planar complex to yield a coordinatively unsaturated 14-electron $[PtMe_2(Me_2SO)]$ species as a reaction intermediate. This strong electrophilic species is able to interact with the alkyl complex either by accepting a phosphine ligand released by the substrate (route A) or by interaction with a lone pair of the coordinated chloride (route B). In route A, the release of the phosphine yields the uncharged "cis-like" 14-electron 3-coordinate [PtL(R)Cl] intermediate. This latter easily interconverts into its "trans-like" analogue that eventually undergoes the reentry of L to yield *trans*-$[PtL_2(R)Cl]$, with a sequence of reaction steps like those described in Scheme III. Electrophilic removal of chloride and interconversion of a cationic $[PtL_2R]^+$ intermediate (route B) leads to the same final trans product. This is in agreement with the low energy barrier found for the fluxionality of coordinatively unsaturated reaction intermediates such as $H(PH_3)_2Pt$,[8] Me_3Au,[9] or $Et_2(PEt_3)Pt$.[10] The mechanism leads to the rate expression

$$k_{obsd} = \frac{k_1}{k_{-1}}\left[\frac{k_2k_3}{k_{-2} + k_3} + \frac{k'_2k'_3}{k'_{-2} + k'_{-3}}\right]\left[\frac{C}{S}\right] \qquad (6)$$

which is consistent with rate law 5, a part from the constant term *a* (the value of the intercept in Figure 4), which represents the contribution of the uncatalyzed pathway to the overall process.

This mechanism is reminiscent of that proposed by Scott and Puddephatt[23] in the study of the methyl for chloro exchange reaction in $CDCl_3$ solution between *cis*-$[PtMe_2(SMe_2)_2]$ and *trans*-$[PtCl_2(SMe_2)_2]$ to yield *trans*-$[Pt(SMe_2)_2MeCl]$ that occurs after preliminary dissociation of the dimethyl sulfide from the dialkyl compound to form a coordinatively unsaturated "cis-like" $[PtMe_2(SMe_2)]$ intermediate. This was borne out by the mass law retardation produced in the rate of exchange by addition of free SMe_2 in solution. A key step of the process is thought to be the attack of the electron-deficient $[PtMe_2(SMe_2)]$ species to either the chloride or the thioether groups bonded to $[PtCl_2(SMe_2)_2]$ to yield a μ-chloro- or μ-SMe_2-bridged adduct. Thus two reaction pathways for the breakdown of the adduct are feasible followed by fast readdition of thioether.

At this stage we are unable to establish whether both pathways in Scheme IV for uncatalyzed isomerization are operative or to infer which is the favored one. Perhaps a detailed investigation of catalyzed isomerization of similar substrates, where the halides or the σ-donor power of the group in trans to the phosphine is alternatively changed, could shed some light on the problem. However, we think that the most significant aspect of this work is the clear demonstration that an electron-deficient 3-coordinate species is acting as a catalyst of isomerization. This adds a new example to the growing list of reactions of d^8 transition-metal complexes in which such 14-electron species are implicated as key intermediates.[11] The use of *cis*-$[PtR_2S_2]$ complexes as precursors of potential catalysts in other processes, where the removal of a phosphine from the coordination sphere of a metal is a critical step, is being investigated.

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Supplementary Material Available: Tables SI and SII, giving primary kinetic data (2 pages). Ordering information is given on any current masthead page.

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Spectroscopy and Electrochemistry of U(IV)/U(III) in Basic Aluminum Chloride–1-Ethyl-3-methylimidazolium Chloride

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The redox chemistry of UCl_4 has been investigated in the solvent $AlCl_3$–1-ethyl-3-methylimidazolium chloride ($AlCl_3$–EMIC), a room-temperature ionic liquid. In basic solutions (<50 mol % $AlCl_3$) the reduction of U(IV) to U(III) on glassy carbon electrodes is reversible. Visible/near-IR spectroscopic data and potentiometric measurements for U(IV)/U(III) as a function of the basic composition of $AlCl_3$–EMIC indicate U(IV) and U(III) are both hexachloro anions. Diffusion coefficients were measured for the U(IV) and U(III) complexes by two methods. The values are comparable to those of transition-metal hexachloro anionic complexes in the same solvent, supporting the assignment of $[UCl_6]^{2-}$ and $[UCl_6]^{3-}$.

Introduction

Mixtures of aluminum chloride and certain organic chlorides (1-butylpyridinium chloride (BPC) and 1-ethyl-3-methylimidazolium chloride (EMIC)) produce room-temperature ionic liquids which exhibit widely varying Lewis acid–base properties depending on their composition.[1] Ionic liquids containing greater than 50 mol % $AlCl_3$ are considered "acidic" because they contain the strongly Lewis acidic species $Al_2Cl_7^-$, whereas those that contain less than 50 mol % $AlCl_3$ are denoted as "basic" because they contain free chloride ion.

Basic $AlCl_3$–BPC and $AlCl_3$–EMIC have been used extensively to study the electrochemistry and spectroscopy of transition-metal,[2] lanthanide,[3] and actinide[4] chloride complexes. These ionic liquids do not undergo solvolysis reactions that are common in aqueous solutions, and they form chloride complexes more readily than in molecular solvents such as acetonitrile or methyl alcohol. The electrochemistry of U(IV) was examined in basic $AlCl_3$–BPC,

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where no reduction to U(III) was observed.[5] However, in basic $AlCl_3$–EMIC, the reduction of U(IV) to U(III) was observed by cyclic voltammetry, as the 1-ethyl-3-methylimidazolium cation (EMI^+) is 800 mV more difficult to reduce than the butylpyridinium cation (BP^+).[6]

The spectroscopy of U(III) has been studied in acidic $AlCl_3$–BPC, and U(III) was found to be uncomplexed. This lack of complexing is evident in the similarity of the visible/near-IR spectrum to that of U(III) in 1 M $HClO_4$.[7] There have been few absorbance spectra of U(III) chloro complexes reported in the literature. Gruen and McBeth reported the visible and near-IR spectra of U(III) in LiCl–KCl eutectic at 400 °C;[8] however, the high temperature significantly broadened the bands in the near-IR spectrum. A visible spectrum of a U(III) chloro complex in basic NaCl–$AlCl_3$ was recorded at 395 °C.[9] The authors indicated the instability of U(III) chloro complexes in the presence of trace amounts of water and oxygen. In the present article, we report definitive visible and near-IR spectra for $[UCl_6]^{3-}$, along with electrochemical data for $[UCl_6]^{2-}$ and $[UCl_6]^{3-}$ complexes. Diffusion coefficients for the U(IV) and U(III) chloro complexes were determined by chronoamperometry and linear sweep voltammetry.

Experimental Section

Apparatus. All liquid mixtures of $AlCl_3$–EMIC were prepared in a Vacuum Atmospheres drybox equipped with a Model HE-495 dry train. Electrochemical leads were introduced into the drybox to allow measurements therein. An argon atmosphere containing less than 5 ppm of O_2 was maintained by continuous circulation of the atmosphere through the purification train.

Conventional cyclic voltammetry and linear-sweep voltammetry were performed with a BAS CV-1B cyclic voltammograph. Data display was accomplished on a Houston Instruments Model 2000 XY recorder. Chronoamperometric measurements were recorded on a Nicolet 310 digital oscilloscope used in conjunction with a PAR 173 potentiostat and PAR 175 universal programmer. Rotating disk electrode (RDE) voltammetry was performed with a Bruker E-RS-1 glassy-carbon rotating disk electrode (GCRDE) and a PAR 174A polarographic analyzer. Coulometry was achieved with a PAR Model 173 potentiostat and a PAR 179 digital coulometer.

The electrolytic cells were made of Pyrex glass, equipped with 7- and 11-mm threaded glass joints with Teflon bushings and FETFE O-ring seals for the working electrodes and reference compartments (Ace Glass, Inc.).[10] The working electrodes were made of glassy carbon (3-mm o.d.) or tungsten (4-mm o.d.). The counter electrode was a coiled tungsten wire (0.5 mm, Alfa, M3N8). The reference electrode consisted of a coiled aluminum wire (0.58 mm, Alfa, M5N) immersed in $AlCl_3$-saturated $AlCl_3$–EMIC, separated from the working solution by a reference compartment with a fine-porosity frit. Electrode wires were sealed with vacuumtight standard tungsten–Pyrex seals. Bulk electrolysis experiments were carried out with the use of a large surface area platinum-gauze electrode or glassy-carbon crucible. All electrochemical measurements were performed at ambient temperature inside the drybox (28 ± 2 °C).

Visible and near-IR spectra were collected by a Cary 14 scanning spectrophotometer converted by On-Line Instrument Systems (OLIS) for data acquisition and analysis by a Zenith 248 computer. Seven millimeter diameter threaded glass joints (Ace Glass, Inc.) were attached to Pyrex graded seals (NSG Precision Cells, Inc.), and the cells were sealed airtight by Teflon stoppers with FETFE O-rings (Ace Glass, Inc.).

To accurately determine the concentrations of U(IV) and U(III) used in obtaining diffusion coefficients for the hexachloro complexes, a method involving the preparation of the arsenazo III complex of the UO_2^{2+} species was employed. The U(IV) or U(III) species in basic $AlCl_3$–EMIC was oxidized to UO_2^{2+} by heating with concentrated HNO_3. The UO_2^{2+} formed a 1:1 complex with arsenazo III which has an absorbance spectrum with a maximum at 656 nm and a molar absorptivity of 59 000 L/(mol·cm).[11] The absorbance was compared to a standard of known concentration.

Chemicals. The synthesis of EMIC was performed at Oak Ridge National Laboratory by the procedure of Smith et al.[12] Aluminum chloride (Fluka, puriss) was sublimed in vacuo from $AlCl_3$–NaCl a minimum of three times.[13] Ethylaluminum dichloride (Aldrich) was used as received. UCl_4 (Cerac) was used without further purification.

Results and Discussion

Voltammetry. A cyclic voltammogram of a solution of UCl_4 in basic $AlCl_3$–EMIC exhibited one reduction wave accompanied by a corresponding oxidation wave when the scan direction was reversed at a glassy-carbon or tungsten disk electrode. This is similar to the behavior observed by Hitchcock et al.[6] The formal potential ($E^{\circ\prime}$) of the U(IV)/U(III) redox couple in a 45:55 $AlCl_3$:EMIC mixture was −1.35 V (vs Al in a 67:33 $AlCl_3$:EMIC mixture).

In rotating disk electrode (RDE) experiments, ethylaluminum dichloride was used to eliminate protonic impurities that obscured the U(IV)/U(III) redox couple. Ethylaluminum dichloride reacts with protons, producing $AlCl_3$ and C_2H_6.[14] Nernst plots (log $((i_L - i)/i)$ vs $E^{\circ\prime}$) for RDE voltammograms in basic $AlCl_3$:EMIC solvent compositions (mol %) of 42.9:57.1, 44.5:55.5, and 46.6:53.4 gave slopes of 63, 64, and 65 mV, respectively, which are close to the theoretical slope of 59 mV for a one-electron reversible charge-transfer reaction at 25 °C. RDE voltammograms of UCl_4 solutions taken at different rotation rates showed that the limiting currents increased linearly with the square root of the rotation rate ($\omega^{1/2}$), as predicted by Levich's equation.[15] Linear behavior was also observed for plots of current vs $\omega^{1/2}$ for currents measured at potentials more positive than that for the limiting current. This demonstrated that the current response was affected only by mass transfer in the vicinity of the electrode, not by the kinetics of electron transfer. The RDE voltammetric data are consistent with the reduction of U(IV) to U(III) in basic $AlCl_3$–EMIC being a reversible one-electron process.

To determine the number of chlorides coordinating to U(IV) and U(III), the formal potential of U(IV)/U(III) was measured as a function of the basic composition of $AlCl_3$–EMIC by cyclic and RDE voltammetry. If it is assumed from previous studies that U(IV) exists as a hexachloro complex[5,6] in basic solutions, then the reduction of U(IV) to U(III) can be written

$$[UCl_6]^{2-} + 1e^- \rightleftharpoons [UCl_x]^{(3-x)+} + (6-x)Cl^-$$

If U(IV) and U(III) both exist as hexachloro complexes in basic $AlCl_3$–EMIC, the slope of a plot of $E^{\circ\prime}$ vs pX_{Cl} should be zero. Results from cyclic and RDE voltammetry indicated a positive shift of 20–25 mV between the formal potentials in the most basic (40:60 $AlCl_3$:EMIC) and almost neutral (49:51 $AlCl_3$:EMIC) compositions. Hussey and co-workers reported shifts of 20–25 mV/pCl unit in the formal potential with changes in chloride ion concentration for transition-metal complexes in which both oxidized and reduced species are known to be hexachloro complexes.[16] Hussey has interpreted this shift in potential as due to Coulombic interactions between the cationic EMI^+ and solute chlorometalate anions.[12b] Presumably, this is the origin of the potential shift in

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Table I. Diffusion Coefficients and Stokes–Einstein Products for $[UCl_6]^{2-}$ and $[UCl_6]^{3-}$ in Basic $AlCl_3$–EMIC

			10^7D,[a] $cm^2 \cdot s^{-1}$		$10^{10}D/T$, $cm^2 \cdot s^{-1} \cdot K^{-1}$	
solute	$AlCl_3$:EMIC	concn, mM	CA	LSV	CA	LSV
$[UCl_6]^{2-}$	45.2:54.8	7.41		2.0 ± 0.4		1.8 ± 0.3
$[UCl_6]^{2-}$	44.8:55.2	8.22	1.85 ± 0.03		1.70 ± 0.03	
$[UCl_6]^{3-}$	44.8:55.2	8.22	1.61 ± 0.03	1.3 ± 0.2	1.48 ± 0.03	1.2 ± 0.2

[a] The uncertainties in the diffusion coefficients are based on 95% confidence limits.

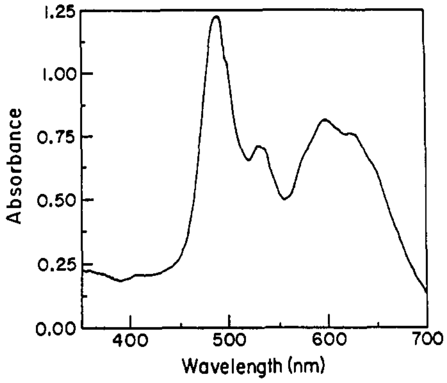

Figure 1. Visible spectrum of U(III) in basic $AlCl_3$ + EMIC.

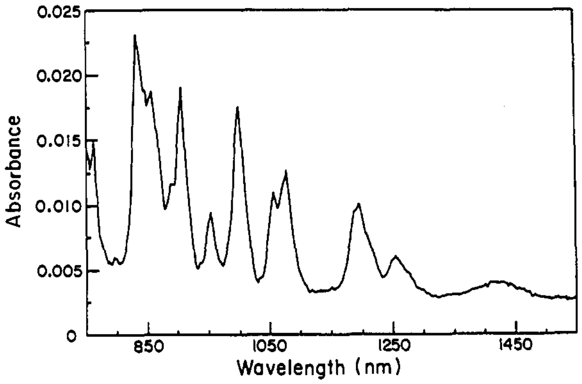

Figure 2. Near-IR spectrum of U(III) in basic $AlCl_3$ + EMIC.

our systems, and like the transition-metal halides, both U(IV) and U(III) complexes are hexachloro species.

Exhaustive Electrolysis. Electrolyses were performed on U(IV) solutions at a constant potential of −1.6 V. During the electrolyses in an open cell, the current did not decay to zero but stabilized at a value approximately 10% of the initial current, indicating the reduction did not go to completion. A possible explanation for this is the presence of oxide or protons in the solvent (presumably, sorbed into the melt from the drybox atmosphere), which reacted with the product of the reduction, U(III), and reoxidized a fraction to U(IV). To minimize this problem, electrolyses were repeated in a closed cell in which the current dropped to approximately 4% of the initial value. However, the inability to completely reduce U(IV) in both closed and open cells prevented determining the amount of charge required to effect the reduction of U(IV). Consequently, we could not obtain the number of electrons involved in the reduction to confirm formation of U(III). However, the electrolysis product could be characterized spectroscopically.

Spectroscopy. D'Olieslager and co-workers published the spectrum of U(IV) in basic $AlCl_3$–BPC and associated it with $[UCl_6]^{2-}$.[5] The spectrum of UCl_4 in basic $AlCl_3$–EMIC obtained in this study was identical with that reported by D'Olieslager. During the electrolysis of U(IV) in basic $AlCl_3$–EMIC, the color of the solution changed from the pale green of U(IV) to a deep blue, assumed to be due to U(III). The near-IR spectrum of the initial solution of UCl_4 compared to that of the electrolysis product indicates the presence of anywhere from 5 to 20% U(IV) in the product solution. However, there is little overlap between the bands due to U(IV) and those of U(III). The visible and near-IR spectra of the electrolysis product are shown in Figures 1 and 2. The near-IR spectrum of U(III) was corrected for absorbance due to U(IV).

The intense broad bands present in the visible spectrum of U(III) in basic $AlCl_3$–EMIC are typical of the LaPorte-allowed $5f^3$–$6d^1$ transitions observed for inner-sphere chloro complexes such as those prepared by Drozdzynski in HCl-saturated anhydrous methyl alcohol and dimethylformamide.[17] Spectra of U(III) chloro complexes in the anhydrous organic solvents[17] bear little similarity to that of U(III) in basic $AlCl_3$–EMIC. It is doubtful that hexachloro complexes were formed in methyl alcohol or DMF due to solvent coordination. Visible spectra of U(III) in high-temperature chloride molten salts[8,9] are more comparable to the spectrum of U(III) in basic $AlCl_3$–EMIC, due to the fact that chloride ion is the only complexing species in such molten-salt systems.

Correction of the near-IR spectrum of U(III) for bands due to U(IV) showed that the residual near-IR spectrum is due to f–f transitions of a U(III) chloro complex. Unfortunately, the broad bands of the spectra of U(III) in LiCl–KCl at 400 °C recorded by Gruen and McBeth[8] did not allow a useful comparison with ours.

The visible/near-IR spectra of U(III) in basic $AlCl_3$–EMIC are notably different from the spectra in acidic room-temperature ionic liquids. The f–f transitions in the near-IR spectrum of U(III) in basic $AlCl_3$–EMIC are less intense than in acidic melt, indicative of the formation of symmetrical octahedral chloro complexes in the former. The absence of chloride ions in acidic ionic liquids accounts for the striking differences between the spectra of U(III) in basic $AlCl_3$–EMIC and in acidic $AlCl_3$–BPC or $AlCl_3$–EMIC. The spectra of U(III) in basic $AlCl_3$–EMIC indicate the presence of a U(III) chloro complex which was not observed in the study of the acidic solvent.

Diffusion Coefficients. Diffusion coefficients were estimated for $[UCl_6]^{2-}$ and $[UCl_6]^{3-}$ in basic $AlCl_3$–EMIC from linear-sweep voltammetry (LSV) and chronoamperometric (CA) data. The diffusion coefficients and Stokes–Einstein products, $D\eta$, which are inversely proportional to the radii of the diffusing species, are included in Table I. The Stokes–Einstein products for the hexachlorouranium complexes agree very well with values obtained by Hussey and co-workers for many transition-metal hexachloro anionic complexes.[18] The agreement between the diffusion coefficients for the uranium and transition-metal hexachloro complexes in basic $AlCl_3$–EMIC is further support of Hussey's proposal of significant ion pairing between the metal anionic complex and the EMI^+ present in the basic system. In comparing diffusion coefficients of anionic complexes of various transition metals in room-temperature haloaluminate ionic liquids, Hussey pointed out that the Stokes–Einstein product depends more on the overall charge of the complex than on the nature of the metal center.[18] The overall negative charge on the hexahalometalate complex determines the number of EMI^+'s that are ion paired. In the case of $[UCl_6]^{2-}$ and $[UCl_6]^{3-}$, two and three EMI^+'s might be associated with the anionic complexes, respectively, accounting for the large difference in their Stokes–Einstein products.

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Conclusions

It has been previously established that U(IV) exists as a hexachloro complex in basic $AlCl_3$–EMIC. Rotating disk electrode voltammetry has confirmed $[UCl_6]^{2-}$ reduces reversibly to $[UCl_6]^{3-}$; however, it is difficult to prepare pure solutions of $[UCl_6]^{3-}$ by electrolysis due to the instability of U(III) chloro complexes in the presence of trace amounts of water and oxygen. Although pure solutions of $[UCl_6]^{3-}$ have not been obtained, subtraction of the absorbance due to the small amount of $[UCl_6]^{2-}$ present has yielded a definitive spectrum of $[UCl_6]^{3-}$.

Potentiometric and diffusion coefficient measurements on U(IV)/U(III) in basic $AlCl_3$–EMIC are consistent with data on hexachloro transition-metal redox couples. The data suggest hexachloro anionic metalate complexes are not present in the ionic liquid as simple anions but are associated with one or more EMI^+'s. The Stokes–Einstein coefficients of $[UCl_6]^{2-}$ and $[UCl_6]^{3-}$ are nearly identical with those of transition-metal hexachloro anions in basic $AlCl_3$–EMIC, demonstrating that the sizes of the diffusing ion-pair complexes containing a particular central metal charge state are the same irrespective of the metal center.

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Stabilization of the Defect ("Lacunary") Complex $PMo_{11}O_{39}{}^{7-}$. Isolation, Purification, Stability Characteristics, and Metalation Chemistry

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All 19 literature citations of the lacunary complex $PMo_{11}O_{39}{}^{7-}$ deal with aqueous solutions, conditions under which this anion is kinetically labile. Kinetic stabilization of $PMo_{11}O_{39}{}^{7-}$, a compound of central value in development of the chemistry and applications of defect polymolybdophosphates, is made possible by precipitation of this polyoxoanion from aqueous solutions containing the requisite proportions of the parent Keggin complex α-$H_3PMo_{12}O_{40}$, and OH^-, by addition of n-Bu_4N^+. The yield of the product, $(Bu_4N)_4H_3PMo_{11}O_{39}$ (**1**), versus the byproducts, principally $P_2Mo_{18}O_{62}{}^{6-}$, varies greatly with the initial concentrations of α-$PMo_{12}O_{40}{}^{3-}$ and base prior to precipitation. All of the redox couples of **1** in acetonitrile are completely irreversible, unlike those of the parent complex, α-$H_3PMo_{12}O_{40}$, and other polyoxometalates whose structures are comprised of MO_6 octahedra with one terminal oxo group. In contrast to $PMo_{11}O_{39}{}^{7-}$ in aqueous solution, **1** in acetonitrile solution can be (a) highly purified by recrystallization with no generation of other polymolybdophosphates, (b) reversibly protonated to $H_4PMo_{11}O_{39}{}^{3-}$, which slowly decomposes to $PMo_{12}O_{40}{}^{3-}$, $P_2Mo_{18}O_{62}{}^{6-}$, and $P_2Mo_5O_{23}{}^{6-}$, and (c) reversibly deprotonated to $H_2PMo_{11}O_{39}{}^{5-}$ by 1 equiv of OH^- and readily converted to α-A-$PMo_9O_{31}(OH)_3{}^{6-}$ and $PMo_{12}O_{40}{}^{3-}$ by >1 equiv of OH^-. **1** can be metalated with several divalent d^n, $n \neq 0$ transition-metal (TM) ions to form the corresponding TM-substituted polymolybophosphates, $PMo_{11}(TM)O_{39}{}^{5-}$. Unlike Co^{II}, Mn^{II}, or Cu^{II}, metalation with Zn^{II} induces the decomposition of **1**. Effective metalations of **1** can be carried out by a homogeneous one-phase procedure (acetonitrile solvent and TM triflate salt) or by a heterogeneous two-phase procedure (treatment of 3:2 acetonitrile–toluene solution of **1** with an aqueous solution of the TM salt). The rates of exchange of terminal axial ligands, L, in $PM_{11}(TM\text{-}L)O_{39}{}^{n-}$ (M = Mo, W), in the aprotic medium, acetonitrile, which depend on the TM, the axial ligand, and on the polyoxometalate ligand environment, are discussed.

Introduction

One of the most cited of all early-transition-metal polyoxometalates is the heteropoly compound dodecamolybdophosphate, α-$PMo_{12}O_{40}{}^{3-}$, or in its protonated form, dodecamolybdophosphoric acid, α-$H_3PMo_{12}O_{40}$. This complex and its derivatives have numerous analytical and chemical applications.[1,2] Most significantly, however, they constitute key components in catalysts for relatively new major heterogeneous catalytic processes.[3,4] In the course of trying to prepare pure samples of the defect of "lacunary" form of the Keggin complex, $PMo_{11}O_{39}{}^{7-}$ (Figure 1), and the d^n, $n \neq 0$, transition-metal- (TM-) substituted complexes derived thereof, $PMo_{11}(TM)O_{39}{}^{n-}$, and to examine their chemical and catalytic properties, it became apparent that no satisfactorily reliable, reproducible, and selective method for the preparation of these complexes existed under conditions in which they were kinetically stable. This is in sharp contrast to the analogous polyoxotungstates. The preparation of the lacunary form of the poly-

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