

New {RuNO} Polyoxometalate $[PW_{11}O_{39}Ru^{II}(NO)]^{4-}$: Synthesis and Reactivity

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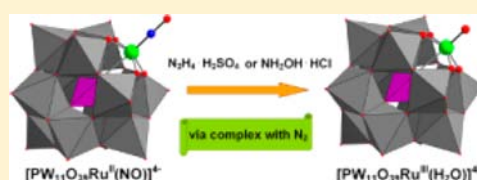
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S Supporting Information

ABSTRACT: New Ru-containing polyoxometalate $[PW_{11}O_{39}Ru^{II}(NO)]^{4-}$ (1^{4-}) was obtained in high yield by reaction of $[Ru(NO)Cl_5]^{2-}$ with $[PW_{11}O_{39}]^{7-}$ and characterized by multinuclear NMR, cyclic voltammetry, IR spectroscopy, and electrospray ionization mass spectrometry (ESI-MS). The intrinsic reactivity of the {RuNO} site in 1^{4-} toward various reagents has been studied using a versatile and simple ESI tandem mass spectrometric methodology for identification of the L attached at the Ru site; this approach relies on the preferential liberation of the L ligands attached at the Ru sites upon mass-selecting desired intermediates and subsequent promotion of their fragmentation. Reactions with both hydrazine and hydroxylamine lead to elimination of the nitroso group and quantitative formation of $[PW_{11}O_{39}Ru^{III}(H_2O)]^{4-}$ (2^{4-}) in aqueous solution. In the reaction with hydroxylamine, an intermediate with coordinated dinitrogen has been detected. An easy access to the NH_3 -coordinated $[PW_{11}O_{39}RuNH_3]^{4-}$ (3^{4-}) complex was achieved upon reduction of 1^{4-} with Sn^{2+} in water.



INTRODUCTION

Polyoxometalates (POM) constitute one of the most important classes of transition metal polynuclear oxocomplexes. This class of compounds is a “front-edge” topic of modern inorganic chemistry, due to a number of unique features such as a remarkable structural diversity and, consequently, a high variety of chemical properties.¹ Research in this field is strongly inspired by its importance both for fundamental chemistry, in particular for developing such basically important concepts like self-assembly,² and for different applied areas such as materials science, magnetism,³ and catalysis,⁴ in particular photocatalysis.⁵

Inside this area, chemistry of POM complexes with noble metals is particularly important.⁶ These complexes are expected to provide a useful synergism from combining reactivity peculiar to POM and noble metal complexes. Many complexes of this kind demonstrate good catalytic activity toward oxidation of various organic substrates⁷ and, what is even more interesting, in water splitting reactions.⁸

The most studied structural type of noble metal POM complexes is based on monolacunary Keggin derivatives $\{EW_{11}M\}$. Though reported examples for M = noble metal also include rhodium,⁹ iridium,¹⁰ palladium,¹¹ and osmium,¹² and, very recently, Kato et al. reported the synthesis of a Pt-containing complex,¹³ the lion's share in this area belongs to the chemistry of ruthenium: there are a number of papers by the groups of Proust, Sadakane, Kortz, and Bonchio dedicated to synthesis and characterization,¹⁴ reactivity studies, i.e., catalytic activity at the Ru site,¹⁵ and DFT calculations.¹⁶

However, despite the outstanding progress achieved in this field there are still several important points to be investigated. The first one is diversification of synthetic approaches to the $[XW_{11}O_{39}Ru(H_2O)]^{n-}$ polyoxoanions which in most cases serve as catalysts or precursors for further transformations. Several methods of incorporation of the $\{Ru(H_2O)\}$ unit have been suggested, but no one can be referred to as “standard” due to various features which restrict their area of application. Some of the described synthetic procedures give good yields of the targeted product, but require use of special techniques [for example, high temperature (220 °C) autoclave treatment^{14c} or microwave irradiation^{14c}] or precursors which require multistep preparation and working under inert atmosphere.^{14a} A very elegant method involving benzene complexes of ruthenium has been put forward,^{15g} which can be considered as the most convenient to date. However, the search for alternative methods to $[XW_{11}O_{39}Ru(H_2O)]^{n-}$ is still ongoing.

The second point for investigation is reactivity of ligands coordinated to Ru atom in $\{EW_{11}O_{39}Ru\}$ -type POM. This area is very promising, taking into account exciting data on reactivity of the nitrido ligand in nitrogen transfer reactions reported by Proust et al.^{15a,b,h} The spectacular synthetic potential of the nitride complex $[PW_{11}O_{39}RuN]^{4-}$ has been demonstrated in the reaction with triphenylphosphine, which ultimately leads to the release of $[PPh_3NPPH_3]^+$ through several intermediates, among which are the phosphoraniminato derivative

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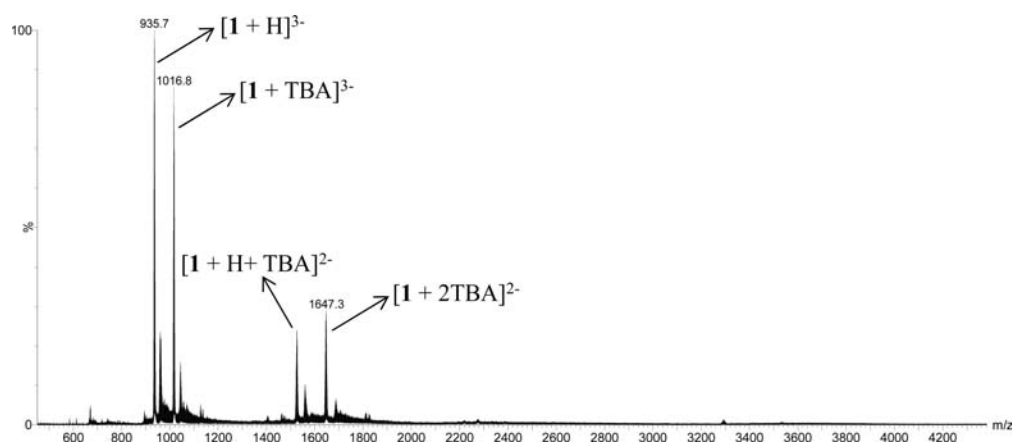


Figure 1. Negative ESI mass spectrum of compound 1a at $U_c = 5$ V in acetonitrile; TBA denotes Bu_4N^+ .

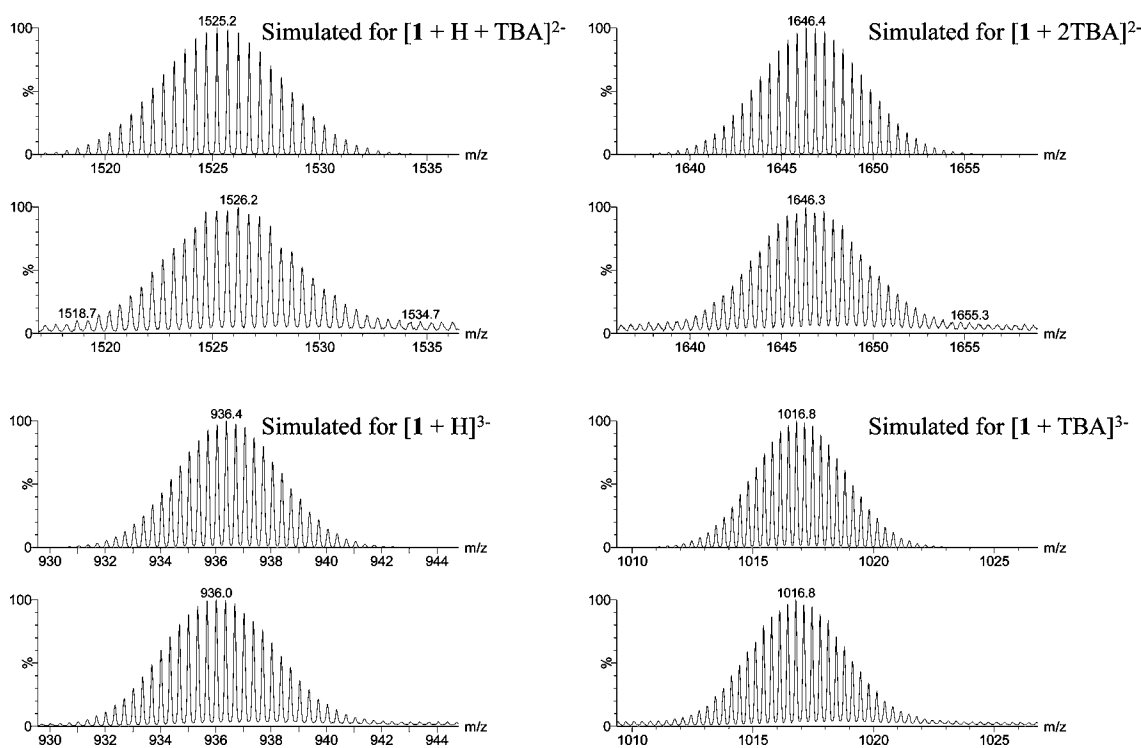


Figure 2. Simulated and experimental peaks for the triply charged $[\mathbf{1} + \text{H}]^{3-}$ and $[\mathbf{1} + \text{TBA}]^{3-}$ (bottom) and doubly charged $[\mathbf{1} + \text{H} + \text{TBA}]^{2-}$ and $[\mathbf{1} + 2\text{TBA}]^{2-}$ (top) anions.

$[\text{PW}_{11}\text{O}_{39}(\text{Ru}^{\text{V}}\text{NPh}_3)]^{3-}$ and such complexes as $[\text{PW}_{11}\text{O}_{39}(\text{RuN}(\text{OH})\text{PPh}_3)]^{4-}$ and $[\text{PW}_{11}\text{O}_{39}(\text{Ru}(\text{OPPh}_3))^{4-}]^{4-}$.^{15a,b} Reaction of $[\text{PW}_{11}\text{O}_{39}\text{RuN}]^{4+}$ with an N-heterocyclic carbene $(\text{CH}_2(\text{Mes})\text{N})_2\text{C}$: yielded $(\text{CH}_2(\text{Mes})\text{N})_2\text{CNH}_2^+$ as final coupling product, formed via $[\text{PW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}\text{NC}(\text{CH}_2(\text{Mes})_2\text{N})_2]^{3-}$ intermediate.^{15h}

More often than not, unambiguous characterization of the species is very difficult, especially with respect to the identity of the terminal ligand attached at the Ru site and the separation of mixtures of isostructural byproducts of essentially the same structure. For this reason, use of novel experimental approaches for the characterization of the ligand attached at the Ru site is desirable.

Focusing upon these two points, we expected that the nitroso complex of ruthenium, $\text{K}_2[\text{RuNOCl}_5]$, would show the behavior similar to that of the nitrido complex^{15a,b} in reacting with $[\text{PW}_{11}\text{O}_{39}]^{7-}$ to form $[\text{PW}_{11}\text{O}_{39}\text{Ru}(\text{NO})]^{4+}$. The strong

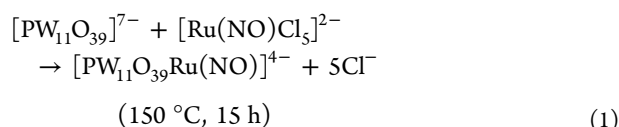
advantage in using the nitroso complex is that it is obtained by a simple procedure in quantitative yield.¹⁷ In addition, the nitroso ligand may be involved in various further chemical transformations; i.e., it can be “removed” from Ru site by reaction with reagents like hydrazine or hydroxylamine,¹⁸ yielding the desired Ru aqua complex, or transformed into other species without rupture of the Ru–N bond.

Here we report the high yield synthesis of $[\text{PW}_{11}\text{O}_{39}\text{Ru}(\text{NO})]^{4+}$ ($\mathbf{1}^+$) for the first time, and reactivity studies at the Ru site, in particular, conversion into aqua complex $[\text{PW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{H}_2\text{O})]^{4+}$ ($\mathbf{2}^+$). The ammonia complex, namely $[\text{PW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}\text{NH}_3]^{4+}$ ($\mathbf{3}^+$), could also be accessed via reduction of $\mathbf{1}^+$ with SnCl_2 in water. A novel experimental approach that enables easy detection and confirmation of the identity of the ligand attached at the Ru site based on ESI tandem mass spectrometry is also presented. This approach is validated by using pure samples of $\mathbf{1}^+$, $\mathbf{2}^+$, and $\mathbf{3}^+$ and was used

to unravel the formation of a first N_2 -ligated POM as an intermediate of the reaction of 1^+ with NH_2OH to yield 2^+ .

RESULTS AND DISCUSSION

As it turned out, the reaction of $[PW_{11}O_{39}]^{7-}$ with $[Ru(NO)Cl_5]^{2-}$ proceeds relatively slowly due to extraordinarily substitutionally inert d^6 electronic configuration of the Ru(II) center. We found that the optimum conditions are hydrothermal (Teflon bomb, 15 h, 150 °C). Experiments aimed at optimization of the yield by carrying out the reaction at lower temperature (close to the boiling point in an open beaker) showed that it required much more time (as monitored with ^{31}P NMR, reaction was not completed even after 31 h, see Figure S2 in Supporting Information, SI).



It is worth stressing that the yield of the $[PW_{11}O_{39}Ru^{II}(NO)]^{4+}$ (1^+) complex at the optimum conditions is quantitative, as can be judged from ^{31}P NMR spectrum, which shows a single peak, whose chemical shift is slightly solvent-dependent (-13.9 ppm in D_2O , -14.6 ppm in d^6 -DMSO, being similar to that observed for the nitrido complex $[PW_{11}O_{39}RuN]^{3-}$ (-13.8 ... -14.5 ppm^{15a}). ^{183}W NMR spectrum contains 6 signals with 2:2:1:2:2:2 relative intensities, which correspond to expected C_s symmetry of a monosubstituted Keggin polyoxoanion. IR spectrum of **1a** (TBA salt of 1^+) contains a strong peak at 1850 cm^{-1} which is unequivocally assigned to the coordinated NO group, being highly characteristic. This value is comparable with the data reported for the only known $\{RuNO\}$ -POM complex, $[SiW_{11}O_{39}Ru(NO)]^{5-}$ (1870 cm^{-1});^{15d} its shift to lower frequency corresponds to a higher electronic density on π^* -orbitals of NO^+ and may indicate that the $[PW_{11}O_{39}]^{7-}$ moiety is a better electron donor than $[SiW_{11}O_{39}]^{8-}$ despite smaller overall charge.

The ESI-MS technique has been applied for characterization of the $\{PW_{11}O_{39}Ru\}$ framework. The negative high resolution ESI mass spectrum of acetonitrile solutions of **1a** (Figure 1) reveals the presence of intact triply charged $[1 + H]^{3-}$ and $[1 + TBA]^{2-}$ species accompanied by doubly charged $[1 + H + TBA]^{2-}$ and $[1 + 2TBA]^{3-}$ peaks. Both m/z values and comparison of simulated and experimental isotopic patterns support these formulations (Figure 2).

The electrochemical behavior of **1** was investigated in CH_3CN solution. The cyclic voltammogram shows a one-electron reversible redox process at $E_{1/2} = 1.29$ V versus Ag/AgCl in the positive region (Figure 3) which belongs to the Ru(III)/Ru(II) couple. The reversibility shows that the oxidized form of the nitroso complex has a certain degree of stability. The reversible redox process at $E_{1/2} = -1.00$ V versus Ag/AgCl has been also detected and corresponds to the reduction of W(VI) atoms. It can be compared to the value of -0.90 V found for $(Bu_4N)_4[PW_{11}O_{39}Ir(H_2O)]$.¹⁰

It is well established that a coordinated NO group can interact with both electro- and nucleophiles.¹⁸ The nucleophiles attack the more positively charged nitrogen atom of the coordinated NO group; in the case of such nucleophiles as N_2H_4 , NH_2OH , or N_3^- , unstable addition products decompose releasing N_2 or N_2O , and leaving a water molecule to occupy the vacated coordination site.¹⁸ This approach can be used for

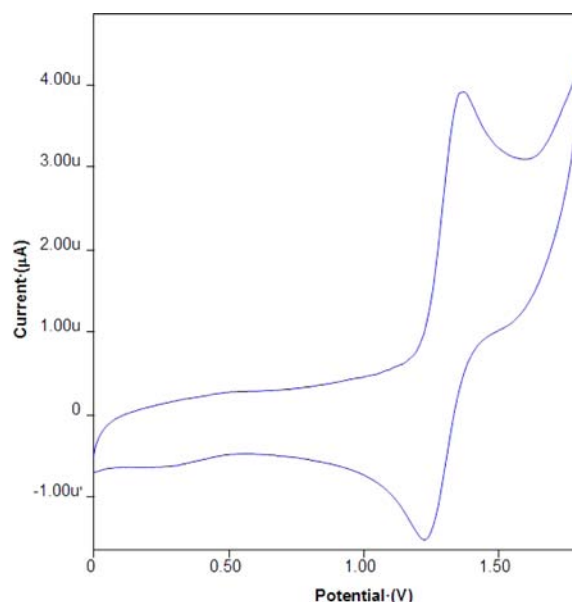


Figure 3. Cyclic voltammogram of **1** in CH_3CN in the potential route of $0 \leftrightarrow 1.8$ V (scan rate of 0.1 V/s).

conversion of the nitroso complexes into aqua complexes in the $\{PW_{11}O_{39}Ru\}$ chemistry, in a way similar to that followed in the preparation of heteroleptic complexes $[Ru^{II}(LL)_2(X)(Y)]$ (LL is a bidentate ligand).^{19,20} We have found that complex 1^+ slowly reacts with both hydrazine and hydroxylamine already at room temperature to yield $[PW_{11}O_{39}Ru^{III}(H_2O)]^{4+}$ as the final product, as judged by ^{31}P NMR and ESI-MS data. The reactions complete after 96 h at RT or after 24 h when run at 60 °C [see Figure 4 and SI (Figures S3–S4) for full details]. Illustrative ESI mass spectrum of **2a** is shown in Figure 5, a and comparison of simulated and experimental peaks is shown in Figure S1 (see SI).

In order to trace intimate mechanism operative in the 1^+ to 2^+ transformation upon reaction with the N-donor reagents, we have followed the reaction by ^{31}P NMR. Shortly after addition of $NH_2OH \cdot HCl$ to a solution of 1^+ , a new peak (A) at -12.2 ppm appeared; no such observation in the case of $N_2H_4 \cdot H_2SO_4$ was made. As the reactions both with $NH_2OH \cdot HCl$ and $N_2H_4 \cdot H_2SO_4$ proceed, there appears a new broad peak which corresponds to the paramagnetic $[PW_{11}O_{39}Ru^{III}(H_2O)]^{4+}$ complex (2^+) as final product; the peak grows simultaneously with the decrease in the intensity of the signal corresponding to starting 1^+ . It is noteworthy that the intensity of peak A at -12.2 ppm does not change significantly during the reaction time, and starts to vanish only after disappearance of 1^+ (Figure 6). Taking into account its position (no paramagnetic shift) and possible mechanisms of the reaction, this peak could correspond to a Ru^{II} complex with coordinated N_2 , formulated as $[PW_{11}O_{39}Ru^{II}(N_2)]^{5-}$, which finally aquates and oxidizes into 2^+ , although we are aware that the identity could not be unequivocally determined on the basis of only NMR data. Attempts to run the reaction under N_2 did not increase in the intensity of A.

ESI mass spectrometry was also employed for the monitoring of the reaction between 1^+ with hydrazine and hydroxylamine. For this purpose, reactions were quenched at different time intervals by precipitation of POMs with excess of Bu_4NBr . The samples were then dissolved in CH_3CN and directly introduced into mass spectrometer. The resulting ESI(–) mass spectra

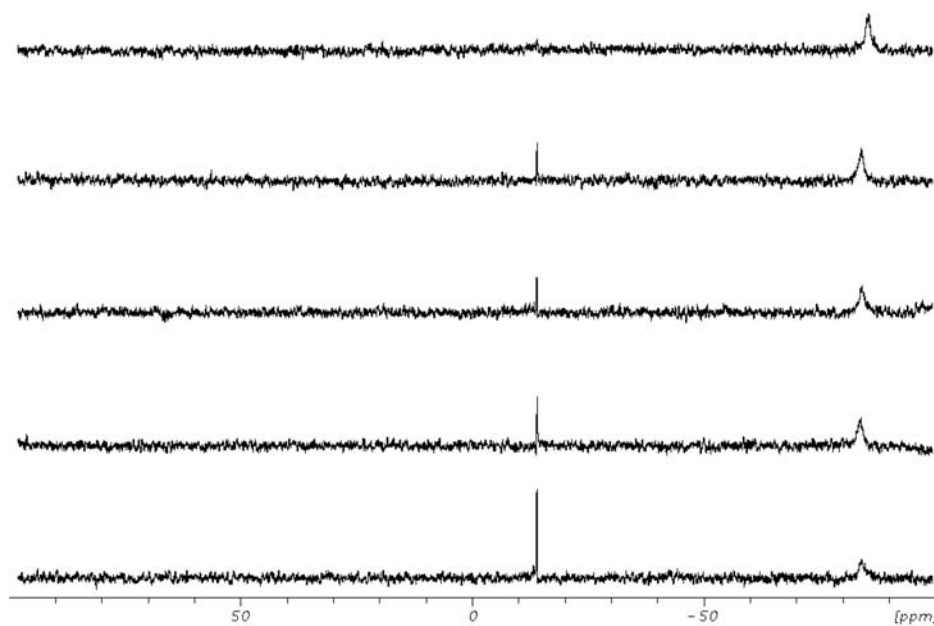


Figure 4. ^{31}P NMR monitoring of reaction between $[\text{PW}_{11}\text{O}_{39}\text{Ru}(\text{NO})]^{4+}$ and $\text{NH}_2\text{OH}\cdot\text{HCl}$ at $60\text{ }^\circ\text{C}$ (after 2.5, 5, 6, and 24 h).

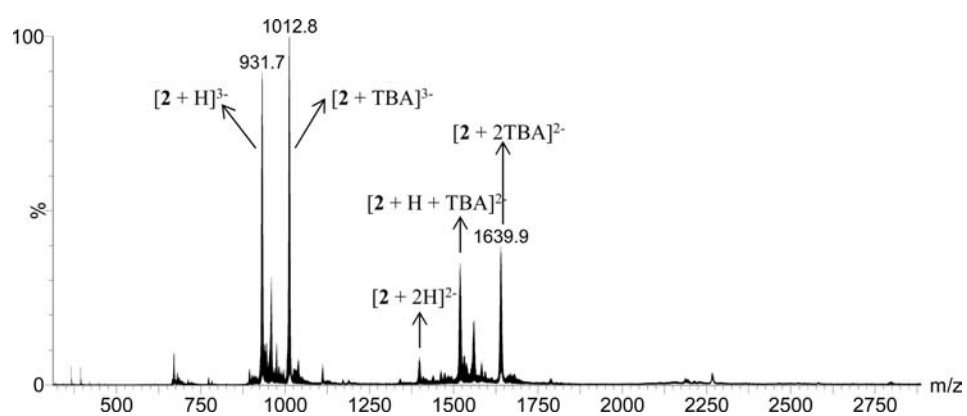


Figure 5. Negative ESI mass spectrum of **2a** at $U_c = 5\text{ V}$ in acetonitrile, TBA denotes Bu_4N^+ .

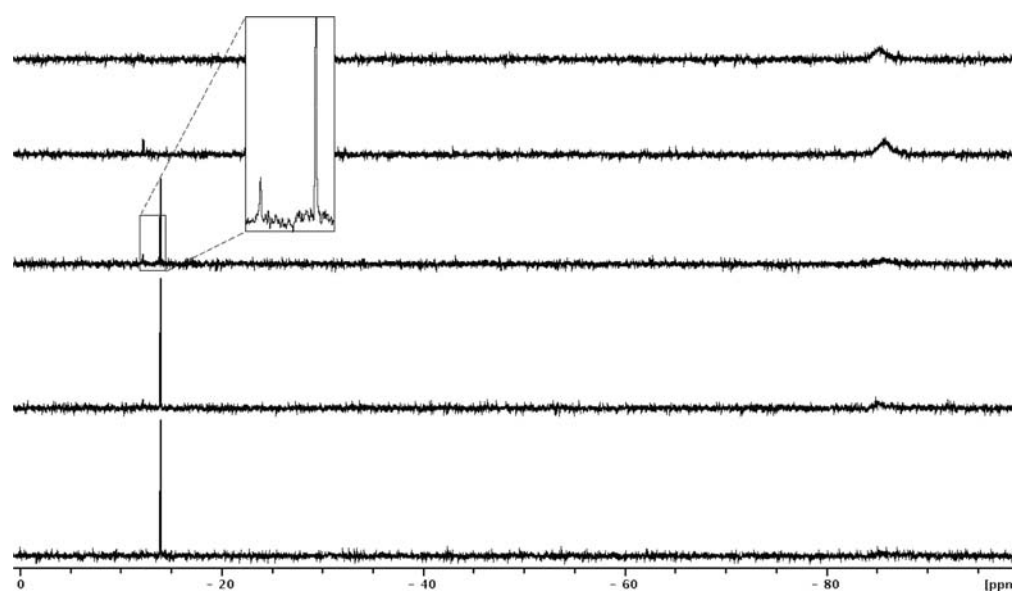


Figure 6. ^{31}P NMR monitoring of the reaction between $[\text{PW}_{11}\text{O}_{39}\text{Ru}(\text{NO})]^{4+}$ and $\text{NH}_2\text{OH}\cdot\text{HCl}$ in water at room temperature [recorded after 45 min (bottom), 1.5 h, 80 h, and 96 h (top), respectively]. Peak A (small peak) is to the left from the peak of 1^- (sharp intense peak).

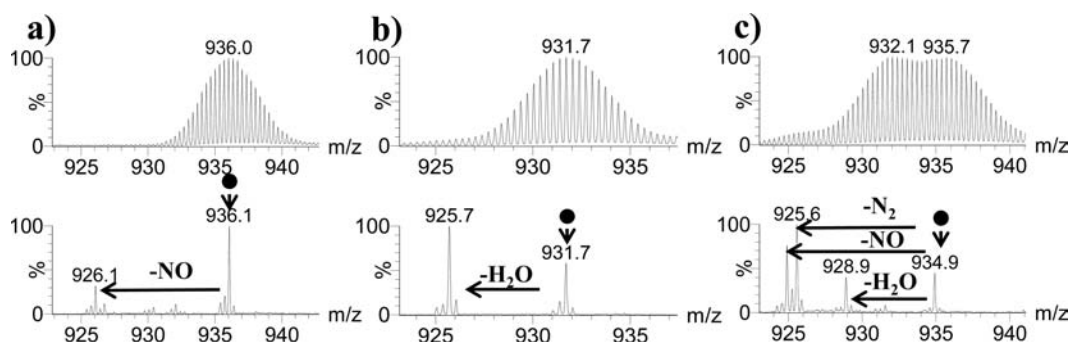


Figure 7. (a) Expanded region of the ESI mass spectrum of pure **1a** (top) and CID mass spectrum after mass-selecting $[1 + H]^{3+}$ m/z 936.1 at a collision energy ($E_{lab} = 5$ eV). (b) Expanded region of the ESI mass spectrum of pure **2a** (top) and CID mass spectrum after mass-selecting $[2 + H]^{3+}$ m/z 936.1 at a collision energy ($E_{lab} = 5$ eV). (c) Expanded region of the ESI mass spectrum of the resulting mixture of the reaction of **1**⁴⁺ and hydroxylamine (top), and CID mass spectrum after mass-selecting m/z 934.9 at a collision energy ($E_{lab} = 10$ eV).

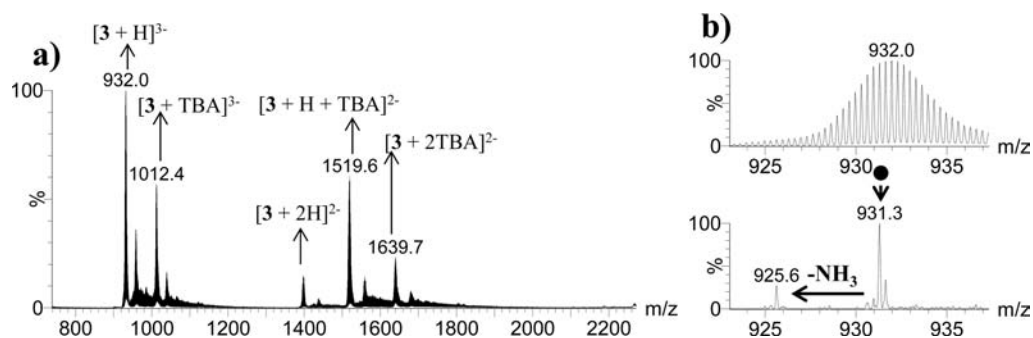


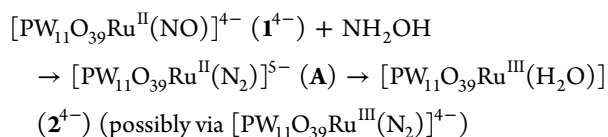
Figure 8. (a) Negative ESI mass spectrum of **3**⁺ at $U_c = 5$ V in acetonitrile, TBA denotes Bu_4N^+ . (b) Expanded region of the ESI mass spectrum of **3**⁺ (top) and CID mass spectrum after mass-selecting $[3 + H]^{3+}$ m/z 931.3 at a collision energy ($E_{lab} = 5$ eV).

revealed very slight differences due to the intrinsic wide isotopic pattern envelope of each of the proposed $\{PW_{11}O_{39}RuL\}$ species and the small molecular weight difference of all the potential L ligands attached at the Ru site (i.e., potentially L = NO, NH_3 , H_2O , N_2 , N_2O). Since single stage ESI-MS did not provide the definitive proof of the identity of the ligand attached at the Ru site, we investigated the gas-phase dissociation of these ions in order to deconvolute the partially overlapped peaks, provided that the release of the neutral (L) ligand at the Ru site occurs under collision induced dissociation (CID) conditions.²¹ This approach was initially validated by investigating the CID mass spectra of pure samples of **1a** and **2a**. Figure 7a shows expanded portion of the ESI mass spectrum of pure **1**⁴⁺ in the region of the $[1 + H]^{3+}$ (top) and the CID mass spectrum after mass-selecting $[1 + H]^{3+}$ at m/z 936.1 (bottom) which clearly reveals the exclusive liberation of NO, thus confirming that the starting sample comprises a single product, namely, with L = NO. The same applies when gas-phase dissociation experiments were carried out on mass-selected $[1 + TBA]^{3+}$ and $[1 + H + TBA]^{2-}$ and $[1 + 2TBA]^{2-}$, although for the alkylammonium adducts, additional fragmentation channels are observed that comprise liberation of tributylamine NBu_3 and butanal C_4H_8O ; this gas-phase behavior of the alkylammonium moieties has been previously observed.²²

Identical results were obtained for a sample of **2a** (see Figure 7b), for which the CID mass spectrum after mass-selecting $[2 + H]^{3+}$ at m/z 931.7 revealed the exclusive liberation of H_2O (L = H_2O).

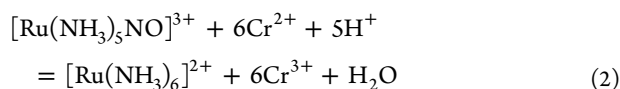
The progress of the reaction after addition of $N_2H_4 \cdot H_2SO_4$ or $NH_2OH \cdot HCl$ to a solution of **1a** can be conveniently followed

by monitoring the CID spectra. As the reaction proceeds, the product ions corresponding to the release of H_2O become evident, accompanied by the disappearance of the product ions due to the liberation of NO. This approach was particularly fruitful to identify $[PW_{11}O_{39}Ru^{III}(N_2)]^{4+}$, which is the oxidized form of $[PW_{11}O_{39}Ru^{II}(N_2)]^{5-}$, to which peak A in ³¹P NMR spectrum had been assigned, at intermediate stage of the reaction, from the characteristic mass loss of 28, corresponding to N_2 . This is illustrated for the reaction of **1**⁴⁺ with hydroxylamine (see CID spectrum in Figure 7 c). In this case, CID mass spectrum of mass-selected peak with m/z 934.9 revealed the liberation of neutral H_2O , N_2 , and NO fragments. At this point, we notice that both ESI and ESI tandem mass spectrometry did not provide information about the *initial* net charge of the N_2 -ligated complex (4− or 5−) because redox interconversion is ubiquitous during the ESI process itself; however, the diamagnetic nature of the intermediate detected by ³¹P NMR (see above) and the known preference of N_2 ligand for coordination with Ru(II), not to Ru(III), led us to postulate the N_2 -ligated complex as $[PW_{11}O_{39}Ru^{II}(N_2)]^{5-}$, which is oxidized under ESI-MS condition to the $[PW_{11}O_{39}Ru^{III}(N_2)]^{4+}$ species. An alternative explanation would be that the $[PW_{11}O_{39}Ru^{III}(N_2)]^{4+}$ species were already present in the reaction solution, but the corresponding signal, being broad, overlapped with the broad, paramagnetically shifted signal from $[PW_{11}O_{39}Ru^{III}(H_2O)]^{4+}$. As a whole, from ³¹P NMR, ESI, and ESI tandem MS monitoring, the following transformation steps are proposed:



It is known that the nitroso compound which we used as starting reagent, $\text{K}_2[\text{Ru}(\text{NO})\text{Cl}_5]$, reacts with SnCl_2 to give a binuclear nitrido complex $[\text{Ru}_2\text{NCl}_8(\text{H}_2\text{O})_2]^{3-}$.²³ Motivated by the successful adaptation of the previous reactivity of mononuclear $\text{Ru}(\text{NO})$ -complexes with N_2H_4 or NH_2OH to the corresponding POM chemistry, we expected that reaction of $\mathbf{1}^{4-}$ with $\text{Sn}(\text{II})$ might lead to similar products. For this purpose, we reacted complex $\mathbf{1}^{4-}$ with SnSO_4 in water, and the resulting product was precipitated with Bu_4NBr . The ESI(−) mass spectrum of this product was virtually identical to that found for pure samples of $\mathbf{2}^{4-}$ as illustrated in Figure 8a; however, we found that CID experiments did reveal the exclusive formation of an ammonia rather than water ligated compound, as judged by the characteristic liberation of 17 mass units (see Figure 8 b). IR data also support NH_3 coordination as evidenced by the strong peak at 1666 cm^{-1} characteristic for coordinated NH_3 , thus strongly supporting that the new NH_3 -ligated $[\text{PW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{NH}_3)]^{4-}$ POM has been obtained.

The mechanism of the formation of $\mathbf{3}^{4-}$ may be related to that proposed for known conversion of $[\text{Ru}(\text{NH}_3)_5\text{NO}]^{3+}$ into $[\text{Ru}(\text{NH}_3)_6]^{2+}$, as depicted in eq 2:²⁴



We assume that the reaction of $\mathbf{1}^{4-}$ with $\text{Sn}(\text{II})$ involves the following: (1) deoxygenation of the nitroso group, (2) protonation of N atom, and (3) oxidation of $\text{Ru}(\text{II})$ to $\text{Ru}(\text{III})$ by O_2 (in air). As expected, $[\text{PW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{NH}_3)]^{4-}$ is paramagnetic. The EPR spectrum (Figure S5, SI) is similar to that for $[\text{PW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{H}_2\text{O})]^{4-}$ and is typical for low-spin d^5 $\text{Ru}(\text{III})$ species. Sample solutions of $\mathbf{3}^{4-}$ in $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (3:7 v/v) were stable for several days at room temperature as judged by ESI and ESI-MS/MS mass spectrometry. This stability is in perfect agreement with kinetic inertness of the low-spin d^5 configuration of $\text{Ru}(\text{III})$.

CONCLUSIONS

A new monoruthenium-substituted Keggin type POM complex with nitroso ligand has been obtained in high yield through a synthetic route that involves hydrothermal reaction of $[\text{Ru}(\text{NO})\text{Cl}_5]^{2-}$ and $[\text{PW}_{11}\text{O}_{39}]^{7-}$. The nitroso ligand can be easily removed with hydrazine or hydroxylamine; this approach may be considered as an alternative efficient route to the $[\text{PW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{H}_2\text{O})]^{4-}$ ($\mathbf{2}^{4-}$) complex which serves as common precursor in this area of chemistry and in catalytic applications. The nitroso ligand is reduced with Sn^{2+} to yield the NH_3 which remains coordinated in $[\text{PW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{NH}_3)]^{4-}$ ($\mathbf{3}^{4-}$). The temporal evolution of the species formed during the $\mathbf{1}^{4-}$ to $\mathbf{2}^{4-}$ transformation has been monitored using NMR, ESI, and ESI tandem mass spectrometric techniques. ESI tandem mass spectrometry has been particularly useful for determination of the L ligand attached at the Ru site. It has been successfully applied to deconvolute partially overlapped peaks typically observed in the reaction mixtures and has allowed us to postulate a N_2 -ligated Ru-containing POM en route to the $[\text{PW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{H}_2\text{O})]^{4-}$ complex ($\mathbf{2}^{4-}$).

EXPERIMENTAL SECTION

General Comments. All reactions and manipulations were carried out in air. Solvents were purified using standard procedures. Most reagents were obtained from commercial sources and used as purchased. $\text{K}_2[\text{Ru}(\text{NO})\text{Cl}_5]$ was prepared according to the published procedure.¹⁷

Electrospray Ionization Mass Spectrometry. A Q-TOF premier mass spectrometer with an orthogonal Z-spray electrospray source (Waters, Manchester, U.K.) was used. The temperature of the source block was set to $100\text{ }^\circ\text{C}$ and the desolvation temperature to $120\text{ }^\circ\text{C}$. A capillary voltage of 3.3 kV was used in the negative scan mode, and the cone voltage was set to 5 V to control the extent of fragmentation of the identified species. TOF mass spectra were acquired in the W-mode operating at a resolution of ca. 15000 (fwhm). Mass calibration was performed using a solution of sodium iodide in isopropanol/water (50:50) from m/z 50 to 3000. Sample solutions were infused via syringe pump directly connected to the ESI source at a flow rate of $10\text{ }\mu\text{L}/\text{min}$. The observed isotopic pattern of each compound perfectly matched the theoretical isotope pattern calculated from their elemental composition using the MassLynx 4.1 program. For ESI tandem MS/MS experiments, the anions of interest were mass-selected using the first quadrupole (Q1) and interacted with argon in the T-wave collision cell at variable collision energies ($\text{CE} = 0\text{--}20\text{ eV}$). The ionic products of fragmentation were analyzed with the time-of-flight analyzer. The isolation width was reduced to mass-select a single isotopomer in the first quadrupole analyzer.

Cyclic Voltammetry. Cyclic voltammetry experiments were performed with a 797 VA Computrace electrochemical analyzer (Metrohm, Switzerland). All measurements were carried out with a conventional three-electrode configuration consisting of glassy carbon working and platinum auxiliary electrodes and a Ag/AgCl reference electrode containing aqueous 3 M KCl. The supporting electrolyte was 0.05 M tetrabutylammonium hexafluorophosphate. $E_{1/2}$ values were determined as $1/2(E_a + E_c)$, where E_a and E_c are the anodic and cathodic peak potentials, respectively.

Synthesis of $\mathbf{1}^{4-}$ and $\mathbf{1a}$. A 500 mg (0.17 mmol) portion of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was dissolved in 10 mL of H_2O . Portions of Li_2CO_3 were added under stirring until the pH reached 4.8. A solution of 66 mg (0.17 mmol) of $\text{K}_2[\text{Ru}(\text{NO})\text{Cl}_5]$ in 1.0 mL of H_2O was added dropwise under stirring. Resulting violet solution was placed into a Teflon-lined Parr digestion bomb and kept at $150\text{ }^\circ\text{C}$ for 15 h. Resulting dark red solution contains $[\text{PW}_{11}\text{O}_{39}\text{Ru}(\text{NO})]^{4-}$ ($\mathbf{1}^{4-}$) as the only heteropolyanion form. TBA salt of $\mathbf{1}^{4-}$ ($\mathbf{1a}$) was obtained by adding of an excess of TBA bromide or nitrate to solution; resulting red-brown precipitate was collected on glass frit, washed with water, and dried over P_2O_5 *in vacuo*. Yield 93%. For $\text{C}_{64}\text{H}_{144}\text{RuN}_5\text{O}_{40}\text{PW}_{11}$ Calcd, %: C, 20.3; H, 3.8; N, 1.9; Ru, 2.7; W, 53.5. Found, %: C, 20.1; H, 4.0; N, 2.0; Ru, 2.7; W, 53.9. IR (KBr , cm^{-1}): 2961 m, 2934 m, 2873 m, 1850 s, 1631 w, 1483 s, 1380 m, 1152 w, 1091 s, 1037 s, 965 s, 887 s, 803 s, 666 m, 652 m, 594 w, 497 m, 386 s. ^{31}P NMR: -13.9 (1, $\text{H}_2\text{O} + \text{D}_2\text{O}$); -14.3 ($\mathbf{1a}$, CD_3CN), -14.65 ppm ($\mathbf{1a}$, d^6 -DMSO). ^{14}N NMR: -67 ppm ($\mathbf{1a}$, d^6 -acetone + CD_3CN , NO group signal). ^{183}W NMR (20.805 MHz): -83.2 (2), -86.0 (2), -90.0 (1), -113.0 (2), -115.1 (2), -130.4 (2) ppm.

Synthesis of $\mathbf{2}^{4-}$ and $\mathbf{2a}$. In typical experiment aimed at preparation of $[\text{PW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{H}_2\text{O})]^{4-}$, solution of $\mathbf{1}$ was used, obtained as mentioned above. Stoichiometric amount of N_2H_4 , H_2SO_4 or $\text{NH}_2\text{OH}\cdot\text{HCl}$ was added; the solution was kept at $60\text{ }^\circ\text{C}$ for 24 h. Purity was checked by ^{31}P NMR. TBA salt $\mathbf{2a}$ was obtained as mentioned above for $\mathbf{1a}$; its purity was checked by ESI-MS and elemental analysis. Conversion of $\mathbf{1}$ to $\mathbf{2}$ is quantitative; yield of $\mathbf{2a}$ is 90–95%.

Synthesis of $\mathbf{3}^{4-}$ and $\mathbf{3a}$. A 45 mg (0.2 mmol) portion of solid SnSO_4 was added to solution containing 0.1 mmol of $\mathbf{1}^{4-}$ (5 mL). Resulting solution was stirred at room temperature for 1 h. The color of the solution turned dark brown. TBA salt of $\mathbf{3a}$ was obtained by adding of an excess of TBA bromide or nitrate to solution; resulting red-brown precipitate was collected on glass frit, washed with water, and dried over P_2O_5 *in vacuo*. Yield 75%. For $\text{C}_{64}\text{H}_{147}\text{RuN}_5\text{O}_{39}\text{PW}_{11}$

Calcd, %: C, 20.4; H, 3.9; N, 1.9. Found, %: C, 20.5; H, 4.1; N, 2.0. IR (KBr, cm^{-1}): 3347 s, 3189 s, 2961 s, 2935 s, 2873 s, 1666 s, 1911 m, 1483 s, 1382 s, 1347 w, 1285 w, 1152 w, 1079 s, 1050 s, 962 s, 881 s, 796 s, 588 s, 512 m, 498 m. ^{31}P NMR (3^+ , $\text{H}_2\text{O} + \text{D}_2\text{O}$): -92.7 (broadened). EPR: $g_1 = 2.73$, $g_2 = 2.378$, $g_3 = 1.7$.

■ ASSOCIATED CONTENT

Supporting Information

Additional ESI-MS data, ^{31}P monitoring data, and EPR spectrum of **3a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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