Inorg. Chem. **2008**, *47*, 365–372

Inorganic Chemistry
Article

Reactivity of Niobium and Tantalum Pentahalides with Cyclic Ethers and the Isolation and Characterization of Intermediates in the Polymerization of Tetrahydrofuran

Fabio Marchetti,[†,§] Guido Pampaloni,*[,†] and Stefano Zacchini[‡]

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

Received June 22, 2007

The complexes $MX_5(THF)$ (M = Nb, X = Cl, **2a**; M = Ta, X = F, **2c**, X = Cl, **2d**) and $[MX_4(THF)\{O(CH_2)_4\text{-}\overline{O(CH_2)_3CH_2}\}][MX_6]$ (M = Nb, X = Cl, **3a**; M = Ta, X = Cl, **3d**, X = Br, **3e**, X = I, **3f**) result from reactions of MX_5 with 0.5 and 1.5 equiv of THF, respectively. Compounds **3** contain the unprecedented 4-(tetrahydrofuran-1-ium)-butan-1-oxo ligand and are likely to play a role in the course of THF polymerization catalyzed by MX_5. The addition of L (L = 2,5-dimethyltetrahydrofuran, tetrahydropyran, 1,4-dioxane) to MX_5 results in the formation of the hexacoordinated complexes $MX_5(L)$. The molecular structures of **2d**, **3d**, and $NbCl_5$(dioxane), **6a**, have been ascertained by X-ray diffraction studies.

Introduction

The halides of early transition elements are often used as starting materials for the synthesis of inorganic or organometallic compounds, although they can induce parasitic reactions when contacted with species containing Lewis basic functionalities. This is particularly true in the case of the halides of the Group 5 metals in the highest oxidation state, MX_5, M = Nb, Ta.[1] For example, deoxygenation reactions[2] have been observed with these powerful Lewis acids, and examples have been reported regarding sulfoxides and phosphine oxides,[3] ketones,[4] and crown ethers.[5] Therefore, the coordination chemistry of MX_5, M = Nb, Ta, with oxygen donor ligands is scarcely developed, if we except alcohols or diols.[6]

In the framework of our research on the chemistry of early transition elements, we became interested in the reactivity of MX_5 (M = Nb, X = Cl, **1a**, Br, **1b**; M = Ta, X = F, **1c**, Cl, **1d**, Br, **1e**, I, **1f**) with aliphatic cyclic ethers and with THF in particular. This interest has stemmed from the observation that, although THF is widely used as solvent and it forms complexes with many transition metals,[6a] 1:1 adducts with the general formula $MCl_5(THF)$ have been identified (^1H NMR) only in diluted solution at ca. −60 °C.[7] A reason for this lack of studies may be related to the known tendency of niobium and tantalum pentachlorides to cause ring-opening and polymerization of THF.[8]

In this paper, we report on the reactivity of MX_5 with

---

[*] To whom correspondence should be addressed. E-mail: pampa@dcci.unipi.it. Tel: +39 050 2219 219. Fax: +39 050 2219 246.

[†] Università di Pisa.

[§] Born in Bologna (Italy) in 1974.

[‡] Università di Bologna.

(1) 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 but mononuclear in the vapor phase [Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, 1993]. For the sake of simplicity, the formula MX_5 will be used in this paper when dealing with the niobium(V) and tantalum(V) halides.

(2) Hubert Pfalzgraf, L. G.; Postel, M.; Riess, J. G. Niobium and Tantalum. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, 1987; Vol 3, pp 594, 631.

(3) (a) Copley, D. B.; Fairbrother, F.; Grundy, K. H.; Thompson, A. *J. Less-Common Met.* **1964**, *6*, 407. (b) Copley, D. B.; Fairbrother, F.; Thompson, A. *J. Less-Common Met.* **1965**, *8*, 256.

(4) Gill, M. S.; Ahuja, H. S.; Rao, G. S. *J. Indian Chem. Soc.* **1978**, *55*, 875.

(5) Bulychev, B. M.; Bel'skii, V. K. *Russ. J. Inorg. Chem.* **1995**, *40*, 1765.

(6) (a) *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T, J., Eds.; Pergamon: Oxford, 2004. (b) For a review on the reactivity of MCl_5 with alcohols or phenols see: Bradley, D. C.; Merhotra, R. C.; Singh, A.; Rothwell, I. P. *Alkoxo and Phenoxo Derivatives of Metals*; Academic Press: London, 2001. (c) See also M. J. Heeg, M. J.; Williams, D. S.; Korolev, A. quoted as Private communication, 2005 on the Cambridge Structural Database (CSD), 2005. Refcodes KARCEM and RATPEI.

(7) Merbach, A.; Bünzli, J. C. *Helv. Chim. Acta* **1972**, *55*, 580.

(8) Fairbrother, F.; Nixon, J. F. *J. Chem. Soc.* **1962**, 150. Takegami, Y.; Ueno, T.; Hirai, R. *J. Pol. Sci. Polym. Chem.* **1966**, *4*, 973.

10.1021/ic7012254 CCC: $40.75

limited amounts of THF on changing the nature of the halide and the solid-state characterization of $TaCl_5(THF)$, **2d**, and $[TaCl_4(THF)\{O(CH_2)_4\overline{O(CH_2)_3CH_2}\}][TaCl_6]$, **3d**, an ionic compound containing the unprecedented 4-(tetrahydrofuran-1-ium)-butan-1-oxo ligand. Moreover, the chemistry of MX_5 with a series of different aliphatic cyclic ethers [2,5-dimethyltetrahydrofuran (THF*), tetrahydropyran (THP), 1,4-dioxane (diox)] will be presented and discussed.

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} mm Hg), and then filled with argon. Niobium and tantalum pentafluorides were commercial products (Aldrich) of the highest purity available. The pentachlorides MCl_5 were commercial products (Fluka), sublimed at 100−110 °C/10^{-2} Torr before use. $NbBr_5$ (**1b**), $TaBr_5$ (**1e**), and TaI_5 (**1f**) were prepared according to published procedures.[9] Solvents and liquid reagents were distilled before use under argon atmosphere from appropriate drying agents: CH_2Cl_2, CD_2Cl_2, and $CDCl_3$ from P_4O_{10}, THF from Na/benzophenone, pentane from $LiAlH_4$, and THF*, THP, and 1,4 dioxane from metallic sodium. Infrared spectra were recorded at 298 K either on a FTIR Perkin-Elmer spectrometer equipped with a UATR sampling accessory (solid samples) or on a FTIR Perkin-Elmer Paragon 500 spectrometer (nujol mulls). NMR measurements were performed either on Mercury Plus 400 instrument or on Varian Gemini 200BB spectrometer. The chemical shifts for ^1H, ^{13}C, or ^{19}F were referenced to internal TMS or to $CFCl_3$, respectively. Unless otherwise specified, NMR measurements were recorded at 298 K.

Carbon and hydrogen analyses were performed at the Dipartimento di Chimica Farmaceutica of the University of Pisa on a Carlo Erba model 1106 instrument, paying particular attention to the more sensitive compounds which were weighed and directly introduced into the analyzer. The halide content was determined by the Volhardt method[10] after exaustive hydrolysis of the sample. Niobium and tantalum were analyzed as M_2O_5 obtained by hydrolysis of the sample followed by calcination in a platinum crucible. The halide and the metal analyses were repeated twice in order to get reproducible results.

1. Preparation of $MX_5(THF)$ Complexes. Only the preparation of $TaCl_5(THF)$, **2d**, is described in detail, the others being performed in a similar way.

1.A. $TaCl_5(THF)$, 2d. A suspension of $TaCl_5$ (0.450 g, 1.26 mmol), in CH_2Cl_2 (10 mL), was treated with THF (0.050 mL, 0.62 mmol), and the resulting mixture was stirred at room temperature for 30 min. Hence, the mixture was filtered in order to remove unreacted $TaCl_5$, and the solution was dried in vacuo, affording a colorless solid. Crystallization from CH_2Cl_2/pentane at ca. −30 °C gave moisture-sensitive crystals of **2d** suitable for X-ray analysis. Yield: 0.240 g (90%). Anal. Calcd for $C_4H_8Cl_5OTa$: C, 11.2; H, 1.9; Ta, 42.0; Cl, 41.2. Found: C, 11.1; H, 1.8; Ta, 42.3; Cl, 41.0. IR (nujol mull): 1044w, 817m-s cm^{-1} (THF). ^1H NMR (200 MHz, $CDCl_3$): δ 4.82 (m, 4H, OCH_2), 2.21 (m, 4H, OCH_2CH_2). ^{13}C NMR (200 MHz, $CDCl_3$): δ 81.6 (OCH_2), 26.2 (OCH_2CH_2).

1.B. $NbCl_5(THF)$, 2a. Yellow, air-sensitive solid; 83% yield from **1a** (0.350 g, 1.30 mmol) and THF (0.050 mL, 0.62 mmol). Anal. Calcd for $C_4H_8Cl_5NbO$: C, 14.0; H, 2.4; Nb, 27.1; Cl, 51.8. Found: C, 13.9; H, 2.3; Nb, 27.2; Cl, 51.7. IR (solid): 1017w, 865s, 841s cm^{-1} (THF). ^1H NMR (200 MHz, $CDCl_3$): δ 4.69 (m, 4H, OCH_2), 2.19 (m, 4H, OCH_2CH_2). ^{13}C NMR (200 MHz, $CDCl_3$): δ 80.7 (OCH_2), 26.0 (OCH_2CH_2).

1.C. $TaF_5(THF)$, 2c. Light brown, air-sensitive solid; 79% yield from **1c** (0.320 g, 1.16 mmol) and THF (0.100 mL, 1.24 mmol). Anal. Calcd for $C_4H_8F_5OTa$: C, 13.8; H, 2.3; Ta, 52.0. Found: C, 13.6; H, 2.2; Ta, 51.6. ^1H NMR (200 MHz, $CDCl_3$): δ 4.44 (m, 4H, OCH_2), 2.19 (m, 4H, OCH_2CH_2). ^{13}C NMR (200 MHz, $CDCl_3$): $\delta = 75.7$ (OCH_2), 25.1 (OCH_2CH_2). ^{19}F NMR (200 MHz, $CDCl_3$): δ 80.1 (br, 1F, *trans*-F), 39.2 (br, 4F, *cis*-F).

1.D. $TaBr_5(THF)$, 2e. Reaction performed at 0 °C. Orange, air-sensitive solid; 82% yield from **1e** (0.300 g, 0.517 mmol) and THF (0.010 mL, 0.13 mmol). Anal. Calcd for $C_4H_8Br_5OTa$: C, 7.4; H, 1.2; Ta, 27.7; Br, 61.2. Found: C, 7.3; H, 1.3; Ta, 27.4; Br, 61.0. ^1H NMR (200 MHz, $CDCl_3$): δ 4.97 (m, 4H, OCH_2), 2.25 (m, 4H, OCH_2CH_2).

2. Preparation of $[MX_4(THF)\{O(CH_2)_4\overline{O(CH_2)_3CH_2}\}][MX_6]$ Complexes. Only the preparation of $[TaCl_4(THF)\{O(CH_2)_4\overline{O(CH_2)_3CH_2}\}][TaCl_6]$, **3d**, is described in detail, the others being performed in a similar way.

2.A. $[TaCl_4(THF)\{O(CH_2)_4\overline{O(CH_2)_3CH_2}\}][TaCl_6]$, 3d. A suspension of $TaCl_5$ (0.650 g, 1.81 mmol), in CH_2Cl_2 (10 mL) was treated with THF (0.220 mL, 2.73 mmol), and the mixture was stirred at room temperature for 15 min. The final resulting solution was dried in vacuo, and a colorless solid was obtained. A ^1H NMR spectrum of this solid dissolved in CD_2Cl_2 evidenced the presence of **2d** and **3d** in a 2:1 molar ratio. Crystallization from CH_2Cl_2/pentane at room temperature gave moisture-sensitive crystals of **3d** suitable for X-ray analysis. Yield: 0.412 g (49%). Anal. Calcd for $C_{12}H_{24}Cl_{10}O_3Ta_2$: C, 15.5; H, 2.6; Ta, 38.8; Cl, 38.0. Found: C, 15.4; H, 2.4; Ta, 38.4; Cl, 37.7. IR (solid): 2982w, 2958w, 2876w, 1443m-w, 1248s, 1083vs, 1046m-w, 985m-s (THF), 948m, 926m cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 5.45, 4.88, 4.42, 3.66 (m, 12 H, OCH_2), 2.23, 1.83 (m br, 12 H, CH_2). ^{13}C NMR (200 MHz, $CDCl_3$): δ 85.7, 80.4, 71.5, 69.4 (OCH_2), 32.7, 29.9, 28.2, 26.2 (CH_2).

2.B. $[NbCl_4(THF)\{O(CH_2)_4\overline{O(CH_2)_3CH_2}\}][NbCl_6]$, 3a. Yellow, air-sensitive solid; 52% yield from THF (0.240 mL, 2.96 mmol) and **1e** (0.532 g, 1.97 mmol). Anal. Calcd for $C_{12}H_{24}Cl_{10}Nb_2O_3$: C, 19.0; H, 3.2; Nb, 24.6; Cl, 46.9. Found: C, 18.9; H, 3.1; Nb, 24.3; Cl, 46.6. ^1H NMR (200 MHz, $CDCl_3$): δ 5.56, 4.94, 4.31, 3.70 (m, 12 H, OCH_2), 2.20, 1.97, 1.66 (m br, 12 H, CH_2). ^{13}C NMR (200 MHz, $CDCl_3$): δ 86.0, 80.9, 70.8, 70.5 (OCH_2), 31.9, 29.8, 28.2, 26.3 (CH_2).

2.C. $[NbBr_4(THF)\{O(CH_2)_4\overline{O(CH_2)_3CH_2}\}][NbBr_6]$, 3b. Red, air-sensitive solid; 77% yield from THF (0.110 mL, 1.40 mmol) and **1b** (0.405 g, 0.822 mmol). Anal. Calcd for $C_{12}H_{24}Br_{10}Nb_2O_3$: C, 12.0; H, 2.0; Nb, 15.5; Br, 66.5. Found: C, 11.9; H, 1.9; Nb, 15.3; Br, 66.3. IR (nujol mull): 1096w, 816ms cm^{-1} (THF). ^1H NMR (200 MHz, $CDCl_3$): δ 5.42, 4.90, 3.60, 3.43 (m, 12 H, OCH_2), 2.23, 1.90, 1.58 (m, 12 H, CH_2). ^{13}C NMR (200 MHz, $CDCl_3$): δ 86.6, 81.2, 71.2, 69.1 (OCH_2), 32.5, 29.0, 28.1, 26.3 (CH_2).

2.D. $[TaBr_4(THF)\{O(CH_2)_4\overline{O(CH_2)_3CH_2}\}][TaBr_6]$, 3e. Yellow, air-sensitive solid; 82% yield from THF (0.063 mL, 0.78 mmol) and **1e** (0.300 g, 0.517 mmol). Anal. Calcd for $C_{12}H_{24}Br_{10}O_3Ta_2$: C, 10.5; H, 1.8; Ta, 26.3; Br, 58.0. Found: C, 10.5; H, 1.7;

---

[9] Calderazzo, F.; Pallavicini, P.; Pampaloni, G.; Zanazzi, P. F. *J. Chem. Soc. Dalton Trans.* **1990**, 2743.

[10] Skoog, D. A.; West, D. M. *Fundamentals of Analytical Chemistry*, 2nd ed.; Holt, Rinehart and Winston: Chatham, U.K., 1974; p 233.

Ta, 26.0; Br, 57.8. IR (solid): 2959w, 2901w, 2875w, 1453wm, 1260s, 1083vs, 1044wm, 990ms (THF), 950m, 926ms cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.51, 4.93, 3.55, 3.46 (m, 12 H, OC*H*$_2$), 2.20, 1.93, 1.69 (m, 12 H, C*H*$_2$). ^{13}C NMR (400 MHz, CD_2Cl_2): δ 85.5, 81.4, 71.7, 70.8 (O*C*H$_2$), 31.4, 29.3, 28.6, 26.4 (*C*H$_2$).

2.E. $[TaI_4(THF)\{O(CH_2)_4\overline{O(CH_2)_3CH_2}\}][TaI_6]$, 3f. Dark red, air-sensitive solid; 81% yield from THF (0.045 mL, 0.59 mmol) and **1f** (0.280 g, 0.343 mmol). Anal. Calcd for $C_{12}H_{24}I_{10}Ta_2O_3$: C, 7.8; H, 1.3; Ta, 19.6; I, 68.7. Found: C, 7.6; H, 1.2; Ta, 19.4; I, 68.4. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.50, 4.31, 3.47, 3.24 (m br, 12 H, OC*H*$_2$), 2.15, 1.91, 1.77 (m, 12 H, C*H*$_2$). ^{13}C NMR (200 MHz, $CDCl_3$): δ 85.0, 81.4, 70.2, 69.8 (O*C*H$_2$), 32.8, 29.6, 28.2, 26.0 (*C*H$_2$).

3. Formation of Bis(4-chlorobutyl)ether, $O[(CH_2)_4Cl]_2$ from 3d. To a CH_2Cl_2 solution (20 mL) of **3d** (0.340 g, 0.365 mmol), prepared from $TaCl_5$ and THF as described in Section 2.A., a solution of KOH (0.210 g, 3.74 mmol) in H_2O (7 mL) was added dropwise. The formation of a colorless precipitate occurred immediately. The mixture was filtered on an alumina column (2 × 5 cm), and the column was washed with CH_2Cl_2 (10 mL). A GC/MS analysis of the eluted solution indicated the presence of THF and of bis(4-chlorobutyl)ether, the identity of which was further confirmed by ^{1}H NMR spectroscopy.

4. Preparation of TaX_5(THF*), 4d−e. 4.A. $TaCl_5$(THF*), 4d. To a suspension of $TaCl_5$ (0.375 g, 1.05 mmol) in CH_2Cl_2 (10 mL) THF* (0.200 mL, 1.66 mmol) was added, and the mixture was stirred at room temperature for 30 min. Complex **4d** was isolated as a light-yellow solid upon removal of the solvent and all volatile materials in vacuo. The compound was recrystallized from dichloromethane/pentane. Yield: 0.395 g, 82%. Anal. Calcd for $C_6H_{12}Cl_5OTa$: C, 15.7; H, 2.6; Ta, 39.5; Cl, 38.7. Found: C, 15.5; H, 2.5; Ta, 39.2; Br, 38.6. IR(solid): 2962w, 2931w, 2875w, 1591wm, 1532m, 1486m, 1456m, 1381m-w, 1263m-w, 872vs, 814vs cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ (major isomer) 4.23 (m, 1H, C*H*), 1.98 (m, 2H, C*H*$_2$), 1.54 (m, 3H, Me); δ (minor isomer) 5.69 (m, 1H, C*H*), 2.31 (m, 2H, C*H*$_2$), 1.64 (m, 3H, Me). Isomer ratio 5:2. ^{13}C NMR (200 MHz, $CDCl_3$): δ (major isomer) 88.8 (*C*H), 57.8 (*C*H$_2$), 25.4 (Me); δ (minor isomer) 58.4 (*C*H$_2$), 22.1 (Me).

4.B. $TaBr_5$(THF*), 4e. Compound **4e** was obtained as a yellow solid by the same procedure as that described for **4d**, by reacting $TaBr_5$ (0.270 g, 0.465 mmol) with THF* (0.095 mL, 0.79 mmol). Yield: 0.269 g, 85%. Anal. Calcd for $C_6H_{12}Br_5OTa$: C, 10.6; H, 1.8; Ta, 26.6; Br, 58.7. Found: C, 10.5; H, 1.7; Ta, 26.4; Br, 58.5. IR(solid): 2944wm, 2865w, 1429w, 1380w-br, 1261s, 1183m-sh, 1074vs, 1036vs, 952vw, 800s, 725m cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ (major isomer) 4.22 (m, 1 H, C*H*), 2.02 (m, 2 H, C*H*$_2$), 1.83 (m, 3 H, Me); δ (minor isomer) 5.86 (m, 1H, C*H*), 2.19 (m, 2H, C*H*$_2$), 1.78 (m, 3H, Me). Isomer ratio 3:1. ^{13}C NMR (200 MHz, $CDCl_3$): δ 94.2 (*C*H), 39.5, 38.7 (*C*H$_2$), 26.6 (Me).

5. Preparation of TaX_5(THP), 5d−e. 5.A. $TaCl_5$(THP), 5d. A suspension of $TaCl_5$, (0.400 g, 1.12 mmol), in CH_2Cl_2 (15 mL), was treated with THP (0.180 mL, 1.85 mmol). After 30 min of stirring, the solvent was removed in vacuo and a colorless residue was obtained. The residue was washed with pentane (2 × 10 mL), giving a colorless microcrystalline compound identified as **5d** (0.390 g, 76% yield). Anal. Calcd for $C_5H_{10}Cl_5OTa$: C, 13.5; H, 2.3; Ta, 40.7; Cl, 39.9. Found: C, 13.3; H, 2.2; Ta, 40.4; Cl, 39.4. IR(solid): 2962m, 2916m, 2848m, 1259s, 1079s, 1014vs, 863m, 792vs cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.01 (m, 4H, OC*H*$_2$), 1.63 (m, 6H, OCH$_2$C*H*$_2$ and OCH$_2$CH$_2$C*H*$_2$). ^{13}C NMR (200 MHz, $CDCl_3$): δ 71.0 (TaO*C*H$_2$), 26.3, 22.5 (*C*H$_2$).

5.B. $TaBr_5$(THP), 5e. Compound **5e** was obtained in 70% yield as a yellow solid by the same procedure as that described for **5d**, by reacting $TaBr_5$ (0.480 g, 0.827 mmol) with THP (0.130 mL, 1.33 mmol). Anal. Calcd for $C_5H_{10}Br_5OTa$: C, 9.0; H, 1.5; Ta, 27.1; Br, 59.9. Found: C, 8.9; H, 1.5; Ta, 26.8; Br, 59.6. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.86 (m, 4H, OC*H*$_2$), 1.70 (m, 6H, OCH$_2$C*H*$_2$ and OCH$_2$CH$_2$C*H*$_2$). ^{13}C NMR (200 MHz, $CDCl_3$): δ 70.0 (TaO*C*H$_2$), 26.1, 22.7 (*C*H$_2$).

6. Preparation of MCl_5(diox), 6a,d. 6.A. $NbCl_5$(diox), 6a. A suspension of $NbCl_5$ (0.350 g, 1.30 mmol) in CH_2Cl_2 (10 mL) was treated with diox (0.160 mL, 1.88 mmol). The mixture was stirred for 1 h, and then the solvent was removed. A light-yellow solid, identified as **6a** (0.368 g 79% yield), was obtained upon washings with pentane (2 × 10 mL). X-ray quality crystals of **6a** were obtained at ca. 253 K from a CH_2Cl_2 solution layered with pentane. Anal. Calcd for $C_4H_8Cl_5NbO_2$: C, 13.4; H, 2.3; Nb, 25.9; Cl, 49.5. Found: C, 13.2; H, 2.2; Nb, 25.6; Cl, 49.1. IR (solid): 2962w, 2934w, 2864w, 1445m, 1367m, 1332m, 1289m, 1254s, 1117s, 1077m, 1015m, 964m, 890m-s, 861vs, 799vs cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 4.12 (br). ^{13}C NMR (200 MHz, $CDCl_3$, 298 K): δ 67.8 (br). ^{1}H NMR (200 MHz, $CDCl_3$, 323 K): δ 4.13 (s). ^{1}H NMR (200 MHz, $CDCl_3$, 243 K): δ 4.67 (br, 4H), 4.00 (s, 4H), 3.76 (s, 8H). ^{1}H NMR (200 MHz, $CDCl_3$, 213 K): δ 4.98 (s, 2H), 4.36 (s, 2H), 3.99 (s, 4H), 3.77 (s, 8H).

6.B. $TaCl_5$(diox), 6d. Compound **6d** was obtained as a colorless microcrystalline solid by the same procedure as that described for **6a**, by reacting $TaCl_5$ (0.335 g, 0.935 mmol) with diox (0.120 mL, 1.41 mmol). Yield: 0.334 g (80%). Anal. Calcd for $C_4H_8Cl_5O_2Ta$: C, 10.8; H, 1.8; Ta, 40.5; Cl, 39.7. Found: Ta, C, 10.6; H, 1.7; Ta, 40.2; Cl, 39.4. IR (solid): 2963w, 2920w, 1599w, 1450wm, 1372w, 1296w, 1257s, 1111s, 1077m-s, 1041s, 890s, 860vs, 794vs cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.79 (m, 4H, TaOC*H*$_2$), 3.98 (m, 4H, TaOCH$_2$C*H*$_2$). ^{13}C NMR (200 MHz, $CDCl_3$): δ 79.1 (TaO*C*H$_2$), 65.6 (TaOCH$_2$*C*H$_2$).

X-ray Crystallography. Crystal data and collection's details for **2d**, $[TaCl_4(THF)\{O(CH_2)_4\overline{O(CH_2)_3CH_2}\}][TaCl_6]\cdot 0.5CH_2Cl_2$, **3d·0.5CH$_2Cl_2$**, and **6a** are listed in Table 1. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector using Mo Kα radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS[11]). Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[12] Hydrogen atoms bonded to carbon atoms were fixed at calculated positions and refined by a riding model. The crystal of **3d·0.5CH$_2$Cl$_2$** was racemically twinned with a refined Flack parameter of 0.228(18),[13] and it was refined using the TWIN refinement routine of SHELXTL. Restraints were applied to bond distances and anisotropic displacement parameters of carbon and oxygen atoms in **3d·0.5CH$_2$Cl$_2$** in order to obtain a satisfactory model (empirical, SADABS[11]). The structures were solved by direct methods and refined by full-matrix least-squares procedures (SHELX97[12]). Due to the strong absorptions of tantalum and niobium, some high electron densities, all located close to the heavy atoms, remained in the structures of **3d·0.5CH$_2$Cl$_2$** and **6a**, respectively. They could not completely corrected by SADABS[11] even by using different sets of parameters.

---

(11) Sheldrick, G. M. *SADABS, Program for Empirical Absorption Correction*; University of Göttingen: Göttingen, Germany, 1996.

(12) Sheldrick, G. M. *SHELX97, Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1997.

(13) Flack, H. D. *Acta Crystallogr., Sect. A* **1983**, *39*, 876.

Table 1. Crystal Data and Details of the Structure Refinement for Compounds **2d**, **3d·0.5CH$_2$Cl$_2$**, and **6a**[a]

	2d	**3d·0.5CH$_2$Cl$_2$**	**6a**
formula	$C_4H_8Cl_5OTa$	$C_{12.5}H_{25}Cl_{11}O_3Ta_2$	$C_4H_8Cl_5NbO_2$
fw	430.30	975.18	358.26
T, K	100(2)	100(2)	100(2)
λ, Å	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1$	$P\bar{1}$
a, Å	7.8854(5)	7.2577(13)	8.0208(19)
b, Å	30.843(2)	47.516(8)	8.565(2)
c, Å	9.0224(6)	8.0971(14)	9.074(2)
α, °	90	90	62.346(3)
β, °	98.2410(10)	97.411(2)	86.328(3)
γ, °	90	90	84.782(3)
cell volume, Å^3	2171.7(2)	2769.0(8)	549.7(2)
Z	8	4	2
D_c, g cm^{-3}	2.632	2.339	2.165
μ, mm^{-1}	11.300	8.973	2.269
F(000)	1584	1828	348
crystal size, mm^3	0.22 × 0.14 × 0.12	0.22 × 0.16 × 0.12	0.22 × 0.13 × 0.11
θ limits, °	1.32−27.00	1.71−25.03	2.53−25.03
reflns collected	23 875	24 639	3786
independent reflns	4725	9763	1892
	[$R_{int} = 0.0286$]	[$R_{int} = 0.0593$]	[$R_{int} = 0.0254$]
data/restraints/params	4725/36/199	9762/312/515	1892/0/109
GOF on F^2	1.087	1.122	1.214
R1 ($I > 2\sigma(I)$)	0.0279	0.0685	0.0471
wR2 (all data)	0.0620	0.1734	0.1472
largest diff. peak and hole, e Å^{-3}	1.076/−2.354	3.179/−4.188	3.34/− 0.882

[a] $R1(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2(F_o^2) = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; $GOF = [\Sigma[w(F_o^2 - F_c^2)^2]/(N-P)]^{1/2}$, where N and P are the number of observations and parameters, respectively.

Results and Discussion

The THF adducts MCl$_5$(THF) (M = Nb, **2a**; M = Ta, **2d**) were obtained by treating dichloromethane suspensions of MCl$_5$ (M = Nb, **1a**; M = Ta, **1d**) with THF in a 2:1 metal/THF molar ratio, eq 1.

$$\mathrm{MCl_5 + THF \xrightarrow[M\,=\,Nb,\ Ta]{CH_2Cl_2} \underset{\mathbf{2}}{MCl_5(THF)}} \qquad (1)$$

Solvent removal afforded colorless solids, which were recrystallized from dichloromethane/pentane and characterized by analytical and spectroscopic methods and by X-ray diffraction analyses for M = Ta.

The most salient spectroscopic features of **2** are represented by the ^{1}H and ^{13}C NMR resonances of the coordinated THF molecule. Such resonances appear downfield shifted with respect to uncoordinated THF [δ 3.76, 1.85 (^{1}H) and δ 68.0, 25.6 (^{13}C) in CDCl$_3$]; the electronic effect due to the coordination being more relevant for the O-adjacent CH$_2$ units [e.g., for **2d**, ^{1}H NMR (CDCl$_3$ solution): δ 4.82, 2.21; ^{13}C NMR (CDCl$_3$ solution): δ 81.6, 26.2].

The unit cell of **2d** contains two independent molecules with similar geometries and bond distances and angles (Figure 1 and Table 2). The tantalum atom is hexacoordinated to five chloride anions [Ta−Cl average 2.315(3) and 2.316(3) Å for the two independent molecules, respectively] and a THF unit [Ta(1)−O(1) 2.146(6) Å; Ta(2)−O(2) 2.149(4) Å] in a slightly distorted octahedral geometry. The bond distances and angles are in the range observed for similar tantalum(V) compounds, such as TaCl$_4$(THF)(NPCl$_3$),[14] TaCl$_3$(NPh)(THF)(PEt$_3$),[15] TaCl$_3$(2,2′-ethylenebis(6-isopropylphenolate)(THF),[16] and TaCl$_3$(η^5-C$_5$Me$_5$)(OCHCHC$_6$H$_4$-p-Me)(THF).[17]

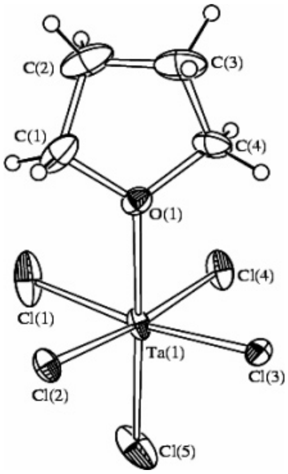


Figure 1. Molecular structure of TaCl$_5$(THF), **2d**. Displacement ellipsoids are at the 30% probability level. Only one of the two independent molecules present in the unit cell is represented.

We found that the THF adducts **2** promote the THF polymerization under experimental conditions analogous to those reported for the reactions catalyzed by **1a**,**d**,[8] thus suggesting that these species are probably involved in the

---

(14) Rivard, E.; Honeyman, C. H.; McWilliams, A. R.; Lough, A. J.; Manners, I. *Inorg. Chem.* **2001**, *40*, 1489.

(15) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1982**, *21*, 223.

(16) Anthis, J. W.; Filippov, I.; Wigley, D. E. *Inorg. Chem.* **2004**, *43*, 716.

(17) Meyer, T. Y.; Garner, L. R.; Baenziger, N. C.; Messerle, L. *Inorg. Chem.* **1990**, *29*, 4045.

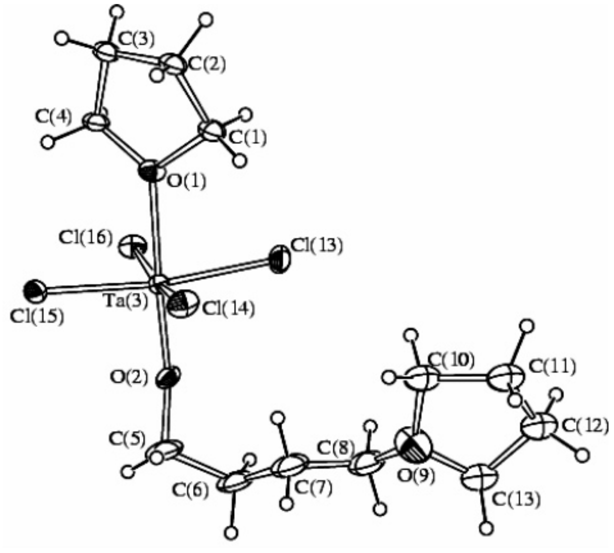


Figure 2. View of the $[TaCl_4(THF)\{O(CH_2)_4\overline{O(CH_2)_3CH_2}\}]^+$ cation in **3d·0.5CH$_2$Cl$_2$**. Only one of the two independent cations is represented. Displacement ellipsoids are at the 30% probability level.

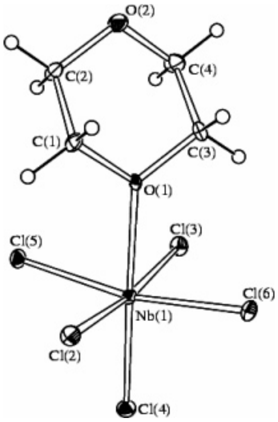


Figure 3. View of the molecular structure of **6a**. Displacement ellipsoids are at the 30% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Two Independent Molecules of $TaCl_5(THF)$, **2d**

Ta(1)−Cl(1)	2.3324(18)	O(1)−C(1)	1.488(7)
Ta(1)−Cl(2)	2.3301(12)	O(1)−C(4)	1.486(8)
Ta(1)−Cl(3)	2.3218(13)	Ta(1)−Cl(4)	2.3194(14)
Ta(1)−Cl(5)	2.2727(19)	Ta(1)−O(1)	2.146(4)
Ta(2)−Cl(6)	2.3238(13)	Ta(2)−Cl(7)	2.3155(14)
Ta(2)−Cl(8)	2.3269(15)	Ta(2)−O(2)	2.149(4)
Ta(2)−Cl(9)	2.3288(12)	O(2)−C(8)	1.480(6)
Ta(2)−Cl(10)	2.2866(15)	O(2)−C(5)	1.483(6)
C(4)−O(1)−C(1)	108.9(5)	C(8)−O(2)−C(5)	109.6(4)
O(1)−C(1)−C(2)	104.3(6)	O(2)−C(5)−C(6)	104.1(4)
O(1)−C(4)−C(3)	103.9(6)	O(2)−C(8)−C(7)	104.1(5)

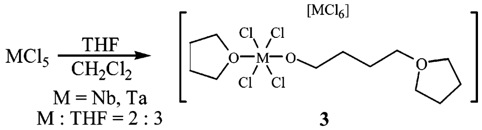
Table 3. Selected Bond Lengths (Å) for the Two Independent Molecules of **3d·0.5CH$_2$Cl$_2$**

Ta(1)−Cl(1)	2.336(6)	Ta(2)−Cl(7)	2.356(5)
Ta(1)−Cl(2)	2.366(5)	Ta(2)−Cl(8)	2.341(6)
Ta(1)−Cl(3)	2.332(6)	Ta(2)−Cl(9)	2.352(6)
Ta(1)−Cl(4)	2.349(6)	Ta(2)−Cl(10)	2.336(5)
Ta(1)−Cl(5)	2.346(5)	Ta(2)−Cl(11)	2.345(6)
Ta(1)−Cl(6)	2.344(6)	Ta(2)−Cl(12)	2.355(5)
Ta(3)−Cl(13)	2.372(7)	Ta(4)−Cl(17)	2.328(7)
Ta(3)−Cl(14)	2.356(6)	Ta(4)−Cl(18)	2.338(6)
Ta(3)−Cl(15)	2.335(6)	Ta(4)−Cl(19)	2.351(6)
Ta(3)−Cl(16)	2.340(6)	Ta(4)−Cl(20)	2.360(6)
Ta(3)−O(1)	2.180(15)	Ta(4)−O(3)	2.196(15)
Ta(3)−O(2)	1.821(16)	Ta(4)−O(4)	1.797(14)
O(1)−C(1)	1.446(14)	O(3)−C(21)	1.438(14)
O(1)−C(4)	1.448(14)	O(3)−C(24)	1.438(14)
O(2)−C(5)	1.430(10)	O(4)−C(25)	1.433(10)
C(5)−C(6)	1.531(10)	C(25)−C(26)	1.528(10)
C(6)−C(7)	1.531(10)	C(26)−C(27)	1.536(10)
C(7)−C(8)	1.526(10)	C(27)−C(28)	1.527(10)
C(8)−O(9)	1.427(10)	C(28)−O(29)	1.432(10)
O(9)−C(13)	1.433(10)	O(29)−C(33)	1.445(9)
O(9)−C(10)	1.433(10)	O(29)−C(30)	1.432(9)

Table 4. Selected Bond Distances (Å) and Angles (deg) for **6a**

Cl(2)−Nb(1)	2.3237(14)	C(1)−O(1)	1.476(6)
Cl(3)−Nb(1)	2.3265(15)	C(1)−C(2)	1.509(8)
Cl(4)−Nb(1)	2.2637(15)	C(2)−O(2)	1.431(7)
Cl(5)−Nb(1)	2.3245(15)	C(3)−O(1)	1.469(6)
Cl(6)−Nb(1)	2.3259(14)	C(3)−C(4)	1.505(8)
Nb(1)−O(1)	2.206(4)	C(4)−O(2)	1.421(7)
O(1)−C(1)−C(2)	108.4(4)	O(2)−C(4)−C(3)	110.7(5)
O(2)−C(2)−C(1)	110.8(5)	C(3)−O(1)−C(1)	108.8(4)
O(1)−C(3)−C(4)	108.8(4)	C(4)−O(2)−C(2)	109.7(4)

Scheme 1

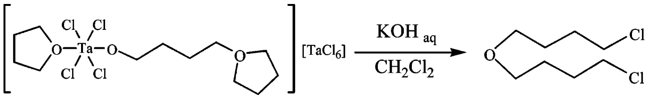


initial steps of the polymerization of tetrahydrofuran carried out in the presence of MCl_5 (M = Nb, Ta).

In order to identify and to isolate further intermediates involved in such reactions, compounds **1a**,**d** were treated with a slight excess of THF. By operating under these conditions, the formation of **2** was accompanied by the production of a minor compound, **3**, as indicated by NMR spectroscopy. The relative amounts of **2** and **3** depend on the metal/THF molar ratio, and the yield of **3** was optimized by using a 2:3 metal/THF stoichiometry, see Scheme 1. Operating with this metal/THF molar ratio, compounds **3** were obtained in satisfactory-to-good yields, identified as $[MCl_4(THF)\{O(CH_2)_4\overline{O(CH_2)_3CH_2}\}][MCl_6]$ (M = Nb, **3a**; M = Ta, **3d**), and fully characterized by analytical and spectroscopic methods (IR, ^{1}H NMR, ^{13}C NMR and 2D NMR investigations).

An X-ray diffraction study carried out on **3d** showed that it crystallizes with two independent cations and anions and one CH_2Cl_2 molecule per unit cell. The $[TaCl_4(THF)\{O(CH_2)_4\overline{O(CH_2)_3CH_2}\}]^+$ cation contains an almost octahedral Ta(V) center coordinated to four nearly coplanar chloride ligands, a THF molecule, and the zwitterionic $[(O^-)(CH_2)_4\overline{(O^+)(CH_2)_3(CH_2)}]$ group, vide infra. The Ta−Cl bonds [average 2.351(13) and 2.344(13) Å, for the two independent cations, respectively] compare well with those observed in the two independent $[TaCl_6]^-$ anions present in the unit cell [average 2.341(14) and 2.348(14) Å] and those observed in **2d**. The Ta(3)−O(2) and the Ta(4)−O(4) bonds [1.821(16) and 1.797(14)Å, respectively] are significantly shorter than the bond with the oxygen atom of the THF molecule [Ta(3)−O(1) 2.180(15) Å; Ta(4)−O(3) 2.196(15)

Scheme 2



3d

Å] and are typical of Ta(V)−OR bonds, involving an alcoholate ligand.[18]

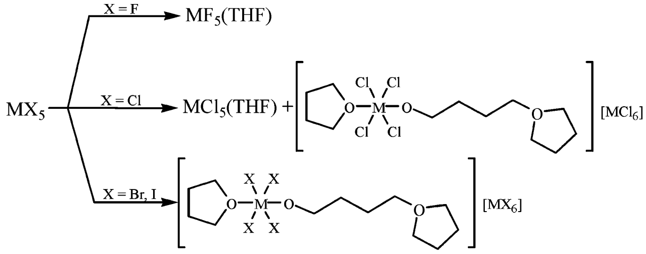
The zwitterionic ligand $[(\mathrm{O}^-)(\mathrm{CH}_2)_4\overline{(\mathrm{O}^+)(\mathrm{CH}_2)_3(\mathrm{CH}_2)}]$, represents a rare example of structurally characterized 1-tetrahydrofuranium species, the only other case being 1,1′-(1,4-butanediyl)bis(tetrahydrofuranium), recently reported by Beckmann and co-workers.[19] The C−O [1.427(10)−1.445(9) Å] and the C−C distances [1.522(10)−1.536(10) Å] within $[(\mathrm{O}^-)(\mathrm{CH}_2)_4\overline{(\mathrm{O}^+)(\mathrm{CH}_2)_3(\mathrm{CH}_2)}]$ are similar to those observed in the bis(tetrahydrofuranium) dication[19] and agree with an sp^3 hybridization of the carbon atoms.

The NMR features of **3a**,**d** are well in agreement with the structure of **3d** in the solid state. More in detail, the ^{1}H NMR spectra contain multiplets which account, respectively, for six OCH_2 units (e.g., for **3d** at δ 5.45, 4.88, 4.42, 3.66) and six CH_2 groups not vicinal to oxygen (at δ 2.23 and 1.83 in the case of **3d**). The ^{13}C NMR resonances of **3d** have been assigned as follows, δ 85.7, 80.4, 71.5, 69.4 (O*C*H$_2$); δ 32.7, 29.9, 28.2, 26.2 (*C*H$_2$). These attributions have been established by comparison with the NMR data collected for compound **3e** (see below).

The zwitterionic ligand $[(\mathrm{O}^-)(\mathrm{CH}_2)_4\overline{(\mathrm{O}^+)(\mathrm{CH}_2)_3(\mathrm{CH}_2)}]$ rearranges to bis-(4-chlorobutyl)ether (GC-MS and ^{1}H NMR) by the treatment of a CH_2Cl_2 solution of **3d** with aqueous KOH, see Scheme 2. This result is in agreement to previous findings[20] and is explicable by admitting that the hydrolysis of **3d** causes the release of the ligands from the metal center and the C−O bond cleavage within the tetrahydrofuranium fragment.

According to the generally accepted mechanism proposed for the polymerization of THF catalyzed by Lewis acids, the reaction catalyzed by $TaCl_5$ ($NbCl_5$) should occur through initial coordination of THF to the metal, followed by sequential steps consisting of ring-opening and C−O bond formation with the incoming monomer, giving a tertiary oxonium ion.[21] We found that **3d**, clearly the result of ring-opening of THF followed by C−O coupling with an additional THF ring, likewise $TaCl_5$ and **2d**, is active in promoting THF polymerization, thus suggesting that the formation of **2** and **3** may occur stepwise in the early stages of the THF polymerization catalyzed by MX_5 (M = Nb, Ta).

Scheme 3



M	X	M:THF		M:THF	
Nb	Cl	2:1	**2a**	2:3	**3a**
Nb	Br	-	**2b**	2:3	**3b**
Ta	F	1:1	**2c**	-	**3c**
Ta	Cl	2:1	**2d**	2:3	**3d**
Ta	Br	-	**2e**	2:3	**3e**
Ta	I	-	**2f**	2:3	**3f**

The formation of compounds **3** should proceed via halide migration from one metal center to another. With the aim to evidentiate the effect of the halide, we decided to extend the present study to the other niobium(V) and tantalum(V) halides.

Suspensions of TaF_5 in CH_2Cl_2 react with THF in a nearly 1:1 molar ratio to give the adduct **2c** in high yield. The ^{1}H and ^{13}C NMR data of **2c** resemble those related to **2a**,**d**, and do not deserve further comments. The ^{19}F NMR spectrum of **2c** exhibits two broad peaks, at δ 80.1 and 39.2, which have been attributed to the fluorides located in trans and in cis positions with regards to the coordinated THF, respectively. This feature is in agreement with the results reported for analogous octahedral $TaF_5(L)$ species.[22]

Compound **2c** is the only product which can be isolated by reacting TaF_5 with limited amounts of THF. Attempts to obtain **3c** failed. The reaction of TaF_5 with 2 equiv of THF afforded **2c** only, even in boiling $CHCl_3$ solution. When TaF_5 was treated with major amounts of THF, formation of viscous solutions occurred and the isolation of metal adducts was no longer possible.

On the other hand, the reactions of MX_5 with 0.5 equiv of THF gave exclusively the ionic species $[\mathrm{MX}_4(\mathrm{THF})\{\mathrm{O}(\mathrm{CH}_2)_4\overline{\mathrm{O}(\mathrm{CH}_2)_3\mathrm{CH}_2})\}][\mathrm{MX}_6]$ (M = Nb, X = Br, **3b**; M = Ta, X = Br, **3e**, I, **3f**) (Scheme 3), the yields being optimized by using 3:2 THF/metal molar ratios. The identities of **3b**,**e**,**f** were established by IR and NMR spectroscopy and elemental analysis.

The identities of **3b**,**e**,**f** were established by IR and NMR spectroscopy and elemental analysis. The NMR characterization of **3e** has been supported by DEPT and 2D experiments. The DEPT experiment (in $CDCl_3$ solution) revealed a total of eight resonances, all ascribable to the same type of carbons (CH_2 groups, on the basis of the X-ray analysis related to **3d**, see above). The ^{1}H and the ^{13}C NMR resonances of compound **3e** have been assigned as follows, δ 5.51, 4.93, 3.55, 3.46 (m, 12 H, OC*H*$_2$), 2.20, 1.93, 1.69 (m, 12 H, C*H*$_2$),

---

(18) Some selected examples are: (a) Tatsumi, K.; Tahara, A.; Nakamura, A. *J. Organomet. Chem.* **1994**, *471*, 111. (b) Abbenhuis, H. C. L.; Rietveld, M. H. P.; Haarman, H. F.; Hogerheide, M. P.; Spek, A. L.; van Koten, G. *Organometallics* **1994**, *13*, 3259. (c) Rietveld, M. H. P.; Hagen, H.; van der Water, L.; Grove, D. M.; Kooijman, H.; Veldman, N.; Spek, A. L.; van Koten, G. *Organometallics* **1997**, *16*, 168. (d) Davies, H. O.; Leedham, T. J.; Jones, A. C.; O'Brien, P.; White, A. J. P.; Williams, D. J. *Polyhedron* **1999**, *18*, 3165. (e) Boyle, T. J.; Andrews, N. L.; Alam, T. M.; Rodriguez, M. A.; Santana, J. M.; Scott, B. L. *Polyhedron* **2002**, *21*, 2333.

(19) Akkerman, K.; Beckmann, J.; Duthie, A. *Acta Crystallogr., Sect. E* **2006**, *62*, o2781.

(20) Belgian Patent BE634194 to CIBA Ltd, Basel, 1963.

(21) Dreyfuss, P.; Dreyfuss, M. P. *Adv. Polym. Sci.* **1967**, *4*, 528. Panczek, S.; Kubisa, P.; Matyjaszewski, K. *Adv. Polym. Sci.* **1980**, *37*, 1.

(22) Buslaev, Y. A.; Ilyin, E. G. *J. Fluorine Chem.* **1974**, *4*, 271.

85.5, 81.4, 71.7, 70.8 (OCH_2), 31.4, 29.3, 28.6, 26.4 (CH_2), respectively. These attributions have been corroborated by gs-HSQC and gs-HMBC experiments.[23] More in detail, the gs-HSQC experiment has pointed out the following $^1H-^{13}C$ correlations: δ 5.51−85.5, 4.93−81.4, 3.55−70.8, 3.46−71.7, 2.20−26.4, 1.93−31.4, 1.93−29.3, 1.69−28.6. Moreover, the gs-HMBC experiment has allowed us to reject some signals due to impurities and it has given confirmation of the assignments listed above. Finally, the NMR attributions of **3b**,**f** have been based on the comparison with the data available for **3e**.

The outcomes of the reactions summarized in Scheme 3 do not depend on the metal but are strongly influenced by the nature of the halide: the tendency to the formation of the ionic adducts of type **3** increases along the series F < Cl < Br,I. This fact may be reasonably correlated to the metal−halide bond energy, which decreases on increasing the atomic weight of the halide:[24] since the syntheses of compounds **3** require halide migration from one metal center to another, this step would be slowed by a relatively high M−X bond energy.

Although compounds **3b**,**e**,**f** were formed even when using a THF/MX_5 = 0.5 molar ratio, compounds with the general formula MX_5(THF) such as **2b**,**e**,**f** could be isolated when a large excess of the metal halide was used. For example, **2e** was formed when THF was added to a 4-fold excess of $TaBr_5$ in dichloromethane at 0 °C. As expected, the treatment of **2e** with 0.5 equiv of THF readily yielded **3e**; therefore, adding additional support to the idea that THF polymerization promoted by $TaBr_5$ is likely to proceed through intermediates analogous to those found in the case of $TaCl_5$.

The details of the mechanism producing **3**, the possibility to isolate longer-chain intermediates, and the relative properties of the poly-THF produced by MX_5 catalysis are at present under investigation.

In order to check if MX_5 could promote ring-opening reactions of aliphatic cyclic ethers different from THF, we decided to extend the study to the reactions of MX_5 with THP and diox.[25] The reactions were performed by using a 2:3 metal/cyclic ether ratio (in analogy to the syntheses of **3a**−**f**), but only the neutral species MX_5(L) were obtained, see Scheme 4. THF* behaves analogously, since it is known that disubstituted THF species, by contrast with simple THF, do not polymerize.[27]

Scheme 4

$$MX_5 + L \rightarrow MX_5(L)$$

	M	X	L	
1d	Ta	Cl	THF*	**4d**
1e	Ta	Br	THF*	**4e**
1d	Ta	Cl	THP	**5d**
1e	Ta	Br	THP	**5e**
1a	Nb	Cl	diox	**6a**
1d	Ta	Cl	diox	**6d**

Complexes **4**−**6** were characterized by elemental analysis, IR and NMR spectroscopy, and X-ray diffraction in the case of compound **6a.** The molecular structure of **6a** is similar to that of compound **2d** with the niobium(V) center coordinated to five chloride anions [Nb−Cl average 2.313(3) Å] and a dioxane molecule [Nb(1)−O(1) 2.206(4) Å] which adopts the generally observed chair conformation.[28] By taking into consideration that the ionic radii of hexacoordinated Nb(V) and Ta(V) have the same value (0.64 Å),[29] the M−O bond distances in **6a** are longer than in **2d** [2.146(6) and 2.149(4) Å in the two independent molecules]. A similar increase of the M−O bond distance on going from THF to dioxane complexes has been observed also in $MoCl_3(N_3S_2)(L)$[28a] and in Cd(Tp^{Ph})(acetate)(L),[28c] L = THF, dioxane; Tp^{Ph} = (3-phenylpyrazol-1-yl)hydroborate.

Compounds **4d**−**e** have been isolated as mixtures of two isomeric forms (^1H NMR) since they have been prepared by reacting TaX_5 (X = Cl, Br) with a mixture of *cis*- and *trans*-THF*. The NMR spectra of **5d**−**e**, **6d**, which show single sets of resonances, are similar to those of the analogous species **2a**,**d**. For instance, compound **6d** exhibits two ^1H NMR resonances at δ 4.79 ($TaOCH_2$) and 3.98 ($TaOCH_2CH_2$),[30] the nonequivalence of the two methylenic units being a consequence of dioxane coordination (the ^1H NMR spectrum of uncoordinated diox consists of a single peak at δ 3.69 in $CDCl_3$). At variance to **6d**, the niobium derivative **6a** shows a temperature-dependent ^1H NMR spectrum. At 298 K only one broad peak is observed (δ 4.12), which turns into a sharp singlet at almost the same frequency on increasing the temperature to 323 K. On cooling to 243 K, the spectrum does show two peaks at δ 4.67 and 4.00, with the former broader than the latter, and a resonance at δ 3.76, attributable to free dioxane.[30] Furthermore, the ^1H NMR spectrum recorded at 213 K reveals four signals, at δ 4.98, 4.36, 3.99, and 3.77 (relative integral values 2:2:4:8). Although possible niobium quadrupolar effects cannot be excluded, the dependence of the NMR spectrum of **6a** on temperature may be explained by considering the presence in solution of free

---

(23) Willker, W.; Leibfritz, D.; Kerssebaum, R.; Bermel, W. *Magn. Reson. Chem.* **1993**, *31*, 287.

(24) *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1996; pp 9−51.

(25) The adducts MCl_5(diox) (M = Nb, Ta) were described some years ago[8,26] and characterized by elemental analysis and ^1H NMR at room temperature in the case of $NbCl_5$(diox).

(26) Feenan, K.; Fowles, G. W. A. *J. Chem. Soc.* **1965**, *2449*.

(27) Pruckmayr, G.; Dreyfuss, P.; Dreyfuss, M. P. *Encyclopedia of Chemical Technology*, 4th ed.; J. Wiley and Sons: New York, 1996; Vol. 19, p 743.

(28) (a) Dietrich, A.; Neumüller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **2002**, *628*, 243. (b) Noll, A.; Müller, U. *Z. Anorg. Allg. Chem.* **1999**, *625*, 803. (c) Darensbourg, D. J.; Niezgoda, S. A.; Holtcamp, M. W.; Draper, J. D.; Reibenspies, J. H. *Inorg. Chem.* **1997**, *36*, 2426. (d) Micklitz, W.; Lippard, S. J. *Inorg. Chem.* **1988**, *27*, 3067. (e) Evenhuis, C. J.; Hitchman, M. A.; McDonald, R. G.; Goodgame, D. M. L.; Kwiatkowski, E, Dettlaff-Weglikowska, U.; Pakawatchai, C.; White, A. H. *J. Chem. Soc. Dalton Trans.* **1984**, 943.

(29) Shannon, R. *D: Acta Crystallogr., Sect. A* **1974**, *32*, 751.

(30) Meerbach and Bünzli (see ref 7) reported resonances ($CDCl_3$) at δ 4.71 and 4.03 and at δ 4.83 and 4.04 in the spectra of **6a (**233 K) and **6d** (253 K), respectively.

dioxane and its fast exchange with the coordinated ether. As the temperature goes lower, the rotation of the dioxane ligand around the Nb−O bond turns slower and the nonequivalence of two couples of protons in α-position to the oxygen comes evident by the splitting of the signal at δ 4.67 into two resonances at δ 4.98 and 4.36 (at 213 K). The observation that samples containing a large excess (ca. 5:1) of $NbCl_5$ have NMR patterns identical to those described for **6a**, suggests that the free dioxane detected in the $CDCl_3$ solutions of **6a** is not probably formed by fortuitous hydrolysis (the large excess of $NbCl_5$ actually acts as drying agent). Taking into account that the ^1H NMR spectrum of the tantalum derivative **6d** at 298 K (δ 4.79 and 3.98) looks similar to that of **6a** at 243 K (δ 4.67 and 4.00), the presence of free dioxane in the $CDCl_3$ solutions of **6a** should be more properly related to the higher lability exhibited by the compounds of **4d** elements with respect to those containing the heavier congeners.[31]

Conclusions

This paper represents an attempt to shed some light on the reactivity of Group 5 metal pentahalides with cyclic ethers, a topic scarcely discussed in the literature.

We have shown that the reactions of MX_5 with diluted solutions of cyclic ethers give, in the majority of the cases, the stable and somehow expected hexacoordinated $MX_5(L)$ complexes **2**. However, when THF is used in 50% excess with respect to the metal, a second product is formed corresponding to the ionic species **3**. Both types of compounds **2** and **3** are active in the THF polymerization; therefore, they may be considered as intermediate species involved in the early stages of the polymerization of THF promoted by MX_5. The formation of **3** requires halide migration from one metal center to another and appears to be accelerated on decreasing the metal−halide bond energy. The structure of **3**, characterized in the solid state in the case of M = Ta and X = Cl, includes the zwitterionic 4-(tetrahydrofuran-1-ium)-butan-1-oxo ligand and represents a noticeable corroboration of the generally accepted mechanism for the cationic polymerization of cyclic ethers, i.e., the propagating species is a tertiary oxonium ion undergoing nucleophilic attack by the monomer at the α-carbon atom of the THF ring.[21]

Acknowledgment. The authors thank the Ministero dell' Istruzione, dell' Università e della Ricerca (MIUR, Roma), Programma di Ricerca Scientifica di Notevole Interesse Nazionale 2004-5, for financial support.

Supporting Information Available: Variable-temperature ^1H NMR spectra of compound **6a**; and X-ray crystallographic data for **2d**, **3d·0.5CH$_2$Cl$_2$**, and **6a** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC7012254

---

(31) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley-Interscience: New York, 1999.