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Solution Phase Cationic Niobium and Tantalum Alkoxide Clusters: Insights into Formation and Structure

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Electrospray mass spectrometry (ESMS) is used to investigate cationic niobium and tantalum alkoxide clusters generated in solution by adding equal molar amounts of $B(C_6F_5)_3$ to the metal ethoxide, $M(OEt)_5$. The dominant metal ethoxide cations that were observed in the electrospray mass spectrum correspond to $M(OEt)_4^+$, $M_2O(OEt)_7^+$, $M_2(OEt)_9^+$, and $M_3O(OEt)_{12}^+$, where M is niobium or tantalum. In separate experiments heterometallic Nb/Ta ethoxide clusters were produced, and the heterometallic cations present in the electrospray mass spectrum are $NbTaO(OEt)_7^+$, $NbTa(OEt)_9^+$, $Nb_2TaO(OEt)_{12}^+$, and $NbTa_2O(OEt)_{12}^+$. Collision-induced dissociation (CID) experiments were completed to provide structural information about the observed metal ethoxide cations. At low collision energy ($E_{CM} < 2$ eV), the CID fragmentation pattern of $Nb_3O(OEt)_{12}^+$ favors loss of $Nb_2(OEt)_9^+$ and neutral $NbO(OEt)_3$, whereas the fragmentation pattern of $Ta_3O(OEt)_{12}^+$ favors loss of $Ta_2O(OEt)_7^+$ and neutral $Ta(OEt)_5$. In addition, the major CID product of $M_2O(OEt)_7^+$ and $M_2(OEt)_9^+$ at low collision energy is $M(OEt)_4^+$. During CID experiments of $M(OEt)_4^+$, four consecutive ethylene molecules were released leaving $M(OH)_4^+$, which at higher collision energies ($E_{CM} > 2$ eV) liberates two water molecules resulting in MO_2^+. The CID fragmentation pattern of crotyl alcohol ($CH_3CH{=}CHCH_2OH$) substituted and *n*-butanol ($CH_3CH_2CH_2CH_2OH$) substituted metal alkoxides resembles the fragmentation pattern proposed for $M(OEt)_4^+$, in which four consecutive organic molecules are shed leaving $M(OH)_4^+$.

Introduction

A limited number of investigations have attempted to characterize inorganic complexes in solution using electrospray mass spectrometry (ESMS).[1] Because the use of ESMS is relatively new to the inorganic chemist, many of these publications have concentrated on validating the use of ESMS to probe solution chemistry.[2−11] One of the benefits of an electrospray source is that pre-existing ions in solution are observed directly as a result of the soft transfer of ionic species in solution into the gas phase. Therefore, the ionic species observed in ESMS experiments are equivalent to those originally in solution. An additional advantage of ESMS to inorganic chemistry is that the technique results in a clean mass spectrum, which is dominated by the principal ions present in solution.

Numerous ESMS studies on inorganic complexes have been performed.[12−15] For example, Hercules and co-workers have characterized tungstate, vanadate, and perrhenate oxyanions using ESMS.[15] From these studies, it was determined that protonated monomeric oxyanions are prevalent in basic tungstate and vanadate solutions and that protonated polymeric species are the major ionic species present in acidic solutions. Monomeric perrhenate was the only ionic species detected in both the acidic and basic perrhenate solutions. From these studies, it was determined that the ionic metalate species detected by ESMS are consistent with the reported speciation in aqueous solutions. Despite the relatively large number of ESMS studies on inorganic complexes, only a few ESMS studies have been performed on metal alkoxides. For example, Løver et al. obtained the electrospray mass spectra of $Zr(OEt)_4$, $Ti(OEt)_4$, $Al(OEt)_3$, and $Si(OEt)_4$ after the addition of chelating agents and sodium ethoxide.[16] The molecular complexity of the dominant ions observed in the electrospray mass spectra agrees with the previously established polymeric nature of these metal alkoxides. Additionally, the ESMS studies confirmed that the oligomeric alkoxides retain their structural integrity in the gas phase.

The current investigation focuses on the production of cationic niobium and tantalum alkoxides in solution via reactions with tris(pentafluorophenyl)borane. Niobium and tantalum alkoxides, $Nb(OR)_5$ and $Ta(OR)_5$, were selected as the inorganic system of interest because these metal alkoxides contain organic groups that may undergo intramolecular C−C and C−H activation analogous to the intermolecular reactivity reported by Castleman and co-workers.[17,18] Moreover, organotransition-metal complexes possessing a high degree of coordinative unsaturation are frequently reactive toward activating C−H and C−C bonds.[19] Therefore, it seems a valuable endeavor to probe the reactivity of niobium and tantalum alkoxide cations toward C−C and C−H bond activation using ESMS techniques.

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Experimental Section

All of the cationic metal alkoxide samples were prepared under nitrogen in an inert atmosphere drybox. Homometallic metal ethoxide cations were generated by combining equal molar amounts of tris(pentafluorophenyl)borane (Aldrich) with niobium or tantalum ethoxide (Aldrich); the mixture was then diluted to 0.1 mM using dichloromethane. Heterometallic Nb/Ta ethoxide clusters were produced by allowing a solution of equal molar amounts of $Nb(OEt)_5$ and $Ta(OEt)_5$ to equilibrate. Additionally, the crotyl alcohol- and *n*-butanol-substituted metal alkoxide clusters were generated by combining 2 equiv of $M(OEt)_5$ with 1 equiv of crotyl alcohol ($CH_3CH{=}CHCH_2OH$) or *n*-butanol ($CH_3CH_2CH_2CH_2OH$) and allowing this solution to equilibrate. The cationic species of the heterometallic ethoxides and alcohol-substituted metal ethoxides were then produced by adding tris(pentafluorophenyl)borane as was previously described. These samples were placed in glass vials, sealed with a rubber septum, and transferred from the drybox to the electrospray mass spectrometer. The conductivity of the solutions was measured in the drybox using a Traceable digital conductivity meter.

The ESMS experiments were performed on a MicroMass Q-TOF mass spectrometer. Solutions of cationic metal alkoxides in dichloromethane were continuously infused into the spray probe by means of a syringe pump (Harvard Apparatus, model 22), typically at a flow rate of 10 μL/min. The desolvation and block temperatures were set at 70 °C to effectively spray the dichloromethane solutions. Additionally, the desolvation gas flow was typically 0−100 L/h, and the nebulizing flow was ~10 L/h. The Q-TOF mass spectrometer is a tandem quadrupole orthogonal acceleration time-of-flight mass spectrometer capable of MS/MS experiments. The cone voltage was typically 30 V in these experiments except during the collision-induced dissociation (CID) experiments on $M(OR)_4^+$, which are described below. The Q-TOF utilizes a high-performance quadrupole mass analyzer, incorporating a prefilter assembly to protect the main analyzer from contaminating deposits, and an orthogonal acceleration time-of-flight mass spectrometer. A hexapole collision cell, which is located between the quadrupole and the time-of-flight region, can be used to induce fragmentation by the addition of nitrogen gas into the cell and by increasing the DC voltage applied to the hexapole rods. The ions are extracted into the TOF mass analyzer, separated in mass by their differing flight times, and detected by a microchannel plate detector and an ion counting system. Finally, it was necessary to increase the cone voltage from 30 to 65 V to perform CID studies on $M(OR)_4^+$.

Results

The electrospray mass spectra of niobium and tantalum ethoxide with tris(pentafluorophenyl)borane are shown in Figures 1 and 2. It is evident from these figures that similar peaks are observed for both $Nb(OEt)_5$ and $Ta(OEt)_5$ with tris(pentafluorophenyl)borane in dichloromethane. The major peaks in the electrospray mass spectrum of $Nb(OEt)_5$ with tris(pentafluorophenyl)borane occur at *m/z* 273, 517, 591, and 835 and are identified as $Nb(OEt)_4^+$, $Nb_2O(OEt)_7^+$, $Nb_2(OEt)_9^+$, and $Nb_3O(OEt)_{12}^+$, respectively. Similarly, the dominant peaks found in the electrospray mass spectrum of $Ta(OEt)_5$ with tris(pentafluorophenyl)borane occur at *m/z* 361, 693, 767, and 1099, which correspond to $Ta(OEt)_4^+$, $Ta_2O(OEt)_7^+$, $Ta_2(OEt)_9^+$, and $Ta_3O(OEt)_{12}^+$, respectively. Additionally, Figure 3 shows the electrospray mass spectrum of the anions present in the solutions of $M(OEt)_5$ with tris(pentafluorophenyl)borane. The major peaks occur at *m/z* 528.8 and 556.8, which correspond to $B(C_6F_5)_3OH^-$ and $B(C_6F_5)_3OEt^-$, respectively.

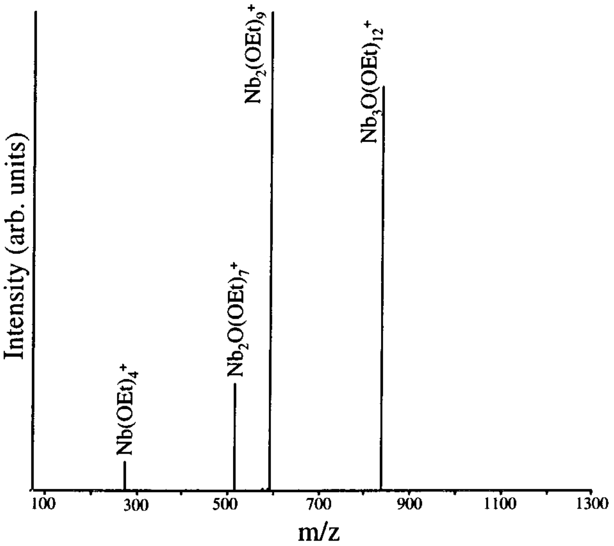


Figure 1. Electrospray mass spectrum of cationic species present in $Nb(OEt)_5$ with tris(pentafluorophenyl)borane in dichloromethane at a cone voltage of 30 V.

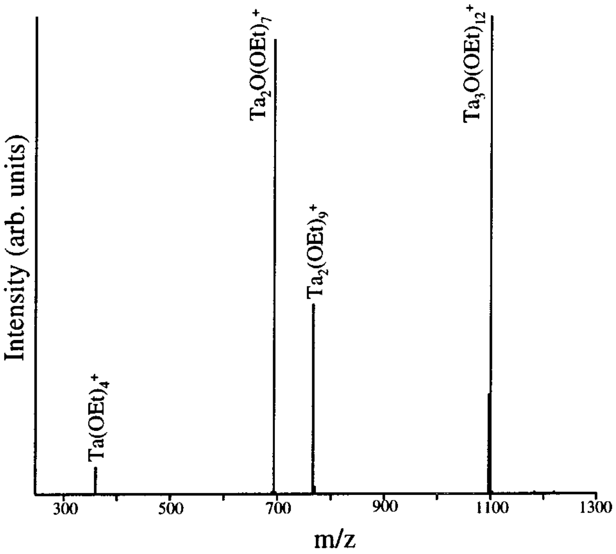


Figure 2. Electrospray mass spectrum of cationic species present in $Ta(OEt)_5$ with tris(pentafluorophenyl)borane in dichloromethane at a cone voltage of 30 V.

Figure 4 shows the CID fragmentation pattern of the cationic species formed upon the reaction of $M(OEt)_5$ with $B(C_6F_5)_3$. It should be mentioned that the collision-induced fragmentation patterns are similar for both niobium and tantalum ethoxide with $B(C_6F_5)_3$ in dichloromethane. The major cations detected during CID experiments on $M_3O(OEt)_{12}^+$ at $E_{CM} < 2$ eV are $M_2O(OEt)_7^+$, $M_2(OEt)_9^+$, and $M(OEt)_4^+$, according to reactions 1−3 in Figure 4. At higher collision energies, $E_{CM} > 2$ eV, the CID pattern described in reactions 6−11 in Figure 4 is followed. Additionally, the major CID product for both $M_2(OEt)_9^+$ and $M_2O(OEt)_7^+$ at $E_{CM} < 2$ eV is $M(OEt)_4^+$, according to reactions 4 and 5 in Figure 4. As the collision energy is increased, fragments according to those described in reactions 6−11 are observed. Finally, the CID fragmentation pattern for $M(OEt)_4^+$ is shown in reactions 6−11 in Figure 4. Loss of an ethoxy group (OEt) was not detected during the CID experiments. Instead, according to Figure 4, four ethylene molecules are sequentially

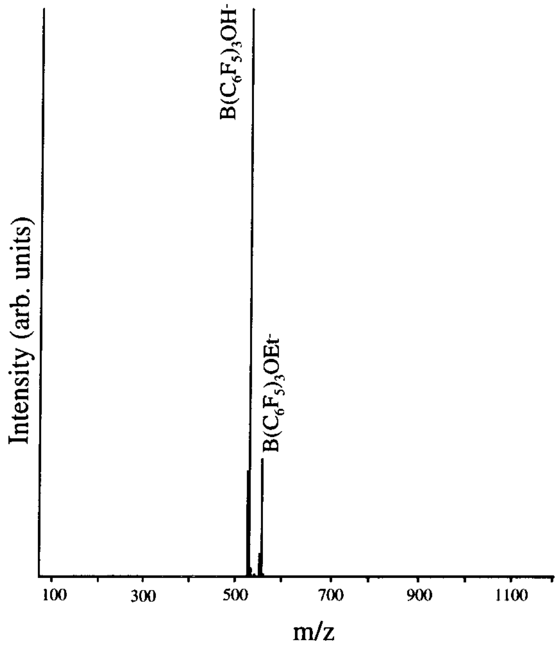


Figure 3. Electrospray mass spectrum of anionic species present in $M(OEt)_5$ with tris(pentafluorophenyl)borane in dichloromethane at a cone voltage of 30 V.

shed, leaving $M(OH)_4^+$, which then further dissociates by liberating two water molecules to form MO_2^+.

The electrospray mass spectrum of heterometallic Nb/Ta ethoxide with tris(pentafluorophenyl)borane is shown in Figure 5. The major peaks present in the electrospray mass spectrum corresponding to heterometallic ethoxide cations occur at *m/z* 605, 679, 923, and 1011, which are identified as $NbTaO(OEt)_7^+$, $NbTa(OEt)_9^+$, $Nb_2TaO(OEt)_{12}^+$, and $NbTa_2O(OEt)_{12}^+$, respectively. Reactions 12−26 in Table 1 display the CID results at $E_{CM} = 2$ eV of cationic species formed upon the reaction of heterometallic Nb/Ta ethoxides with tris(pentafluorophenyl)borane. The fragmentation pathways of the heterometallic Nb/Ta ethoxide clusters are similar to those of the homometallic ethoxide clusters shown in Figure 4. It should be noted that we are unable to detect neutrals in this experimental setup. The neutrals lost, which are listed in Table 1, are simply based upon the difference between the mass-selected cluster and the fragment ion.

Additionally, crotyl alcohol ($CH_3CH{=}CHCH_2OH$)-substituted and *n*-butanol ($CH_3CH_2CH_2CH_2OH$)-substituted metal ethoxide clusters were produced to determine if these species, like the metal ethoxides, would lose the R group, as opposed to the OR group, during CID experiments. It was determined that the dissociation pathways for crotyl alcohol- and *n*-butanol-substituted metal ethoxide clusters are similar to those observed for the metal ethoxide clusters. The main fragmentation channel is loss of a neutral organic molecule at lower collision energies, similar to reactions 6−9 in Figure 4. Particularly, during CID experiments on $M(OEt)_2(OCrotyl)_2^+$, two C_4H_6 species and two C_2H_4 species are released to form $M(OH)_4^+$, which then dissociates into MO_2^+ according to reactions 10 and 11 shown in Figure 4. Likewise during CID experiments on $M(OEt)_2(OButyl)_2^+$, two C_4H_8 species and two C_2H_4 species are liberated to form $M(OH)_4^+$, which then dissociates into MO_2^+ according to reactions 10 and 11 in Figure 4.

Table 2 shows the results of the conductivity measurements on 0.01 M solutions of metal ethoxide with tris(pentafluorophenyl)borane. The conductivities of 0.01 M solutions of niobium ethoxide, tantalum ethoxide, and the heterometallic Nb/Ta ethoxide with tris(pentafluorophenyl)borane in dichloromethane were determined to be 80.2, 99.3, and 88.2 $\mu\Omega^{-1}$, respectively. Conversely, the conductivities of 0.01 M solutions of neat $Nb(OEt)_5$, $Ta(OEt)_5$, and tris(pentafluorophenyl)borane in dichloromethane were determined to be 0.36, 0.47, and 0.52 $\mu\Omega^{-1}$, respectively. Due to the sensitivity of the conductivity meter, the conductivity measurements were not performed on the 0.1 mM solutions that were electrosprayed. For calibration, the measured room-temperature conductivity of 0.01 M tetrabutylammonium hexafluorophosphate in dichloromethane was 142 $\mu\Omega^{-1}$. The conductivity of 1:1 tris(pentafluorophenyl)borane and niobium or tantalum ethoxide is somewhat less, which reflects the fact that a solution 0.01 M in metal alkoxide is actually only 0.005 M in dimer.

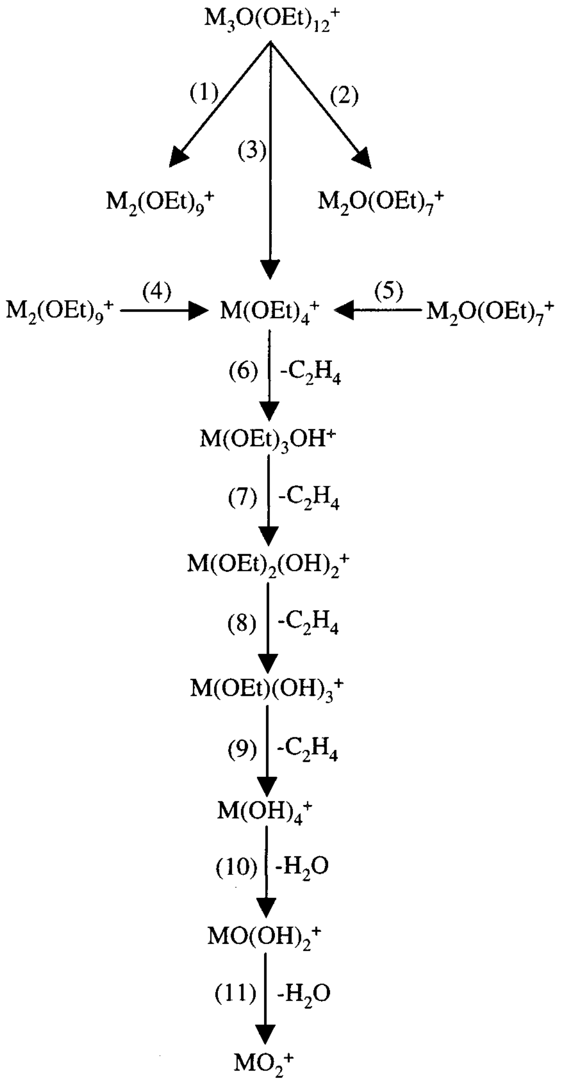


Figure 4. Fragmentation pattern of $M_3O(OEt)_{12}^+$, $M_2(OEt)_9^+$, $M_2O(OEt)_7^+$, and $M(OEt)_4^+$ determined by CID experiments.

Discussion

Numerous past studies have focused on characterizing metal alkoxides using electron ionization sources coupled to mass spectrometers. For example, electron ionization mass spectra have been obtained for various aluminum, gallium, and chromium alkoxides, and the fragmentation patterns of these species during CID processes have been observed.[20−22] Additionally,

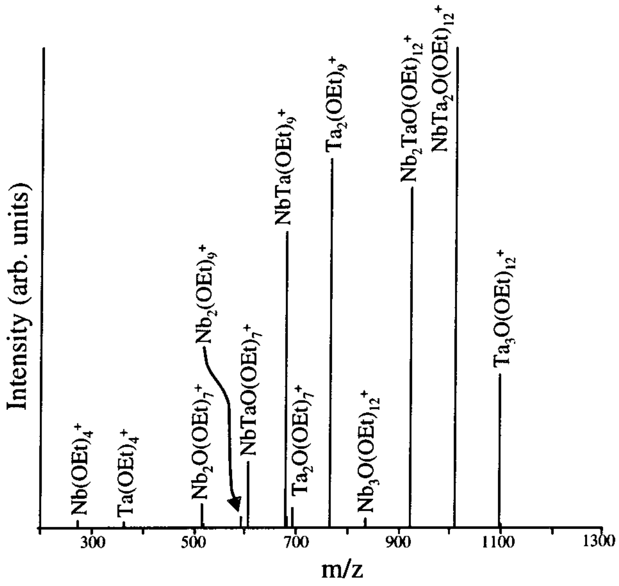


Figure 5. Electrospray mass spectrum of cationic species present in $Nb(OEt)_5$ and $Ta(OEt)_5$ with tris(pentafluorophenyl)borane in dichloromethane at a cone voltage of 30 V.

TABLE 1: CID Results at $E_{CM} = 2$ eV of the Cationic Species Formed upon Reactions of Heterometallic Nb/Ta Ethoxides with $B(C_6F_5)_3$

reaction	cationic heterometallic ethoxide species	product ion	neutral lost[a]
12	$NbTaO(OEt)_7^+$	$Ta(OEt)_4^{+\,b}$	$NbO(OEt)_3$
13		$Nb(OEt)_4^+$	$TaO(OEt)_3$
14	$NbTa(OEt)_9^+$	$Ta(OEt)_4^+$	$Nb(OEt)_5$
15		$Nb(OEt)_4^{+\,b}$	$Ta(OEt)_5$
16	$Nb_2TaO(OEt)_{12}^+$	$NbTa(OEt)_9^{+\,b}$	$NbO(OEt)_3$
17		$NbTaO(OEt)_7^+$	$Nb(OEt)_5$
18		$Nb_2O(OEt)_7^+$	$Ta(OEt)_5$
19		$Ta(OEt)_4^+$	$Nb_2O(OEt)_8$
20		$Nb(OEt)_4^+$	$NbTaO(OEt)_8$
21	$NbTa_2O(OEt)_{12}^+$	$Ta_2(OEt)_9^{+\,b}$	$NbO(OEt)_3$
22		$Ta_2O(OEt)_7^+$	$Nb(OEt)_5$
23		$NbTa(OEt)_9^+$	$TaO(OEt)_3$
24		$NbTaO(OEt)_7^+$	$Ta(OEt)_5$
25		$Ta(OEt)_4^+$	$NbTaO(OEt)_8$
26		$Nb(OEt)_4^+$	$Ta_2O(OEt)_8$

[a] The neutral loss is assigned on the basis of the difference between the selected cluster and the fragment ion formed. [b] Dominant product at $E_{CM} = 2$ eV.

TABLE 2: Conductivity of the 0.01 M Solutions of Group V Transition Metal Ethoxides, $B(C_6F_5)_3$, and Group V Transition Metal Ethoxides with $B(C_6F_5)_3$

solution	conductivity ($\mu\Omega^{-1}$)
$B(C_6F_5)_3$	0.52
$Nb(OEt)_5$	0.36
$Ta(OEt)_5$	0.47
$Nb(OEt)_5$ with $B(C_6F_5)_3$	80.2
$Ta(OEt)_5$ with $B(C_6F_5)_3$	99.3
$Nb(OEt)_5$ and $Ta(OEt)_5$ with $B(C_6F_5)_3$	88.2

lithium *tert*-butoxide, vanadium, zirconium, and hafnium alkoxides, and heterometallic Nb/Ta methoxides have been characterized using electron ionization mass spectrometric techniques.[23−26] One disadvantage of electron ionization sources is that the mass spectra are frequently characterized by intense fragment ions and small molecular ion peaks because of the excess energy that the ion acquires during the ionization process. However, by using ESMS, the principal ions that are present in the solution are observed in the mass spectrum as a result of the soft transfer of ionic species into the gas phase. To the best of our knowledge only a small number of papers have been published on the ESMS examination of metal alkoxides.[16]

When niobium and tantalum ethoxides in dichloromethane, in the absence of tris(pentafluorophenyl)borane, were analyzed using ESMS, poor ion signal was observed, consistent with low conductivity. This is expected because many neutral organometallic complexes cannot be directly observed by ESMS. There are different methods that can be used to produce related ionic species so that these organometallic complexes can be observed using ESMS.[1] For example, β-diketones and Schiff bases can be protonated by the mobile phase to give $[MH]^+$. Also, neutral organometallic complexes can form an adduct with an appropriate metal ion, such as sodium or potassium. Furthermore, generation of cations from neutral organometallics can be achieved by oxidation of the metal center. Finally, sodium methoxide has been used to produce $[M_x(CO)_y]OMe^-$ from neutral metal carbonyl complexes, and sodium ethoxide was used to produce anionic group IV transition metal ethoxide complexes.[16,27] In the current investigation, various strong Brønsted acids, such as triflic acid and hexafluoroantimonic acid, were used in an attempt to produce protonated niobium and tantalum alkoxides, but both the ESMS and conductivity experiments revealed that there were essentially no ions present in these solutions. Therefore, a strong Lewis acid, tris(pentafluorophenyl)borane, was used because a common method to produce transition metal cations in organometallic species is by electrophilic attack of tris(pentafluorophenyl)borane on an M−Me bond to produce $[M]^+[MeB(C_6F_5)_3]^-$.[28] The ESMS data and the conductivity experiments verify that cationic niobium and tantalum ethoxides were produced in solution after the introduction of $B(C_6F_5)_3$.

In the current investigation, the major cationic species present in the electrospray mass spectra of $Nb(OEt)_5$ or $Ta(OEt)_5$ with tris(pentafluorophenyl)borane are $M(OEt)_4^+$, $M_2O(OEt)_7^+$, $M_2(OEt)_9^+$, and $M_3O(OEt)_{12}^+$. It is evident from Figures 1 and 2 that the cationic species observed in the electrospray mass spectrum of both niobium and tantalum ethoxide with $B(C_6F_5)_3$ are similar in nature. This is not unforeseen because the second- and third-row transition series of a given group of the periodic table, especially the early transition metals, tend to possess similar chemical and structural properties.[29]

In Figures 1 and 2, for which the cone voltage is 30 V, the intensity of $M(OEt)_4^+$ is quite small compared to that of the other cations present in the mass spectrum. However, the extent of fragmentation observed in an electrospray mass spectrum can be controlled by varying the voltage applied to the cone. Elevated cone potentials generate ions with increased internal energy where more fragmentation of the principal ions occurs. By increasing the cone voltage from 30 to 65 V, it was found that the relative intensity of $M(OEt)_4^+$ does increase at the expense of $M_2O(OEt)_7^+$, $M_2(OEt)_9^+$, and $M_3O(OEt)_{12}^+$, which indicates that $M(OEt)_4^+$ is a CID product of the larger cations present in the mass spectrum. By increasing the voltage on the cone, it was possible to perform MS/MS experiments on $M(OEt)_4^+$ by selecting this ion using the quadrupole and inducing further CID within the hexapole collision cell. The observed fragmentation pattern during CID experiments of $M(OEt)_4^+$ is consistent with reactions 6−11 in Figure 4. Again, it should be stressed that the CID fragmentation patterns were similar for both niobium and tantalum ethoxides. Figure 6, which shows the CID spectra of $Ta(OEt)_4^+$ at $E_{CM} = 1.1$, 2.9, 5.1, and 7.2 eV, indicates that $M(OEt)_4^+$ sequentially releases four

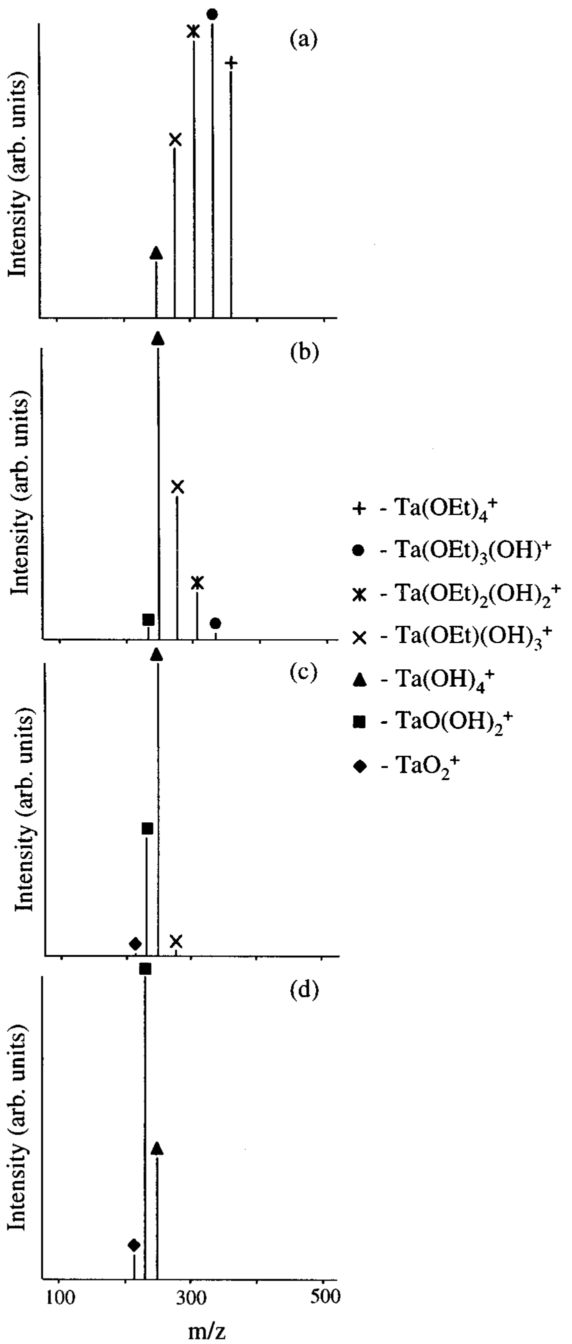
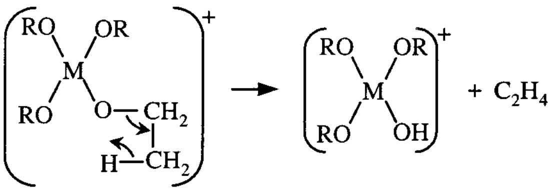


Figure 6. Electrospray mass spectrum of the CID of $Ta(OEt)_4^+$ at center of mass energies of (a) 1.1, (b) 2.9, (c) 5.1, and (d) 7.2 eV.

ethylene molecules to produce $M(OH)_4^+$ at lower collision energies. At higher collision energies $M(OH)_4^+$ further dissociates and liberates two water molecules, leaving MO_2^+. The CID results obtained in this investigation are similar to fragmentation patterns previously observed for chromium and aluminum alkoxide species.[20,22] Alyea et al. investigated the mass fragmentation pattern of chromium *tert*-butoxide, $Cr(O^tBu)_4$, and observed a loss of C_4H_8 to produce the product peak $Cr(O^tBu)_3(OH)^+$.[22] Additionally, Oliver et al. examined the mass fragmentation of aluminum isopropoxide di-*tert*-butoxide, $Al(O^iPr)(O^tBu)_2$, and found that there is loss of C_4H_8 and C_3H_6 units to give the product peak $Al(OR)_2(OH)^+$, which they propose could proceed by a four-centered mechanism.[20] It is possible that the ethylene loss during the CID experiments of $Nb(OEt)_4^+$ and $Ta(OEt)_4^+$ reported herein proceeds by the same β-elimination mechanism, which is shown in Scheme 1. It should be noted that during CID experiments of $M(OEt)_4^+$, loss of an ethoxy group was not observed. This attests to the fact that the M−O bonds in the cationic metal ethoxide are quite strong in nature. In fact, the strength of the HO−CH_2CH_3 bond in ethanol is 3.95 eV, and the strength of the M−O bond is 7.8 or 8.3 eV, where M is Nb or Ta, respectively.[30] Therefore, during CID experiments, it seems probable that loss of the organic molecule from metal ethoxide may occur instead of loss of an ethoxy group. The fragment ion produced at elevated collision energies of $E_{CM} \geq 4$ eV is MO_2^+. This is quite interesting because during CID experiments most gas phase niobium and tantalum oxide cluster cations fragment into MO_2^+, which indicates this is a stable species.[31]

SCHEME 1



Another cationic species that is present in the solutions of niobium and tantalum ethoxides with $B(C_6F_5)_3$ is $M_2(OEt)_9^+$. CID experiments on $M_2(OEt)_9^+$ at low collision energy progress according to reaction 4 in Figure 4, where $M(OEt)_4^+$ and $M(OEt)_5$ are the major products. The presence of $M_2(OEt)_9^+$ in solution is quite interesting because niobium and tantalum alkoxides are known by ebullioscopic measurements to be dimeric, $M_2(OR)_{10}$, in solution.[32] Bradley and co-workers proposed the structure of dimeric niobium and tantalum alkoxides to be a double-bridged alkoxy edge-shared bioctahedral structure, in which each metal atom is bonded to four terminal and two bridging alkoxide groups.[33,34] Additionally, infrared spectroscopy and variable-temperature NMR studies were performed on niobium and tantalum alkoxides, which both confirmed the presence of both bridging and terminal alkoxide groups.[35,36] It is postulated that the structure of $M_2(OEt)_9^+$ is similar to the condensed phase double-bridged alkoxy edge-shared bioctahedral structure proposed by Bradley and co-workers with one ethoxide group missing. Therefore, during CID experiments, fragmentation of $M_2(OEt)_9^+$ could occur at the bridging alkoxy groups, leaving $M(OEt)_4^+$ and the neutral $M(OEt)_5$ molecule.

$M_2O(OEt)_7^+$ and $M_3O(OEt)_{12}^+$ are also observed in the electrospray mass spectrum of both $Nb(OEt)_5$ and $Ta(OEt)_5$ with $B(C_6F_5)_3$. The presence of $M_2O(OEt)_7^+$ and $M_3O(OEt)_{12}^+$ in solution is interesting because these species contain oxy bridges in addition to alkoxy bridges and are therefore referred to as oxo-alkoxides. The alkoxide chemistry of early transition metals contains many examples of oxo-alkoxides, and there are a few ways to explain their presence in solution.[37] Because metal alkoxides are moisture sensitive compounds, oxo-alkoxides can be produced when small amounts of water are added to metal alkoxides due to a partial hydrolysis reaction shown in reaction 27.

$$2M(OEt)_5 + H_2O \rightarrow (OEt)_4M(\mu\text{-}O)M(OEt)_4 + 2ROH \quad (27)$$

However, recently it has been determined that even in the absence of water metal alkoxides can be converted into oxo-alkoxides by an ether elimination reaction, which is shown in reaction 28.

$$2M(OEt)_5 \rightarrow (OEt)_4M(\mu\text{-}O)M(OEt)_4 + R_2O \quad (28)$$

Furthermore, it has also been suggested that the presence of a strong Lewis acid can promote oxide and ether formation from metal alkoxides.[38] Whereas the presence of oxo-alkoxides observed in the current investigation may be due to unintentional hydrolysis, the origin of oxo-alkoxides in the solutions of niobium and tantalum ethoxide with tris(pentafluorophenyl)borane is not clear. It is possible that the solutions of metal ethoxides with tris(pentafluorophenyl)borane in dichloromethane were exposed to water even though precautions were taken to prevent this during sample preparation and analysis. It is also possible that a mechanism similar to the ether elimination shown in reaction 28 produced the oxo-alkoxides present in the solutions of niobium and tantalum ethoxides with tris(pentafluorophenyl)borane. Finally, because $B(C_6F_5)_3$ is present in solution to produce the cationic metal alkoxides, it is possible that this strong Lewis acid promotes oxide and ether formation from the metal ethoxides.

CID experiments were performed on $M_2O(OEt)_7^+$ and proceeded according to reaction 5 in Figure 4 at low collision energy, where $M(OEt_4)^+$ and $MO(OEt)_3$ are the major products. It is thought that the structure of $M_2O(OEt)_7^+$ most likely contains both oxy and alkoxy bridges because this allows the metal atoms to obtain high coordination numbers. During CID experiments, it is postulated that fragmentation occurs at the oxy and alkoxy bridges, leaving $M(OEt)_4^+$ and the neutral $MO(OEt)_3$ molecule. Finally, CID experiments were performed on $M_3O(OEt)_{12}^+$, and the fragmentation pattern proceeded via reactions 1 and 2 in Figure 4 at low collision energy. It is thought that the structure of $M_3O(OEt)_{12}^+$ most likely contains both oxy and alkoxy bridges. It appears that the preferential dissociation pathways are governed by the fact that $Nb_3O(OEt)_{12}^+$ favors losing a neutral $NbO(OEt)_3$ molecule and $Nb_2(OEt)_9^+$, according to reaction 1, with products from reaction 2 being minor. However, $Ta_3O(OEt)_{12}^+$ prefers to lose a neutral $Ta(OEt)_5$ molecule and $Ta_2O(OEt)_7^+$, according to reaction 2, with products from reaction 1 being minor. Furthermore, at elevated collision energies the fragmentation pattern of $M_3O(OEt)_{12}^+$ during CID experiments follows reaction 3 in Figure 4, where $M(OEt)_4^+$ is observed.

The loss of neutral $MO(OEt)_3$ during CID experiments of niobium and tantalum oxo-alkoxides, $M_2O(OEt)_7^+$ and $M_3O(OEt)_{12}^+$, is noteworthy because this molecule, which has a terminal M═O group, is not considered to exist for either niobium or tantalum. As previously mentioned, it seems that the dominant fragments in these CID experiments are governed by the fact that $Nb_3O(OEt)_{12}^+$ prefers to lose $Nb_2(OEt)_9^+$ and neutral $NbO(OEt)_3$ but $Ta_3O(OEt)_{12}^+$ prefers to lose $Ta_2O(OEt)_7^+$ and neutral $Ta(OEt)_5$. This is consistent with the general periodic trend that a 3d transition metal is much more likely than a 5d transition metal to possess a terminal M═O bond.[29] Most of the transition metals form oxide compounds and complexes with bridging oxo-ligands, but only a limited number of these species contain terminal oxo groups, one of which is vanadium. Vanadium is the lighter congener of niobium and tantalum, and the corresponding metal ethoxide is vanadium oxytriethoxide, $VO(OEt)_3$, which possesses a terminal M═O bond. The origin of this periodic trend is not well understood, although it is most likely related to the changes in energy and extension of the metal d orbitals across the periodic table.[39]

In separate experiments heterometallic Nb/Ta ethoxides were produced by allowing a solution of equal molar amounts of neat niobium and tantalum ethoxide to equilibrate. The heterometallic cationic species observed in the electrospray mass spectrum are $NbTaO(OEt)_7^+$, $NbTa(OEt)_9^+$, $Nb_2TaO(OEt)_{12}^+$, and $NbTa_2O(OEt)_{12}^+$. Heterometallic alkoxides typically observed contain a group 1 or 2 metal with a transition metal.[40] However, it has been determined that because the metal−alkoxide bond is labile, formation of heterometallic species is observed even between alkoxides of metals as similar as aluminum and gallium or niobium and tantalum.[38] For example, Hubert-Pfalzgraf et al. synthesized a mixed Nb/Ta methoxide, $NbTa(OMe)_{10}$, which was determined to have a structure analogous to that of $Nb_2(\mu\text{-}OMe)_2(OMe)_8$ but with one niobium atom being substituted by a tantalum atom.[26] CID experiments were performed on $NbTaO(OEt)_7^+$, $NbTa(OEt)_9^+$, $Nb_2TaO(OEt)_{12}^+$, and $NbTa_2O(OEt)_{12}^+$. The major fragment observed at low collision energy during CID experiments of $NbTaO(OEt)_7^+$ is $Ta(OEt)_4^+$, consistent with reaction 12 in Table 1, and the main fragment detected during CID experiments at low collision energy of $NbTa(OEt)_9^+$ is $Nb(OEt)_4^+$ according to reaction 15. Likewise, the main fragment of $NbTa_2O(OEt)_{12}^+$ is $Ta_2(OEt)_9^+$, consistent with reaction 21 in Table 1, and the major fragment of $Nb_2TaO(OEt)_{12}^+$ is $NbTa(OEt)_9^+$ shown in reaction 16. The CID results of heterometallic Nb/Ta ethoxides shown in Table 1 validate the suggestion that $NbO(OEt)_3$ and $Ta(OEt)_5$ are the preferred neutral products during these experiments.

Crotyl alcohol ($CH_3CH{=}CHCH_2OH$)-substituted and *n*-butanol ($CH_3CH_2CH_2CH_2OH$)-substituted metal ethoxide clusters were produced via alcohol exchange reactions primarily to determine if these species, like the metal ethoxides, would lose an R group, as opposed to an OR group, during CID experiments. The reaction of metal alkoxides with an alcohol is generally termed an alcohol exchange reaction, which is shown in reaction 29.[32]

$$M(OR)_n + xR'OH \rightleftarrows M(OR)_{n-x}(OR')_x + xROH \quad (29)$$

The CID results obtained for $M(OEt)_{4-x}(OR)_x^+$, where R is C_4H_7 or C_4H_9, indicate that the primary neutral fragments lost at low collision energies are four organic molecules, leaving $M(OH)_4^+$. For example, $M(OEt)_2(OCrotyl)_2^+$ displayed loss of two 54 Da fragments and two 28 Da fragments during CID experiments, which corresponds to loss of C_4H_6 and C_2H_4. Additionally, during CID experiments on $M(OEt)_2(OButyl)_2^+$, loss of two 56 Da units and two 28 Da units was observed, which corresponds to loss of C_4H_8 and C_2H_4. Whereas the loss of ethylene from these cationic species most likely follows the β-elimination mechanism proposed in Scheme 1, the loss of C_4H_6 and C_4H_8 may occur due to a δ-elimination mechanism.

Figure 3 displays the anions that are present in solution, which correspond to $B(C_6F_5)_3OH^-$ and $B(C_6F_5)_3OEt^-$. The presence of $B(C_6F_5)_3OEt^-$ can be explained by reaction 30

$$(C_6F_5)_3B + M(OEt)_5 \rightarrow (C_6F_5)_3BOEt^- + M(OEt)_4^+ \quad (30)$$

where the Lewis acid, $B(C_6F_5)_3$, directly abstracts an ethoxy group from the metal ethoxide and produces a cationic metal ethoxide species. It is apparent from Figure 3 that the predominant anion in the electrospray mass spectrum is $(C_6F_5)_3BOH^-$. The presence of this particular anion in solution may be explained by a reaction of tris(pentafluorophenyl)borane with contaminant water in the system. In fact, it has been proposed by Danopoulos et al. that upon addition of water to $B(C_6F_5)_3$, reaction 31 occurs.[41]

$$B(C_6F_5)_3 + H_2O \rightleftarrows (C_6F_5)_3B{-}OH_2 \rightleftarrows (C_6F_5)_3B{-}OH^-H^+ \quad (31)$$

The samples might have been exposed to moisture despite the precautions taken to prevent this. Therefore, it is possible that $(C_6F_5)_3BOH^-$ is produced during a reaction of $(C_6F_5)_3B-OH^-H^+$ with the metal alkoxide.

Conclusions

Niobium and tantalum alkoxide cations were produced in solution by the addition of tris(pentafluorophenyl)borane and were investigated using an electrospray mass spectrometer. The major cations present in solution were determined to be $M(OEt)_4^+$, $M_2O(OEt)_7^+$, $M_2(OEt)_9^+$, and $M_3O(OEt)_{12}^+$. CID experiments were performed on the cationic metal alkoxides to provide some structural insight. The fragmentation pattern of $Nb_3O(OEt)_{12}^+$ favored loss of $Nb_2(OEt)_9^+$ and neutral $NbO(OEt)_3$, whereas the fragmentation pattern of $Ta_3O(OEt)_{12}^+$ preferred loss of $Ta_2O(OEt)_7^+$ and neutral $Ta(OEt)_5$. The dissociation patterns of $M_2O(OEt)_7^+$ and $M_2(OEt)_9^+$ revealed that $M(OEt)_4^+$ is the major product at low collision energies. Finally, CID of $M(OEt)_4^+$ revealed that four consecutive ethylene molecules are released to leave $M(OH)_4^+$, which at higher collision energies liberated two water molecules to produce MO_2^+.

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References and Notes

(1) Colton, R.; D'Agostino, A.; Traeger J. C. *Mass Spectrom. Rev.* **1995**, *14*, 79.

(2) Canty, A. J.; Colton, R.; Thomas, I. M. *J. Organomet. Chem.* **1993**, *455*, 283.

(3) Canty, A. J.; Traill, P. R.; Colton, R.; Thomas, I. M. *Inorg. Chim. Acta* **1993**, *210*, 91.

(4) Brown, D. G.; Byers, P. K.; Canty, A. J. *Organometallics* **1990**, *9*, 1231.

(5) Byers, P. K.; Canty, A. J.; Skelton, B. W.; White, A. H. *Organometallics* **1990**, *9*, 826.

(6) Canty, A. J.; Colton, R. *Inorg. Chim. Acta* **1994**, *215*, 179.

(7) Dakternieks, D.; Zhu, H.; Tiekink, E. R. T.; Colton, R. *J. Organomet. Chem.* **1994**, *476*, 33.

(8) Bond, A. M.; Colton, R.; Cooper, J. B.; Traeger, J. C.; Walter, J. N.; Way, D. M. *Organometallics* **1994**, *13*, 3434.

(9) Ahmed, I.; Bond, A. M.; Colton, R.; Jurcevic, M.; Traeger, J. C.; Walter, J. N. *J. Organomet. Chem.* **1993**, *447*, 59.

(10) Traeger, J. C. *Int. J. Mass Spectrom.* **2000**, *200*, 387.

(11) Henderson, W.; Nicholson, B. K.; McCaffrey, L. J. *Polyhedron* **1998**, *17*, 4291.

(12) Lau, T.-C.; Wang, J.; Siu, K. W.; Guevremont, R. *J. Chem. Soc. Chem. Commun.* **1994**, 1487.

(13) Kenny, J. A.; Versiuis, K.; Heck, A. J. R.; Walsgrove, T.; Wills, M. *J. Chem. Soc., Chem. Commun.* **2000**, 99.

(14) Stewart, I. I.; Horlick, G. *Trends Anal. Chem.* **1996**, *15*, 80.

(15) Truebenbach, C. S.; Houalla, M.; Hercules, D. M. *J. Mass Spectrom.* **2000**, *35*, 1121.

(16) Løver, T.; Henderson, W.; Bowmaker, G. A.; Seakins, J. M.; Cooney, R. P. *J. Mater. Chem.* **1997**, *7*, 1553.

(17) Deng, H. T.; Kerns, K. P.; Castleman, A. W., Jr. *J. Phys. Chem.* **1996**, *100*, 13386.

(18) Zemski, K. A.; Bell, R. C.; Castleman, A. W., Jr. *J. Phys. Chem. A* **2000**, *104*, 5732.

(19) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

(20) Oliver, J. G.; Worrall, I. J. *J. Chem. Soc. (A)* **1970**, 845.

(21) Oliver, J. G.; Worrall, I. J. *J. Chem. Soc. (A)* **1970**, 2347.

(22) Alyea, E. C.; Basi, J. S.; Bradley, D. C.; Chisholm, M. H. *J. Chem. Soc. (A)* **1971**, 772.

(23) Hartwell, G. E.; Brown, T. L. *Inorg. Chem.* **1966**, *5*, 1257.

(24) Adler, B.; Bieräugel, I.; Lachowicz, A.; Thiele, K.-H. *Z. Anorg. Allg. Chem.* **1977**, *431*, 227.

(25) Turevskaya, E. P.; Kozlova, N. I.; Turova, N. Y.; Belokon', A. I.; Berdyev, D. V.; Kessler, V. G.; Grishin, Y. K. *Russ. Chem. Bull.* **1995**, *44*, 734.

(26) Hubert-Pfalzgraf, L. G.; Reiss, J. G. *Inorg. Chem.* **1975**, *14*, 2584.

(27) Henderson, W.; McIndoe, J. S.; Nicholson, B. K.; Dyson, P. J. *Chem. Commun.* **1996**, 1183.

(28) Hill, G. S.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 525.

(29) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley: New York, 1988.

(30) *Handbook of Chemistry and Physics*, 67th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1986; F-171.

(31) Unpublished results from our laboratory.

(32) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: New York, 1978.

(33) Bradley, D. C.; Wardlaw, W.; Whitley, A. *J. Chem. Soc.* **1955**, 726.

(34) Bradley, D. C.; Chakravarti, B. N.; Wardlaw, W. *J. Chem. Soc.* **1956**, 2381.

(35) Bradley, D. C.; Westlake, A. H. *Proceedings of the Symposium of Coordination Chemistry*; Hungarian Academy of Science: Budapest, 1965.

(36) Bradley, D. C.; Holloway, C. E. *J. Chem. Soc. (A)* **1968**, 219.

(37) Mehrotra, R. C.; Singh, A. *Chem. Soc. Rev.* **1996**, *25*, 1.

(38) Caulton, K. G.; Hubert-Pfalzgraf, L. G. *Chem. Rev.* **1990**, *90*, 969.

(39) Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds: The Chemistry of Transition Metal Complexes Containing Oxo, Nitrido, Imido, Alkylidene, or Alkylidyne Ligands*; Wiley: New York, 1988; pp 29−32.

(40) Mehrotra, R. C.; Singh, A. In *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; Wiley: New York, 1997; pp 239−454.

(41) Danopoulos, A. A.; Galsworthy, J. R.; Green, M. L. H.; Cafferkey, S.; Doerrer, L. H.; Hursthouse, M. B. *Chem. Commun.* **1998**, 2529.