Synthesis and Characterization of the Keggin-Type Ruthenium-Nitrido Derivative \([\text{PW}_{11}\text{O}_{39}(\text{RuN})]\) and Evidence of Its Electrophilic Reactivity

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Abstract: The ruthenium-nitrido POM derivative \([\text{PW}_{11}\text{O}_{39}(\text{RuN})]\) has been synthesized by reaction between \([\text{PW}_{11}\text{O}_{39}]^{-}\) and \([\text{RuNCl}_{5}]^{2-}\) or \([\text{RuNCl}_{4}]^{-}\). Its molecular structure has been confirmed from multinuclear \(^{31}\text{P}\) and \(^{183}\text{W}\) NMR spectroscopy together with an EXAFS study, while the oxidation state of the ruthenium bearing the nitrido ligand has been inferred both from \(^{183}\text{W}\) NMR and XANES analysis at the Ru-K edge. The potential of \([\text{PW}_{11}\text{O}_{39}(\text{RuN})]\) in N-atom transfer reactions has been demonstrated through reaction with triphenylphosphine, which ultimately leads to the release of the bis(triphenylphosphine)-iminium cation \([\text{PPh}_{3}N\text{PPh}_{3}]^{+}\) through several intermediates, among which the phosphoraniminato derivative \([\text{PW}_{11}\text{O}_{39}(\text{RuNPh}_{3})]\) has been structurally characterized. Its unusual oxidation state is in accordance with its EPR spectrum.

Introduction

Polyoxometalates (POMs) are clusters of early transition metals in their highest oxidation states bound to oxygen atoms. They form a unique class of compounds because of their structural diversity and their tunable properties.\(^1\) They have found numerous applications in analytical chemistry, catalysis, materials science, or medicine.\(^2\) In particular, many Keggin-type polyoxions, incorporating one or several transition metals, have been studied for their catalytic activity in oxygenation reactions.\(^5\) Their thermal stability as well as their robustness under oxidative conditions have then been put forward.\(^5\) Although a few reports of well-described platinum-group derivatives of POMs can be found before 1990, a wider number of studies came out after the seminal publication on the characterization of the phosphotungsto-ruthenate heteropolynanions \([\text{PW}_{11}\text{O}_{39}(\text{RuL})]\) by Rong and Pope.\(^17\) In this paper,\(^17\) the authors showed that the porphyrin-like \([\text{PW}_{11}\text{O}_{39}]^{7-}\) ligand may be successfully used for the coordination of ruthenium cations of different oxidation states (in the range +II to +V), confirming thus that POMs are a versatile class of ligands capable of stabilizing either high or low oxidation state cations. Since then, the analogy between monovacant Keggin anions and porphyrins has also been addressed theoretically.\(^22\) The ability of the thus-stabilized transition metal cations to

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transfer oxygen atom being well established, it seemed interesting to us to explore the nitrogen donor ability of nitrido derivatives of Keggin-type POMs, on which we are now focusing our attention, as part of our general program on nitrogenous derivatives of POMs.23–27 However, up to date, very few metal-nitrido derivatives of polyanions have been synthesized.28,29 We have recently reported the osmium- and rhenium-nitrido derivatives of the Keggin- and Dawson-type anions: [PW11O39(OsN)]4−, α1- and α2-[P2W17O61(OsN)]7−, and [PW11O39(ReN)]4− (n = 4 or 3, for ReVI N and ReVII N, respectively),29–31 the reactivity of the latter being up to now disappointing. Recently, examples of alkene amination and azidination by ruthenium-nitrido porphyrin and ruthenium-nitrido salen complexes have been reported.32,33 These illustrate the versatility of the reactivity of the ruthenium-nitrido function from electrophilic, in the direct azidination of alkynes,32 to nucleophilic, with prior activation by trifluoroacetic anhydride.33

The possibility to tune the reactivity of the ruthenium-nitrido function by playing with the ligand or the oxidation state of the metal prompted us to study the synthesis of ruthenium-nitrido derivatives of Keggin-type POMs. We thus describe here the synthesis and full characterization of [PW11O39(RuVIII N)]4−, which has been isolated as cesium or n-tetraethylammonium (TBA) salts. The nitrido derivative was obtained by direct reaction of K7[PW11O39] with a ruthenium-nitrido precursor, either Cs2[RuNCl5] or Rb2[RuNCl4]. We also report herein that [PW11O39(RuN)]4− contains an electrophilic nitrogen atom, which reacts with phosphines.

Results and Discussion

Synthesis and Stability of [PW11O39(RuVIII N)]4− (1) in Water. Cesium and rubidium salts of [PW11O39(RuVIII N)]4− were synthesized by direct reaction of K7[PW11O39] with Cs2[RuNCl5] or Rb2[RuNCl4] in water. This reaction resulted in the immediate precipitation of the cesium (Cs-I) or rubidium (Rb-I) salt as a greyish-green solid, in a fairly good yield. However, because compounds Cs-I and Rb-I are insoluble in all solvents (including water), their characterization in solution was rendered impossible. In the case of Cs-I, its purity was ascertained by 31P MAS NMR, since only one isotropic signal was observed at −14.5 ppm, and by EDX spectroscopy (ratio W:Ru identical to the previously characterized ruthenium derivative of the [PW11O39]− anion, Cs3[PW11O39(Ru(p-cymene)H2O)],34 see Supporting Information). The reaction of [PW11O39]− with an equimolar amount of K2[RuVIIICl5] was followed by 31P NMR spectroscopy at regular intervals of time. In this case, no precipitation occurred, and the 31P NMR spectrum of the mother solution, recorded after 15 min, displayed two signals with a relative intensity of 3:1 at −10.6 ppm and −14.4 ppm, corresponding to [PW11O39]−, and most probably to the functionalized polyanion [PW11O39(RuVIIICl)4]− (I), respectively. The chemical shift of the latter signal, as well as that observed in the solid-state above, is indeed characteristic of a refilled polyanion, (see below the 31P NMR spectrum of TBA-I and the IR spectra of Cs-I and TBA-I). The 31P NMR spectra obtained after every 35 min are represented in Figure 1. These spectra clearly illustrate that while I is formed almost immediately, it is rather unstable in aqueous solution and is progressively converted to a third, yet unidentified, species, characterized by a signal at −12.7 ppm. Moreover, the [PW11O39]− anion remains the major species in solution in this case.35 These results thus prompted us to investigate the synthesis of the ruthenium-nitrido POM in organic solvents in order to increase the yield of the reaction and to avoid the evolution of the product.

Synthesis of TBA4[PW11O39(RuVIII N)] (TBA-I). While the synthesis of TBA4[PW11O39(ReVII N)] has been achieved by the reaction of TBA4[H3PW11O39] with TBA[ReVIIICl4] in acetonitrile and in the presence of triethylamine,30 no reaction was observed between TBA4[H3PW11O39] and TBA[RuVIIICl4] even after 4 days, be it at room temperature or under reflux. This lack of reactivity is surprising since ligand substitution on [RuVIIICl4]− is known to be easy and has previously been reported in the literature.30 Considering the reactivity observed in water, we thus turned to a mixed organic/water medium: K7[PW11O39] reacted with an equimolar amount of TBA[RuVIIICl4] in a H2O/CH3CN mixture so as to produce TBA4[PW11O39(RuVIII N)] (TBA-I) as a green precipitate, which could be recrystallized from acetonitrile. Its 31P NMR spectrum, recorded in CD3CN at room temperature, is characterized by a signal at −13.8 ppm. Adventitious contamination by [PW11O39]− or [PW12O40]3− could be checked at −12.0 ppm and −14.1 ppm, respectively.

Figure 1. 31P NMR monitoring of the reaction of K7[PW11O39] with K2[RuNCl5] in aqueous solution (spectra recorded every 35 min) at the concentration of 5 × 10−2 mol L−1.

(35) After 24 h, the 31P NMR spectrum of the solution no longer showed any signal at −14.4 ppm. In a similar manner the IR spectrum showed the disappearance of the band at 1072 cm−1.
The ratio of acetonitrile to water in the solvent mixture used for the reaction, which is a compromise between solubility and reactivity, as well as the duration of the stirring, has been improved to maximize product, in the highest purity. However, the overall yield remains low, 32% based on the limiting TBA, and only 8% based on Ru. Attempts to increase the yield by adding TBABr resulted in the precipitation of less pure samples. After filtration of TBA-1, the 31P NMR spectrum of the mother liquor displayed almost no signal that can be attributed to [PW11O39]7− or to [PW11O39(RuVI)N]4+, but rather several extra peaks of unidentified compounds. This demonstrates that (i) it is indeed not worth adding TBABr to increase the yield in TBA-1, and (ii) it is not worth adding an excess of TBA[RuVI(NCl)]4−, since all the [PW11O39]7− has already been transformed. Once separated from the mother liquor, TBA-1 is stable in acetonitrile solution for several days, as checked by 31P NMR.

Structural Characterization of TBA[RW11O39(RuVI)N] (TBA-1). IR Spectroscopy. The infrared spectrum of TBA-1 (see Supporting Information) shows as expected the characteristic features of a Keggin-type structure with strong vibrational bands at 811 cm−1, 889 cm−1, and 962 cm−1 corresponding to ν(W=O−W) and ν(W=O=O) stretching frequencies. The incorporation of the [RuN] function in the lacunary [PW11O39]7− restores partially a pseudo-tetrahedral geometry for I. This is clearly seen by the relatively low splitting of the ν(P=O) stretching mode in [PW11O39(RuVI)N]4+ (ΔP ca. 20 cm−1) by comparison with the lacunary one (ΔP 45 cm−1). The residual splitting observed in I arises most likely from the smaller size of Ruψ+ (r = 53 pm) with respect to Wψ+ (r = 60 pm); the ruthenium cation is not able to completely refill the lacuna and to interact efficiently with the oxygen atom of the central PO₄ unit. The presence of the RuN bond cannot be ascertained by IR spectroscopy because its stretching mode is expected around 1050 cm−1 as a weak band, which is eventually hidden by the strong ν(P=O) band at 1072 cm−1.

183W NMR. The relatively high solubility of TBA-1 in dimethylformamide gives 183W NMR spectra with good signal/noise ratio as required to observe tungsten–tungsten satellites. The 0.12 mol L−1 DMF solution spectrum of TBA-1 obtained at 262 K (−11 °C) exhibits six major lines A, B, C, D, E, and F at −86.9 (2W), −91.0 (2W), −95.7 (1W), −104.1 (2W), −133.0 (2W), and −134.4 (2W) ppm. Minor signals are also present at −80.8, −88.0, −93.6, −94.1, −98.2, −111.8, and −118.2 ppm, which correspond to less than 15% (from 31P NMR) of the lacunary Keggin anion [H₆PW₁₁O₃₉]₇⁻ and to residual amount (less than 2% of [PW₁₁O₃₉]³⁻) (Figure 2 bottom). The 183W NMR spectrum of I fully agrees with the C₄ symmetry of a monosubstituted Keggin anion. Moreover the narrow δ range (less than 50 ppm), without any strongly shifted resonance, is consistent with a diamagnetic compound. While many ruthenium derivatives of POMs have been reported to be paramagnetic, there are relatively few diamagnetic Ru-substituted Keggin compounds which were investigated by 183W NMR: the diamagnetic anions [PW₁₁O₃₉(RuL)]4+ reported until now display strongly positively shifted signals assigned to the tungsten nuclei in the neighborhood of the Ru metal. (L = H₂O, δ = 292.8 and 159.3 ppm; L = DMSO, δ = 117.4 and −2.7 ppm). Although it is unlikely that a ruthenium atom bearing a nitrido ligand could be a Ruψ+, the question of its oxidation state has to be addressed owing to the wide range of available oxidation states for Ru and the many examples of redox processes occurring during the synthesis of Ru derivatives. 183W NMR seems to be able to answer this question; actually the 183W NMR spectrum of I is reminiscent of that of [PW₁₁O₃₉(O₅N₅)]⁴⁺ while it deviates markedly from those of [PW₁₁O₃₉(RuL)]³⁻ by the absence of any positively shifted signal. It appears then more likely that the ruthenium.

References:
atom retains a $d^2$ configuration (Ru$^{VI}$) during the synthesis of I. The great similarity between the $^{183}$W spectra of $[\text{PW}_{11}\text{O}_{39}]^-$ and $[\text{PW}_{11}\text{O}_{39}(\text{Ru}^{VI}N)]^-$ is beneficial to assign the resonances of the latter, by comparison with the former.

The strategy for the assignment is based upon the observation and quantification of $W-W$ satellites and is developed in the Supporting Information. The attribution to the W atoms labeled as in Figure 3 is displayed in Table 1, along with that of $[\text{PW}_{11}\text{O}_{39}(\text{Os}^{VI}N)]^-$ for comparison.

Table 1. Experimental Tungsten–Tungsten Connectivity Matrix for [α-PW$_{11}$O$_{39}$(Ru$^{VI}$N)]$^{4-}$ (at 262 K) and in Brackets for [α-PW$_{11}$O$_{39}$(Os$^{VI}$N)]$^{4-}$ (at 300 K): On-diagonal Terms, Chemical Shifts (in ppm); Off-diagonal Terms, Coupling Constants (in hertz)

<table>
<thead>
<tr>
<th>nucleus</th>
<th>line</th>
<th>2.3</th>
<th>4.9</th>
<th>5.8</th>
<th>6.7</th>
<th>10.12</th>
<th>11</th>
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<tbody>
<tr>
<td>2,3</td>
<td>F</td>
<td>$-134.4$</td>
<td>($-216.6$)</td>
<td>$\approx 10$</td>
<td>$\approx 10$</td>
<td>$\approx 20$</td>
<td>AB</td>
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<tr>
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<td>B</td>
<td>$-91.0$</td>
<td>($-148.3$)</td>
<td>$\approx 23$</td>
<td>($23.5$)</td>
<td>($20.2$)</td>
<td>(AB)</td>
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<tr>
<td>5.8</td>
<td>E</td>
<td>$\approx 10$</td>
<td>$\approx 20$</td>
<td>$-133.0$</td>
<td>$\approx 10$</td>
<td>$??$</td>
<td></td>
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<tr>
<td>6.7</td>
<td>A</td>
<td>$\approx 10$</td>
<td>($11.2$)</td>
<td>($23.5$)</td>
<td>($146.4$)</td>
<td>($11.2$)</td>
<td>(21)</td>
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<tr>
<td>10,12</td>
<td>D</td>
<td>$\approx 20$</td>
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<td>($100.2$)</td>
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![Figure 3](image-url) Postulated structure of $[\text{PW}_{11}\text{O}_{39}(\text{Ru}^{VI}N)]^{4-}$ with W labels according to IUPAC convention.

The origin of the deshielding (i.e., paramagnetic shift) experienced by W nuclei close to d$^6$ addenda atoms in diamagnetic $[\text{PW}_{11}\text{O}_{39}][\text{ML}]^{4-}$ has been discussed by Rong and Pope and may be accounted for by a delocalization of the d-electrons from the metal to the POM framework. The extent of this delocalization and consequently the amplitude of the paramagnetic shift depend on the electron density in the HOMO and on the donor–acceptor ability of the ligand L. For the POM nitrido species the corresponding W nuclei experience opposite (i.e., diamagnetic) shifts, which may be due to the different symmetry properties of the HOMO of the d$^2$ metal centers; the difference observed between Os and Ru is likely due to a better delocalization of the electronic density for Os (difference of energy levels of HOMOs).

**XAS Measurements.** Solid-state absorption spectra were recorded at room temperature for TBA-1 and Cs-1 so as to confirm the oxidation state of the incorporated Ru and the structure of the formed polyanion. The spectra of both compounds are clearly superimposable (see Supporting Information). The conclusions arising from the study of TBA-1 are then valid for Cs-1. Figure 4 shows the Ru-K X-ray absorption near-edge spectra for reference compounds containing ruthenium in different valence states (Ru$^0$, Ru$^{II}$(acac)$_3$, Ru$^{IV}O_2$), and [(salchda)Ru$^{VI}$N](ClO$_4$)$_2$, (salchda $= N,N'$-bis(salicylidene)-$o$-cyclohexyldiamine) as well as that of compound TBA-1. As expected, the position of the absorption edge is dependent on the oxidation state of the ruthenium; the higher the oxidation state the higher its energy. As the absorption edge of compound TBA-1 is close to that of [(salchda)Ru$^{VI}$N](ClO$_4$), and lies higher in energy, it strongly suggests a +VI oxidation state for the ruthenium center in the polyanion, in accordance with the NMR data. Also interestingly, compound TBA-1 and [(salchda)Ru$^{VI}$N](ClO$_4$)$_2$ both exhibit in the Ru-K near-edge absorption spectra according to the inset of Figure 4, the shoulder might be pointed at ca. 22120 eV instead of 22124 eV. In a general way, this part of the spectrum is very sensitive to the local symmetry
around the cation. The observation of such shoulders is well documented for transition-metal cations.\(^{(50,51)}\) They are almost independent of the electronic state of the metal but are due to the lowering of the local symmetry. In our particular case, this lowering of symmetry is directly related to the presence of the very short metal-nitrido bond, as systematically observed for other metal-nitrido-containing compounds.\(^{(52,53)}\)

The geometric parameters around the ruthenium atom in TBA-1\(^{(54)}\) were then obtained from the extended X-ray absorption fine structure (EXAFS) study of this compound (Figure 5). Many metallic derivatives of the \([\text{XW}_{11}\text{O}_{39}]^{n-}\) anions have been described in the literature. In a general way, the \([\text{XW}_{11}\text{O}_{39}]^{n-}\) anion may be considered as a tetradentate or a pentadentate ligand, depending on the nature of the cation incorporated into the structure. For instance, the polyanion behaves as a tetradentate ligand in \([\text{Ce}\{\text{PW}_{11}\text{O}_{39}\}]^{2-}\),\(^{(54)}\) but as a pentadentate ligand.


\(\text{Figure 4.}\) Ru-K edge XANES spectra of Ru\(^0\) (in gray), [Ru\(^{III}\)(acac)\(_3\)] (in blue), Ru\(^{IV}\)O\(_3\) (in black), [(salchda)RuN(ClO\(_4\))] (in red), and TBA\(_4[\text{PW}_{11}\text{O}_{39}-\{\text{Ru}^{IV}\text{N}\}](\text{TBA-1})\) (in green).

\(\text{Figure 5.}\) (a) Ru-K edge EXAFS signal and (b) the corresponding Fourier transform (modulus and imaginary part) of TBA\(_4[\text{PW}_{11}\text{O}_{39}-\{\text{Ru}^{IV}\text{N}\}](\text{TBA-1})\).
in \([\text{SiW}_{11}\text{O}_{39}]^{7-}\) (DMSO = dimethyl sulfoxide), with four Ru–O distances in the range 1.90–2.01 Å and a longer one at about 2.14 Å.

As in the latter example, \([\text{PW}_{11}\text{O}_{39}]^{7-}\) may be considered as a pentadentate ligand in compound TBA-1. Figure 6 shows the experimental and simulated filter (between 1 and 2.5 Å) of the EXAFS signal for TBA-1. The corresponding modulus and imaginary part of the Fourier transform are given in the Supporting Information. Because the simulated FT of the spectrum is in close agreement with the experimental data, the peaks can be unambiguously assigned. As expected, three different distances were observed around the Ru cation corresponding to four Ru–O bonds at 1.97 Å, one Ru–O bond at 2.53 Å, with the tetrahedral PO\(_4^{3-}\) unit, and a short Ru–N triple bond at 1.67 Å, which is in good agreement with the reported ruthenium-nitrido distances ranging from 1.592(4)\(^{32}\) to 1.656(5) Å determined by X-ray crystallography.

Reactivity of TBA\(_4\)\([\text{PW}_{11}\text{O}_{39}]\{\text{Ru}^{\text{VI}}\text{N}\}\) (TBA-1). In a first attempt to study its ability in nitrogen-atom transfer, TBA-1 was reacted with cyclohexene in the presence of trifluoroacetic anhydride, at low temperature. No reaction at all was observed in this case, suggesting TBA-1 to be poorly reactive toward electrophiles. This lack of reactivity might be due to the electron-withdrawing properties of the POM causing the nitrogen atom to be electrophilic rather than nucleophilic. Indeed ruthenium-nitrido complexes are expected to be more electrophilic than the corresponding osmium-nitrido complexes, whose reactivity can be finely tuned by the ancillary ligands from nucleophilic to electrophilic.\(^{56}\) We therefore investigated the reactivity of TBA-1 with phosphines.

Hence, the reaction of TBA\(_4\)\([\text{PW}_{11}\text{O}_{39}]\{\text{Ru}^{\text{V}}\text{NPPh}_3\}\) with increasing amounts of triphenylphosphine was monitored by \(^{31}\)P NMR (Figure 7, see Supporting Information for an extension in the +30–15 ppm region) in a 3:1 mixture of CH\(_3\)CN:CD\(_3\)CN. For small amounts of phosphine added (less than half an equivalent), \(^{31}\)P NMR indicates the formation of only one species \(^2\), characterized by a signal at 322 ppm (\(\Delta\nu_{102} = 90\) Hz). Compound \(^2\) was separated from unreacted TBA-1 by silica column chromatography and recrystallized from acetonitrile/ether. A preliminary single crystal analysis of \(^2\) proved it to be the phosphoraniminato derivative TBA\(_3\)\([\text{PW}_{11}\text{O}_{39}]\{\text{Ru}^{\text{V}}\text{NPPh}_3\}\)]. Unfortunately, the poor quality of the crystals, which showed decomposition even when placed in the mother liquor in a sealed tube, and some disorder encountered within the phenyl rings and the tetrabutylammonium cations prevented the structural analysis from being completed (\(R = 0.0554, Rw = 0.1536\), see Supporting Information). Other attempts of recrystallization from other solvents or with other phosphines are in progress. However, even if they are not definitive, the Ru–N and N–P bond lengths of 1.923(16) and 1.499(18) Å (average value), respectively, and the RuNP bond angle of 138.1(11)° (average value) are reliable and fall within the range of reported values for related osmium complexes.\(^{57,58}\) To the best of our knowledge,

compound 2 is indeed the first ruthenium-phosphoraniminato derivative formed by phosphine reduction of a ruthenium(VI)-nitrido species to be structurally characterized. According to the number of tetrabutylammonium cations around the polyanion, the Ru center should be assigned a +V, rather than the expected +IV, oxidation state. Although most of nitrido-osmium-(VI) complexes are reduced by phosphines to give osmium-(IV)-phosphoraniminato derivatives, [Os(VI)(N(DBCat))2]2− (DBCat = 3,5-di-tert-butylcatecholate) unusually reacts with triphenyolphosphate to yield [Os(VI)(NPPPh)3(DBCat)]5−.56 Spontaneous oxidation in the presence of a POM is also reported: for example, we have shown that the reaction between [Re(VI)Cl2-(PPh3)3] and [H3PW11O39]5− yields [PW11O39(Re(VI))1+].30,59 Since the relatively narrow signal observed in the 31P NMR spectrum of 2 (Δν/2 = 90 Hz) shows no narrowing during 1H decoupling, it was attributed to the polyoxometalate core, while the signal of the phosphoraniminato phosphorus is probably too broad to be observed, because of the vicinity of the paramagnetic ruthenium center.

The X-band EPR spectrum of 2, recorded in the solid state at 100 K, is represented in Figure 8 (up). This spectrum shows features at g1 = 2.51, g2 = 2.32, and g3 = 1.68. It is in agreement with a rhombic S = 1/2 spin system (see simulation Figure 8, down). The large g-anisotropy clearly indicates that the spin density is mainly metal-centered and thus supports a +V oxidation state for the ruthenium (d5 low spin). This, to our knowledge, the first example of a Ru(V)-phosphoraniminato EPR spectrum. Furthermore, there are few examples of EPR spectra of Ru(V) complexes in the literature.60–63 Among these, the two structurally characterized61,64 species are pentacoordinated Ru=O complexes with low g anisotropy (for example g1 = 2.08, g2 = 1.98 and g3 = 1.91).63 In those cases, the low g-anisotropy indicates that the electronic ground state is well removed from excited states, consistent with the observed distorted trigonal bipyramidal geometry, resulting only in second-order contribution of the spin-orbit coupling to the g-matrix. On the contrary, in our case, the large g-anisotropy is indicative of strong spin–orbit interactions. This is in agreement with the pseudo C3v geometry deduced from the preliminary X-ray study. Indeed, in such a geometry, the near degeneracy of the dxz and dyz orbitals should lead to two nearly degenerated ground states and in turn to first-order perturbation of the g-tensor by the spin-orbit coupling, a well-known effect in low spin Fe60 species,65 resulting in large g-anisotropy.

Further additions of phosphine result in the subsequent formation of several species (see Figure 7). Among the final products [PW11O39Ru(VI)(NCCH3)3]2− (−70 ppm, Δν/2 = 1000 Hz)17 is identified by 31P NMR as well as the bis(triphenylphosphine)iminium cation ([PPh3P=N=PPh3]+ = PPNN+)(22 ppm, Δν/2 = 0.7 Hz). The latter was identified by adding a small amount of an authentic sample of PPNCI in the NMR tube and checking that the only effect was the increase of the intensity of the signal at 22 ppm, with no new signal appearing (see Figure 9). According to 31P NMR spectroscopy, the amount of PPNN+ produced by addition of 3 equiv of PPh3 is nearly twice that of starting 1. This in turn suggests that the signals at 195 and −415 ppm correspond to species without nitrogenous ligands. Formation of the iminium, although not reported until now (to our knowledge) from ruthenium-nitrido complexes, is not without precedent for osmium derivatives: [Os(V)(tpy)(Cl2)-(NPPPh3)]+ (tpy = terpyridine) was shown to release PPN+ through the reaction with an excess of phosphine.57 Although the reactivity of ruthenium-nitrido complexes toward phosphine has already been addressed in the literature, little is described about the characterization of the products, the characterization of ruthenium-phosphoraniminato relying only on IR and 31P NMR spectroscopy. This is at variance with the chemistry of osmium-nitrido complexes, which has been extensively studied in the group of T. J. Meyer.56 In one case, the ruthenium-phosphoraniminato derivative has been reported to evolve upon standing with release of the free phosphinimine Ph3PNH.56 In our case no Ph3PNH could be detected (31P NMR signal at 22.6 ppm, according to a freshly prepared authentic sample). Forma-

(59) Following a question from one of the reviewers, we can exclude the concomitant reduction of the polyoxometalate on the basis of optical features: one-electron-reduced polyanion states are deep blue because of the intervalence charge transfer (see for example, Livage, J.; Launay, J.-P. J. Am. Chem. Soc. 1983, 105, 6817−6823), at variance with compound 2, which is orange with an electronic absorption at 442 nm (log ε = 3.7, see Experimental Section).
tion of Ru(III) complexes in the presence of an excess of phosphine is also preceded.67 Identification of the different species and their thorough characterization together with their interplay are under current investigation and will be reported in a subsequent paper.

Summary and Conclusion

In this paper, we describe a very simple method for the synthesis of the ruthenium-nitrido derivative [PW_{11}O_{39}(RuV\text{NCl})\text{]}^{4-} (1), which can be obtained either as an alkaline cation salt (Cs or Rb) or as a tetrabutylammonium salt. In this compound, the oxidation state of the Ru cation has been proved to be +VI by XAS and NMR spectroscopy. Furthermore, we have also demonstrated for the first time that a metal-nitrido function could still be reactive after its incorporation into a polyoxometalate core. Indeed, TBA-1 reacts with triphenylphosphine to generate the first ruthenium-phosphiniminato derivative of a polyoxometalate: [PW_{11}O_{39}(RuNPPh_{3})\text{]}^{3-}. In the course of the reaction of 1 with PPh_{3} the bis(triphenylphosphane)iminium cation [\text{Ph}_{3}P+N=PPh_{3}]^{+} is ultimately released. Much is still to be understood in the reactivity of TBA-1 with PPh_{3} or other phosphines and it is under investigation.

The cleavage of the ruthenium–nitrogen bond and the formation of PPN^{+} validate the potential use of nitrido derivatives of polyoxometalates in nitrogen-atom transfer reactions, a type of reaction still under active investigations.68 Albeit interesting from a mechanistical point of view, phosphines are probably not the most synthetically attractive substrate for this transfer. Our goal will now be to transfer this reactivity to other nucleophilic substrates, such as carbanions or enriched alkenes.

Experimental Section

Instrumentation and Techniques of Measurement. IR spectra were recorded from KBr pellets, on a Bio-Rad Win-IR FTS 165 FT-IR spectrophotometer. UV–visible spectra were recorded on a Shimadzu UV-2101 spectrophotometer. The 31 P (121.5 MHz) NMR spectra were recorded from KBr pellets, on a Bio-Rad Win-IR FTS 165 FT-IR spectrophotometer. Under current investigation and will be reported in a subsequent paper.

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CN) λmax, nm (log ε): 605 (1.5), 380 (sh, 2.7). 31P NMR (121.5 MHz, CD3CN, 300 K) δ (ppm): –13.8 (Δν1/2 = 1 Hz). 183W NMR (12.5 MHz, CD3CN/CD3CN, 300 K) δ (ppm): –87.3, –90.8, –96.4, –104.7, –133.2, –133.9, (12.5 MHz, DMF/d6-acetone, 262 K) δ (ppm): –86.9 (2W), –91.0 (2W), –95.7 (1W), –104.1 (2W), –133.0 (2W), –134.4 (2W). Crystallographic data: cubic, space group: I43m, a = 17.755-(2) Å, V = 5597(2) Å3.

Monitoring of the Reaction of TBA-1 with Triphenylphosphine. In a 5 mm NMR tube were introduced 0.3 mL of a solution of TBA2[PW11O39(Ru)] (263 mg in 5 mL of acetonitrile) and 0.1 mL of CH2Cl2. A control NMR spectrum indicated the presence of about 25% [PW11O39]6+ and traces of [PW12O40]3−. In the NMR tube, 3.48 µL of a solution of triphenylphosphine (474 mg in 20 mL acetonitrile) was slowly added to a solution of TBA2[PW11O39(Ru)] (263 mg in 5 mL of acetonitrile) and 0.1 mL of CD3CN. A control NMR spectrum indicated the presence of about 25% TBA3[PW11O39] and traces of [PW12O40]3−. This process took between 15 and 20 min and was repeated until 3 equiv of triphenylphosphine had been added.

Isolation of TBA3[PW11O39(RuPPh3)] (2). Triphenylphosphine (1 mL of a 0.067 mol L−1 acetonitrile solution) was slowly added to a solution of TBA2[PW11O39(RuPPh3)] (505 mg, 0.13 mmol dissolved in 15 mL acetonitrile). The green solution turned red. The brown solid formed by addition of 40 mL of diethyl ether was separated by centrifugation, redissolved in a minimum of 1:1 mixture of acetonitrile and dichloromethane. Elution over a silica column (silica gel 60, 0.063 mm, eluant CH2Cl2 / CH3CN 1/2) separated two fractions, the first one orange and the second one green (unreacted TBA2[PW11O39(Ru)] and TBA3[PW11O39(RuPPh3)]). The first fraction was concentrated to dryness by rotary evaporation at room temperature, yielding 0.118 g (48% relative to PPh3) of 2 as a red-orange powder. Slow diffusion of diethyl ether in a 6 mM acetonitrile solution yielded the red crystals of 2 used for the X-ray diffraction study. IR (KBr) νmax (cm−1): 388 (s), 518 (m), 690 (w), 724 (w), 806 (vs), 886 (s), 969 (s), 1049 (m), 1087 (s), 1114 (w), 1381 (w), 1438 (w), 1484 (m), 2874 (w), 2833 (w), 2962 (m). UV (CH3CN) λmax, nm (log ε): 442 (3.7). 31P RMN (121.5 MHz, CD3CN, 300 K) δ (ppm): 322 (Δν1/2 = 90 Hz). 1H NMR (300.13 MHz, CD3CN, 300 K) δ (ppm): 1.00 (t, 36H, \((CH3(CH2)2)3N^−\)), 1.41 (h, 24H, \((CH2(CH2)2)3N^−\)), 1.67 (m, 24H, \((CH2(CH2)2)3N^−\)), 3.16 (m, 24H, \((CH2(CH2)2)3N^−\)), 7.57 (t, J = 7.0 Hz, 3H, p-C6H5), 9.44 (d, J = 5.6 Hz, 6H, m-C6H5), 12.05 (s, Δν1/2 = 25 Hz, 6H, o-C6H5).

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Supporting Information Available: EDX spectrum of Cs2[PW11O39(RuVI)] and Cs2[PW11O39(RuPPh3)]; IR and 31P MAS spectra of Cs2[PW11O39(RuVI)] and IR spectrum of TBA2[PW11O39(RuVI)]; theoretical matrix connectivity for [α-PW11O39(ML)p−]; modulus and imaginary part of the Fourier transform of 183W NMR spectrum of TBA2[PW11O39(RuVI)]; Ru-K edge XANES spectra of Cs2[PW11O39(RuVI)] and TBA2[PW11O39(RuVI)]; modulus and imaginary part of the Fourier transform of TBA2[PW11O39(RuVI)] filtered between 1 and 2.5 Å; IR, 1H, and 31P NMR spectra of TBA2[PW11O39(RuPPh3)] and single-crystal X-ray analysis. Evolution of the 31P NMR spectrum (Expanded part +30 to −15 ppm) of TBA2[PW11O39(RuVI)] in the presence of increasing amounts of PPh3. This material is available free of charge via the Internet at http://pubs.acs.org.

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