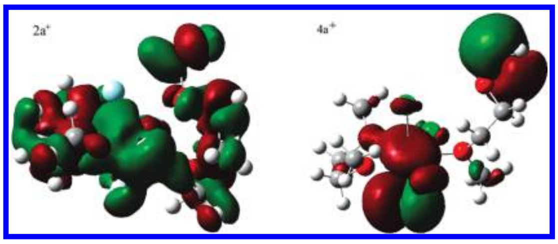
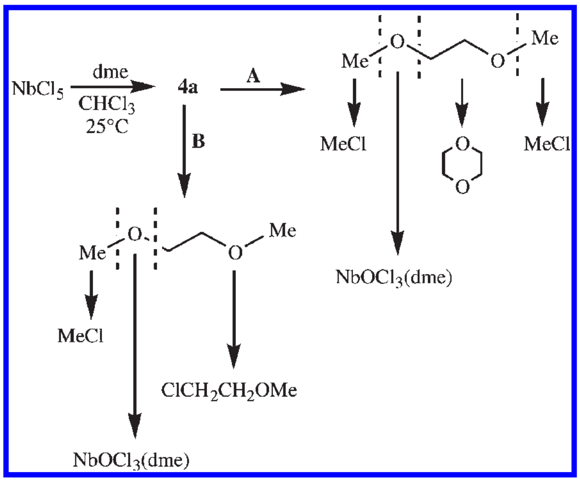


Figure 5. Representation of the LUMO orbitals (isovalue = 0.02) for the cations **2a**$^+$ and **4a**$^+$ [from NBO analysis, calculated with the B3LYP functional using the LANL2DZ basis set and core potential for niobium and the 6-31g(d,p) basis set for the remaining atoms].

Scheme 2. Possible Decomposition Pathways of **4a** in Solution at Room Temperature



dme in chlorinated solvents. In that occasion, the cationic part of **4a** (**4a**$^+$) was claimed to contain an octacoordinated cation on the basis of NMR evidence (the two ^{1}H NMR resonances observed at 253 K in $CDCl_3$ were attributed to two equivalent bidentate dme ligands).[19]

This feature appears to be in contrast with the DFT calculations discussed above, for which we have decided to investigate the low-temperature ^{1}H and ^{13}C NMR spectra of **4a** more deeply. Thus, we have found that at 213 K ($CDCl_3$ solution) the spectra display two singlets due to one κ^2-coordinated dme [^{1}H NMR: δ 3.98 (CH_2), 3.67 (CH_3)] and four additional resonances related to one κ^1-coordinated dme [^{1}H NMR: δ 4.65 (NbO*CH*$_2$), 4.32 (*Me*ONb), 3.88 (*CH*$_2$), 3.41 (*Me*O)]. In summary, an exchange process occurs in **4a**, making the two dme ligands equivalent at room temperature; this process is frozen at 213 K, thus evidencing the presence in solution of $[NbCl_4(\kappa^1\text{-dme})(\kappa^2\text{-dme})][NbCl_6]$, in agreement with what was suggested by the B3LYP/LANL2DZ optimization.

Because of the fact that the nature of the metal atom does not usually influence the chemistry of **1** with O donors, we expected that the reaction of $TaCl_5$ with dme led to the initial formation of an adduct structurally analogous to **4a**. Indeed, the complex **4b** has been identified in a $CDCl_3$ solution at 213 K (see the Experimental Section).

Thermodynamic Stabilities of [NbX$_4$(dme)$_2$][NbX$_6$] (X = F, Cl) Adducts and Thermal Activation of Diethers. In the previous section, we have described the ionic adducts **2a** and **4a**, which form from NbX_5 (X = F, Cl) and dme, showing that the coordination fashion of the O-donor ligands changes according to the nature of the halide.

Then, in order to give thermodynamic support to our discussion, we have calculated the Gibbs free energies involved in the formation of **2a** and **4a** (eqs 1 and 2).[7] On the basis of the data reported in Tables S1 and S2 (see the Supporting Information), we can conclude that both reactions are thermodynamically favored, with that involving the fluoride species being more exoergonic than the other one. Even though the calculations refer to the gas phase, we believe that these results are extensible to the behavior of the species dissolved in a low-polar solvent (e.g., CH_2Cl_2, $CHCl_3$, CD_2Cl_2, and $CDCl_3$).[33]

$$Nb_4F_{20} + 4\text{dme} \rightarrow \underset{\mathbf{2a}}{2[NbF_4(\kappa^2\text{-dme})_2][NbF_6]} \qquad \Delta G_r^\circ = -24.75\ \text{kcal}\cdot\text{mol}^{-1} \tag{1}$$

$$Nb_2Cl_{10} + 2\text{dme} \rightarrow \underset{\mathbf{4a}}{[NbCl_4(\kappa^1\text{-dme})(\kappa^2\text{-dme})][NbCl_6]} \qquad \Delta G_r^\circ = -4.30\ \text{kcal}\cdot\text{mol}^{-1} \tag{2}$$

Once established that the reactions reported in eqs 1 and 2 are spontaneous, we became interested in finding an explanation for the selectivity of the fragmentation reaction occurring when $NbCl_5$ is treated with dme in chlorinated solvents. We have formerly reported[16c] that complex **4a** generates at low temperature but degradates at room temperature with the release of methyl chloride. More precisely, when excess dme is present in the solution, rapid conversion into $NbOCl_3$(dme) and 1,4-dioxane takes place, as depicted in Scheme 2A.[19]

Although several fragmentation ways are possible in principle, our precedent experience in the reactivity of MX_5 (**1**) with polyethers suggested to us the pathway described in Scheme 2B as the most reasonable alternative. The main difference between the two routes lies in the number of the cleaved dme C$-$O bonds: three for reaction A and two for reaction B. In spite of the fact that both reactions considered (Scheme 2A,B) are exoergonic (Table S2 in the Supporting Information), the one leading to 1,4-dioxane (eq 3) is more favored than the alternative one (eq 4), coherently with the experimental evidence.

$$Nb_2Cl_{10} + 4\text{dme} \rightarrow 2NbOCl_3(\text{dme}) + \text{dioxane} + 4MeCl \qquad \Delta G_r^\circ = -106.25\ \text{kcal}\cdot\text{mol}^{-1} \tag{3}$$

$$Nb_2Cl_{10} + 4\text{dme} \rightarrow 2NbOCl_3(\text{dme}) + 2ClCH_2CH_2OMe + 2MeCl \qquad \Delta G_r^\circ = -95.46\ \text{kcal}\cdot\text{mol}^{-1} \tag{4}$$

Analogous calculations have pointed out that the formation of $NbOF_3$(dme) and methyl fluoride, starting

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[33] *Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysic und Technik*, 6th ed.; Landolt-Börnstein Series; Springer Verlag: Berlin, 1969; Vol. *2*.

from Nb_4F_{20},[7] is thermodynamically possible (eqs 5 and 6).

$$Nb_4F_{20} + 8dme \rightarrow 4NbOF_3(dme) + 2dioxane + 8MeF \quad \Delta G_r^\circ = -38.51\ kcal \cdot mol^{-1} \tag{5}$$

$$Nb_4F_{20} + 8dme \rightarrow 4NbOF_3(dme) + 4MeOCH_2CH_2F + 4MeF \quad \Delta G_r^\circ = -27.06\ kcal \cdot mol^{-1} \tag{6}$$

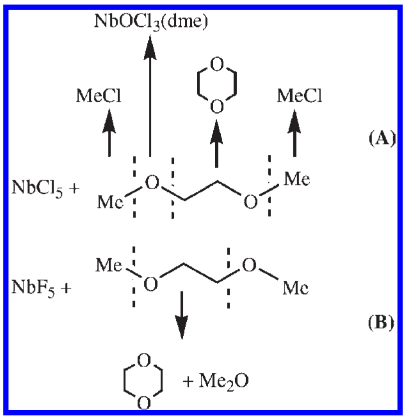
According to the data, both compounds **2a** and **4a** may be viewed as first-step intermediates of a possible reaction involving the dme ligands; the fact that **2a** is isolable at room temperature, while **4a** can be stabilized at low temperature only, should be a consequence of the kinetic inertness of **2a**, induced by the highly energetic M−F bonds (M = Nb, Ta), compared to the M−Cl ones.[34] This observation led us to investigate the thermal stability of the fluorine species $[MF_4(O-O)_2]^+$ ($\mathbf{2}^+$ and $\mathbf{3}^+$; M = Nb, Ta; O−O = diether).

Deuterated chloroform solutions of these cations were obtained by mixing **1a** and **1b** with an equimolar amount of the appropriate diether.[35] The solutions were heated at 70−110 °C in sealed NMR tubes for times variable between 30 min and 4 h (see the Experimental Section). The reactions were monitored by ^1H NMR spectroscopy, observing the progressive disappearance of the starting compounds and contextual formation of colored mixtures of products. The eventual occurrence of redox processes, involving metal reduction, was ruled out in the case of the thermal reaction of **1a** with dme because no signal was detected in the resulting mixture by EPR spectroscopy. Afterward, the final mixtures were treated with an excess of water, in order to make the organic material free from coordination.[17,36] NMR and GC/MS analyses on the resulting solutions revealed the absence of the diether but the presence of different organic substrates (a rough relative quantification of the products was made by using known amounts of CH_2Cl_2 as the NMR standard).

More precisely, at variance to what was described for $NbCl_5$ (Scheme 3A), the heating of dme in the presence of NbF_5 in $CDCl_3$ resulted in the clean formation of 1,4-dioxane and dimethyl ether.[17] The latter were cleanly recovered after hydrolysis and detected in ca. 1:2 ratio (^1H NMR). Coherently, small amounts of the scarcely soluble compounds NbF_5(1,4-dioxane) and $NbF_5(Me_2O)$ were seen by the NMR in solution before the addition of water. Analogous features were found by using TaF_5.

This evidence indicates that, although the coordination compound obtained by the addition of 1 equiv of dme to MF_5 [M = Nb (**2a**), Ta (**2b**)] is stable at room temperature, the dme ligand undergoes modification at higher temperatures. This consists of the breaking of two ethereal C−O bonds (one Me−O and one O−CH_2), the formal combination of the resulting Me and OMe units to give dimethyl ether, and the coupling of two OCH_2CH_2 units to give dioxane (see Scheme 3B). This transformation, proceeding without affecting the M−F bonds, actually occurs selectively in place of those proposed in eqs 5 and 6.

Scheme 3. Fragmentation Reactions of dme in the Presence of NbX_5 (X = F, Cl)



B3LYP/LANL2DZ calculations are in agreement with the fact that the dme fragmentation route, leading to NbF_5(1,4-dioxane) and $NbF_5(Me_2O)$ (eq 7), is more favored than those described in eqs 5 and 6. The situation is reversed when $NbCl_5$ is considered: in such a case, the formation of dioxane, methyl chloride, and $NbOCl_3$(dme), rather than $NbCl_5$(dioxane), $NbCl_5(Me_2O)$, and Me_2O, is more favored by about 70 kcal·mol^{-1}; compare eq 3 with eq 8.

$$Nb_4F_{20} + 4dme \rightarrow 2NbOF_5(dioxane) + 2NbF_5(Me_2O) + 2Me_2O \quad \Delta G_r^\circ = -60.62\ kcal \cdot mol^{-1} \tag{7}$$

$$Nb_2Cl_{10} + 2dme \rightarrow NbCl_5(dioxane) + NbCl_5(Me_2O) + Me_2O \quad \Delta G_r^\circ = -37.07\ kcal \cdot mol^{-1} \tag{8}$$

An overall view of the thermodynamics related to the reaction pathways discussed in the present section is shown in Figure 6. The values of the calculated free energies related to eqs 1−8 are expressed per 1 mol of "NbX_5" unit,[7] in order to make comparisons homogeneous.

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(34) *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1996.

(35) Under the experimental conditions, both $[MF_6]^-$ and $[M_2F_{11}]^-$ anions may coexist as counterions: however, we believe that the nature of the anion does not influence the thermal modification of the O-donor ligand within the cationic unit.

(36) Marchetti, F.; Pampaloni, G.; Zacchini, S. *Polyhedron* **2009**, *28*, 1235.

(37) (a) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *Organometallics* **1991**, *10*, 134. (b) Eaborn, C.; Hitchcock, P. B.; Izod, K.; Smith, J. D. *J. Am. Chem. Soc.* **1994**, *116*, 12071. (c) Deelman, B.-J.; Booij, M.; Meetsma, A.; Teuben, J. H.; Kooijman, H.; Spek, A. L. *Organometallics* **1995**, *14*, 2306. (d) Takaki, K.; Maruo, M.; Kamata, T. *J. Org. Chem.* **1996**, *61*, 8332. (e) Duncalf, D. J.; Hitchcock, P. B.; Lawless, G. A. *Chem. Commun.* **1996**, 269. (f) Cassani, M. C.; Lappert, M. F.; Laschi, F. *Chem. Commun.* **1997**, 1563. (g) Bradley, C. A.; Veiros, L. F.; Pun, D.; Lobkovsky, E.; Keresztes, I.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 16600. (h) La Caër, S.; Mestdagh, H.; Schroeder, D.; Zummack, W.; Schwarz, H. *Int. J. Mass Spectrom.* **2006**, *255−256*, 239. (i) Fedushkin, I. L.; Lukoyanov, A. N.; Hummert, M.; Schumann, H. *Z. Anorg. Allg. Chem.* **2008**, *634*, 357.

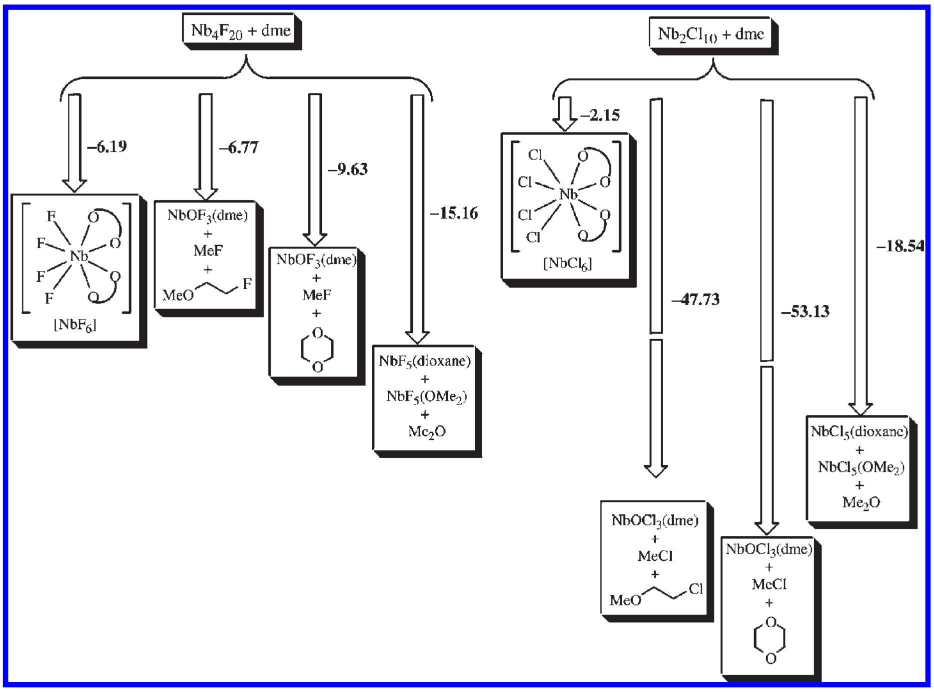

Figure 6. Schematic free-energy scale for the possible reactions of NbX_5 (X = F, Cl) with dme ($\Delta G_r°$ values per 1 mol of NbX_5).

The selective formation of dioxane from dme and MF_5 is noteworthy for two reasons: (i) the MF_5 frame is not affected (coordination adducts of MF_5 with dioxane or dimethyl ether are found as products); (ii) in addition to the cleavage of C−O bonds, new bonds of the same type are formed. Indeed, the direct combination of ethers with compounds containing oxophilic metals (lanthanides, early-transition-metal elements) generally proceeds with the formation of stable metal alkoxides,[37] as a result of C−O bond cleavage. In these cases, the starting ether does not transform into functionalized species but breaks down into smaller fragments. More in particular, dme normally reacts with early-transition-metal compounds with cleavage of either one or two $O-CH_2$ bonds, affording methoxy derivatives.[37e,f,38]

The unusual behavior exhibited by MF_5 when reacted with dme at high temperature should be related to the strongly energetic M−F bond, for which the MF_5 unit comes intact, favoring at the same time some transformation on the organic substrate. These combined features are unprecedented even for other metal fluoride species. For instance, it has been found that TiF_4 is not effective in activating cyclic ethers[39] or dme, whereas the same oxygen compounds may undergo C−O cleavage by means of group 4 tetrachlorides and tetrabromides. Otherwise, tungsten hexafluoride is capable of activating ethers[40a] and dimethyl sulfoxide,[40b] notwithstanding the reactions resulting in the rupture of the WF_6 frame, with the consequent formation of oxyfluoride metal derivatives and fluoro-containing organic molecules.

These considerations outline that the fluorides **1a** and **1b** manifest in their reactivity with oxygen species some precious characteristics that configure them as potential catalysts. This point was investigated in some more detail, and preliminary studies were carried out by using the simplest diether mentioned in this paper, i.e., dme. Hence, we found that heating a $CDCl_3$ solution of complex **2a**, in the presence of ca. 15 equiv of dme, at ca. 363 K in a sealed NMR tube, caused the almost quantitative conversion (93% in 1 h) of dme into dimethyl ether and dioxane. This result indicates that the thermal reaction of **1a** with dme holds the catalytic character (see the Experimental Section for details).

The thermal reaction of TaF_5 with $EtO(CH_2)_2OEt$ provided results similar to those regarding the stability of **2a** and **2b**: 1,4-dioxane and diethyl ether were cleanly recovered in a 1:2 ratio in the final mixture after hydrolysis. Moreover, minor amounts of ethanol were detected, presumably as a result of the hydrolysis of some Ta−OEt moiety. The latter might have been generated in an anhydrous ambient through alternative fragmentation of $EtO(CH_2)_2OEt$.

Although the study of the reactivity of **1a** and **1b** with $MeO(CH_2)_2O(CH_2)_2OMe$ (diglyme) did not allow one to identify any coordination compound,[41] we still tested the

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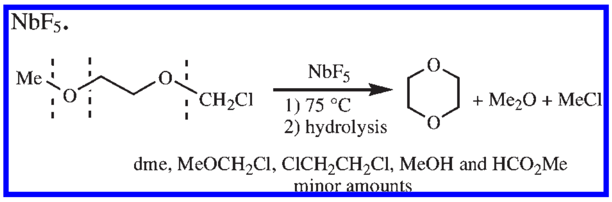
(38) (a) Gun'ko, Y. K.; Hitchcock, P. B.; Lappert, M. F. *J. Organomet. Chem.* **1995**, *499*, 213. (b) Cassani, M. C.; Gun'ko, Y. K.; Hitchcock, P. B.; Hulkes, A. G.; Khvostov, A. V.; Lappert, M. F.; Protchenko, A. V. *J. Organomet. Chem.* **2002**, *647*, 71. (c) Le Caër, S.; Heninger, M.; Lemaire, J.; Boissel, P.; Matre, P.; Mestdagh, H. *Chem. Phys. Lett.* **2004**, *385*, 273. (d) Le Caër, S.; Heninger, M.; Pernot, P.; Mestdagh, H. *J. Phys. Chem. A* **2006**, *110*, 9654. (e) Bradley, C. A.; Veiros, L. F.; Chirik, P. J. *Organometallics* **2007**, *26*, 3191. (f) Fedushkin, I. L.; Girgsdies, F.; Schumann, H.; Bochkarev, M. N. *Eur. J. Inorg. Chem.* **2001**, 2405.

(39) Delaney, P. A.; Johnstone, R. A. W.; Entwistle, I. D. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1855.

(40) (a) Noble, A. M.; Winfield, J. M. *Inorg. Nucl. Chem. Lett.* **1968**, *4*, 339. (b) Darragh, J. I.; Noble, A. M.; Sharp, D. W. A.; Winfield, J. M. *J. Inorg. Nucl. Chem.* **1970**, *32*, 1745.

(41) The characterization of the products of the reactions of NbF_5 with diglyme in different molar ratios failed. However, the ^{19}F NMR spectrum, recorded at 213 K on the mixture obtained from NbF_5 (0.30 mmol) and diglyme (0.40 mmol) in CD_2Cl_2 (0.70 mL), clearly pointed out the formation of the $[NbF_6]^-$ ion (decet centered at 103.5 ppm, $^1J_{Nb-F}$ = 335 Hz). In agreement with the possible formation of ionic species, the molar conductivity (L_M, 293 K) of a CH_2Cl_2 solution of NbF_5 (0.80 mmol) and diglyme (0.85 mmol) resulted in 5.5 $S \cdot cm^2 \cdot mol^{-1}$.

Scheme 4. Fragmentation of $MeO(CH_2)_2OCH_2Cl$ in the Presence of NbF_5



thermal stability of this polyether in the presence of NbF_5. Dimethyl ether and 1,4-dioxane, in a 1:1 ratio, were the only products found in the reaction mixture after treatment with water. This outcome may be explained on the basis of the cleavage of one internal C−O and one external C−O bond, similarly to what was described for $RO(CH_2)_2OR$ (R = Me, Et). Such fragmentation would produce dme and dioxane. Further transformation of the former into dioxane and dimethyl ether (eq 7) could then occur.

The chloromethyl ether $MeO(CH_2)_2OCH_2Cl$ slowly degrades in the presence of **1a** even at room temperature, accounting for the complicated mixtures of products obtained from the reaction (see above). The fragmentation is fast at 75 °C and leads to a mixture of 1,4-dioxane, Me_2O, and MeCl, together with minor amounts of $MeO(CH_2)_2OMe$ (dme), $MeOCH_2Cl$, $ClCH_2CH_2Cl$, MeOH, and HCO_2Me, observed after hydrolysis (see Scheme 4). According to these data, the fragmentation of $MeO(CH_2)_2OCH_2Cl$ is nonselective and seems to involve three of the four C−O bonds of the molecule, i.e., Me−O, $MeO-CH_2$, and $ClCH_2-O$. Actually, the recognition of 1,4-dioxane, dimethyl ether, (chloromethyl)methyl ether, 1,2-dichloroethane, and dme is coherent with this hypothesis. On the other hand, the absence of $ClCH_2OCH_2Cl$ among the organic products supports the idea that the CH_2-OCH_2Cl bond does not break during the process.

Interestingly, CH_3Cl and a small quantity of the complex $NbF_5(HCO_2Me)$[17] have been detected by NMR in the final reaction mixture before treatment with water (see the Experimental Section). The formation of methyl chloride, as well as that of methyl formate, might be explained on the basis of the occurrence of some secondary fragmentation pathway, including C−H bond activation.

The high-temperature activation of 1,2-dimethoxypropane, in the presence of TaF_5, follows a route different from those formulated above: no dioxane-type compounds have been found as products of this thermal reaction. Instead, Me_2O and acetone have been detected, together with some methanol and $MeOCH_2CH(Me)OH$. The production of acetone could be explained on the basis of the formation of the hypothetical transient species $[CH_2CH(CH_3)O]$, which would rearrange to $(CH_3)_2CO$ rather than coupling with another unit of the same type to give methyl-substituted dioxane (see Scheme 5). A summary of the outcomes of the thermal reactions of MF_5 with diethers is given in Table 5.

Scheme 5. Formation of Acetone and Dimethyl Ether by the Thermal Fragmentation of 1,2-Dimethoxypropane in the Presence of TaF_5

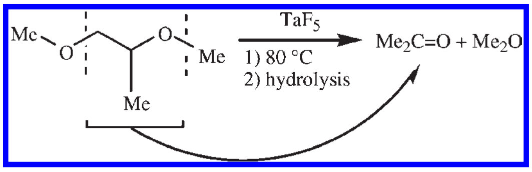
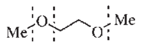
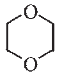
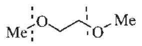
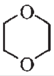
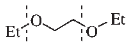
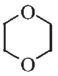
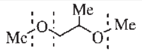
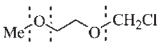
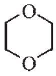
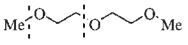
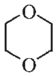


Table 5. Products (after Hydrolysis) of the Thermal Activation of Diethers by MX_5 (M = Nb, Ta; X = F, Cl)[a]

Halide	Diether	Products
MCl_5		MeCl +  [b]
MF_5		Me_2O +  [c]
TaF_5		Et_2O +  [d]
MF_5		$Me_2O + Me_2C=O$ [e]
NbF_5		Me_2O +  + MeCl + dme + MeOH + $ClCH_2CH_2Cl$ + + $MeOCH_2Cl$ + HCO_2Me
NbF_5		Me_2O + 

[a] The bonds undergoing cleavage are indicated. [b] $MOCl_3(dme)$ has been identified before hydrolysis. [c] NbF_5(1,4-dioxane) and $NbF_5(OMe_2)$ have been identified before hydrolysis. [d] Minor amounts of EtOH are produced. [e] Minor amounts of MeOH and $MeOCH_2CH(Me)OH$ (M = Nb) are produced.

Conclusions

The reactions of a variety of simple diethers (O−O) with MF_5 (M = Nb, Ta) to give ionic adducts containing octacoordinated cations of formula $[MF_4(O-O)_2]^+$ have been studied, and the uncommon X-ray structures of the complexes $[MF_4(\kappa^2\text{-dme})_2][MF_6]$ (M = Nb, Ta) have been determined.

The B3LYP/LANL2DZ method has been revealed to be efficient in predicting the structure of the cation $[NbF_4(\kappa^2\text{-dme})_2]^+$ and that of the previously reported $[NbCl_4(\kappa^1\text{-dme})(\kappa^2\text{-dme})]^+$. Although the calculation results refer to the gas phase, they are in good agreement with the experimental evidence, collected both in the solid state and in nonpolar chlorinated solvents.

We have shown that the fragmentation of dme, coordinated to the $[NbX_4]^+$ frame (X = F, Cl), is a thermodynamically spontaneous reaction that is essentially driven by the Nb−X bond energy. Therefore, for the fluoride species, the reaction takes place, preserving the metal−fluorine bonds, and affords, unusually, dioxane and dimethyl ether. Conversely, metal−chlorine bonds are involved in the activation of the $[NbCl_4(dme)_2]^+$ species.

Different diethers, $ROCH_2CH(R')OR''$, can be activated thermally in the presence of MF_5; however, fragmentation routes alternative to that described for dme may be operative, depending on the nature of the substituents R and R′.

Even though the results presented herein refer to stoichiometric reactions involving simple organic molecules, really they indicate that group 5 pentafluorides are capable of promoting unusual transformations on oxygen-containing substrates. Remarkably, such transformations do not affect the MF_5 frame, and, interestingly, we have found that the activation of dme by means of NbF_5 may hold catalytic character. These points suggest that the use of niobium and tantalum pentafluorides in metal-directed reactions involving oxygen species is promising and deserves further deepening. Advancements in this field should be really accomplishable (the chemistry of group 5 pentahalides has not been explored intensively heretofore) and desirable, thinking of the substantial biocompatibility of niobium and tantalum.

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Supporting Information Available: Tables S1 and S2 and X-ray crystallographic data in CIF format [CCDC 750819 (**2a**) and 750820 (**4a**)]. This material is available free of charge via the Internet at http://pubs.acs.org. The atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.