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Functionalized heteropolyanions: high-valent metal nitrido fragments incorporated into a Keggin polyoxometalate structure†

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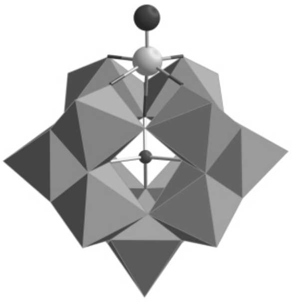
Three examples of nitrido-functionalized polyoxometalate species are reported, namely (n-Bu$_4$N)$_4$[PW$_{11}$O$_{39}$(OsN)] (1), (n-Bu$_4$N)$_4$[PW$_{11}$O$_{39}$(ReN)] (2), and (n-Bu$_4$N)$_3$[PW$_{11}$O$_{39}$(ReN)] (3), which feature the incorporation of [Os^{VI}≡N]$^{3+}$, [Re^{VI}≡N]$^{3+}$ and [Re^{VII}≡N]$^{4+}$ fragments, respectively, into the framework of a Keggin-type heteropolyanion.

The activation of high-valent transition metal nitrido complexes for the aziridination of olefins was first demonstrated in studies by Groves and Takahashi using an [Mn^V≡N]$^{2+}$ porphyrinato system.[1] Although the field remains far less developed than that of the corresponding oxygen atom transfer, recently Carreira *et al.* have broadened the scope and efficiency of these reactions and have shown that co-ligands other than porphyrins are applicable in metal nitrido-mediated aziridination.[2] Our experience in the area of functionalized polyoxometalates (POMs),[3] coupled with the superior oxidative stability of the POM framework,[4] drew our attention to the preparation of substituted POM systems incorporating high-valent metal nitrido functions.[5] Here we describe a general procedure for the synthesis of nitrido derivatives of the Keggin anion by reaction of the monovacant species (n-Bu$_4$N)$_4$[H$_3$PW$_{11}$O$_{39}$] with appropriate metal-nitrido monomers. It is exemplified by the hexavalent species (n-Bu$_4$N)$_4$[PW$_{11}$O$_{39}$(Os^{VI}N)] (**1**) and (n-Bu$_4$N)$_4$[PW$_{11}$O$_{39}$(Re^{VI}N)] (**2**).



Reaction of (n-Bu$_4$N)[Os^{VI}NCl$_4$][6] (0.081 g; 0.14 mmol) with (n-Bu$_4$N)$_4$[H$_3$PW$_{11}$O$_{39}$][7] (0.500 g; 0.14 mmol) in anhydrous CH$_3$CN (15 mL) in the presence of Et$_3$N (0.14 mL; 0.99 mmol) proceeds smoothly at room temperature over 24 h to produce a dark brown solution. After filtration and concentration of the filtrate, Et$_2$O was added to precipitate **1** as an air-stable cocoa-brown powder (0.49 g; 91%). ^{15}N-labelled **1** is prepared analogously. Analytically pure crystals of **1** are readily obtained by diffusion of Et$_2$O vapor into a concentrated CH$_3$CN solution. Calc. for C$_{64}$H$_{144}$N$_5$O$_{39}$OsPW$_{11}$: C, 19.96; H, 3.77; N, 1.82; P, 0.80. Found: C, 20.10; H, 3.98; N, 1.88; P, 1.02%. IR (Nujol; cm^{-1}): 1104sh, 1072s, 1053sh, 961vs, 881s, 811vs. No ^{14}N NMR signal was observable for the nitrido ligand within **1** (presumably due to extreme broadening), but the labelled material displays a ^{15}N NMR resonance at 421.8 ppm; for comparison, the corresponding ^{15}N NMR resonance for [Os^{15}NCl$_4$]$^-$ occurs at 446.5 ppm. In CD$_3$CN solution, **1** is further characterized by a ^{31}P NMR resonance at −14.55 ppm, and by a six-line ^{183}W NMR spectrum (δ −85.5 (2 W), −100.4 (1 W), −101.0 (2 W), −147.2 (2 W), −149.0 (2 W), −217.6 (2 W)) consistent with the expected C_s symmetry. In the absence of excess Et$_3$N, formation of **1** is slow, and an intermediate species can be observed when monitoring the crude reaction mixture by multinuclear NMR spectroscopy. The intermediate species displays a ^{15}N NMR resonance at 428.3 ppm and a ^{31}P NMR resonance at −13.59 ppm; both of these resonances progressively wane over a period of days while resonances corresponding to **1** increase in intensity. The ^{183}W NMR spectrum of the intermediate consists of an eleven-line pattern (δ +88.3, −80.9, −89.4, −92.7, −105.6, −119.6, −120.0, −131.9, −134.3, −194.1, −234.6) indicative of an unsymmetrical (C_1) mono-substituted Keggin system. As shown in Fig. 1, the disappearance of the ^{183}W NMR resonances due to the intermediate is accompanied by growth in the six-line pattern characteristic of **1**. Although we prefer not to speculate

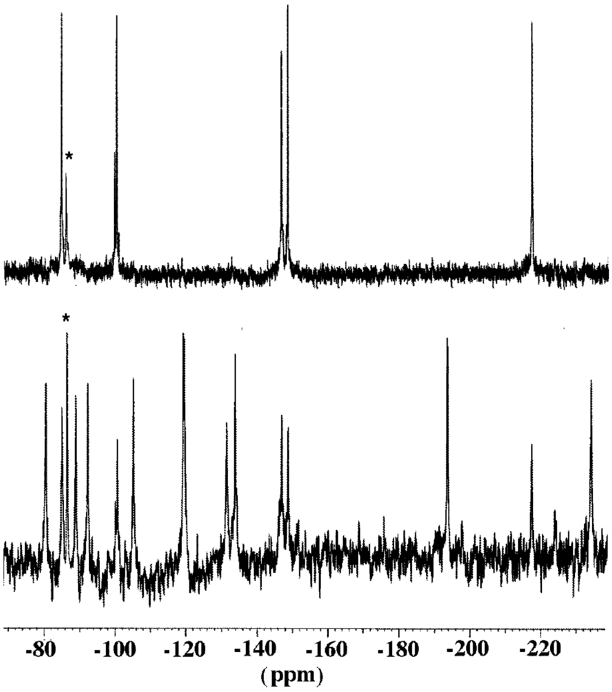


Fig. 1 Stages in the formation of **1** as observed in ^{183}W NMR spectra. Bottom: immediately after preparation of the solution (the deshielded resonance at δ 88.3 is not shown). Top: after standing for 10 d. The resonance indicated by * is due to [PW$_{12}$O$_{40}$]$^{3-}$.

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† Electronic supplementary information (ESI) available: general synthetic and characterization details. See http://www.rsc.org/suppdata/cc/b2/b209173a/

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extensively on the nature of the intermediate, the observance of one strongly deshielded ^{183}W resonance (δ 88.3) implies a peculiar environment for the associated W atom, perhaps one which incorporates a Cl atom.[8]

A similar experimental procedure applies for **2**: to a solution of $(n\text{-Bu}_4\text{N})_4[\text{H}_3\text{PW}_{11}\text{O}_{39}]$ (0.913 g; 0.25 mmol), in distilled CH_3CN (25 mL) are added successively Et_3N (1 mL; 7.10 mmol) and $[\text{Re}^{\text{V}}\text{NCl}_2(\text{PPh}_3)_2]$[9] (0.199 g; 0.25 mmol). Within a few minutes, the initially pink suspension solubilizes to a violet solution which is stirred overnight at room temperature, filtered and evaporated to dryness. Deep violet crystals of $(n\text{-Bu}_4\text{N})_4[\text{PW}_{11}\text{O}_{39}(\text{Re}^{\text{VI}}\text{N})]$ (**2**) are grown from CH_3CN (0.55 g; 57%).‡ Calc. for $C_{64}H_{144}N_5O_{39}PReW_{11}$: C, 19.98; H, 3.77; N, 1.82, P, 0.81. Found: C, 19.98; H, 3.74; N, 1.70, P, 0.62%. IR (KBr; cm^{-1}): 1096sh, 1072s, 963vs, 884s, 802vs. UV/Vis (CH_3CN) λ_{max} = 500 nm (ε = 1150 mol^{-1} L cm^{-1}). In the course of the reaction the Re(V) center undergoes oxidation to Re(VI), presumably by dioxygen. As a consequence, the ^{31}P NMR signal of **2** (CH_3CN–CD_3COCD_3; 2 : 1 v : v) is very broad (−19 ppm; $\Delta\nu_{1/2}$ = 150 Hz). Monitoring the reaction by ^{31}P NMR in degassed acetonitrile in a screw cap NMR tube and under argon shows the formation of a transient species displaying a sharp resonance (−14.05 ppm; $\Delta\nu_{1/2}$ = 5 Hz), which could be the nitrido-rhenium(V) derivative. The paramagnetic character of **2** was confirmed by its EPR spectrum, which displays hyperfine coupling with the spin 5/2 $^{185/187}$Re nuclei and strong second order effects. Its simulation is currently underway.

Cyclic voltammetry studies of **2** were particularly informative. The voltammogram of **2** in CH_3CN displays four reversible waves at +0.49, −0.47, −1.42 and −1.94 V, and an irreversible wave at −2.56 V (*vs.* SCE). The four former waves are one-electron processes, assigned as the $\text{Re}^{7+/6+}$, $\text{Re}^{6+/5+}$, $\text{Re}^{5+/4+}$, and $\text{Re}^{4+/3+}$ couples respectively, while the latter wave is a multi-electron process attributed to the reduction of the polyoxotungstate framework. This assignment follows that of Pope *et al.* for $(n\text{-Bu}_4\text{N})_4[\text{PW}_{11}\text{O}_{39}(\text{Re}^{\text{V}}\text{O})]$.[10] Fig. 2 presents the cyclic voltammograms for the $\text{Re}^{\text{V}}\rightarrow\text{Re}^{\text{VI}}\rightarrow\text{Re}^{\text{VII}}$ processes of both **2** and $[\text{PW}_{11}\text{O}_{39}(\text{Re}^{\text{V}}\text{O})]^{4-}$. The redox potentials for **2** are shifted by *ca.* −0.64 V as compared to those of the oxo-rhenium system. This shift appears to be somewhat larger than can be explained solely by the additional negative charge of the nitrido system (amounting to *ca.* −0.43 V[10]) and therefore likely also comprises the enhanced donation ability of the nitrido ligand *vs.* an oxo ligand. Interestingly, the one-electron oxidation and reduction potentials of **2** (+0.49 and −0.47 V) are in a very accessible range, suggesting that both $[\text{PW}_{11}\text{O}_{39}(\text{Re}^{\text{VII}}\text{N})]^{3-}$ and $[\text{PW}_{11}\text{O}_{39}(\text{Re}^{\text{V}}\text{N})]^{5-}$ can be prepared easily, although we could suspect the latter to be very air-sensitive.

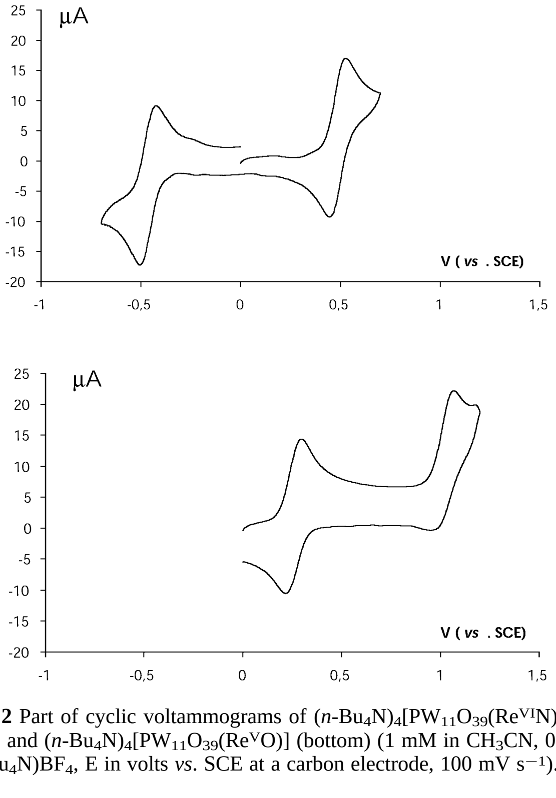

Fig. 2 Part of cyclic voltammograms of $(n\text{-Bu}_4\text{N})_4[\text{PW}_{11}\text{O}_{39}(\text{Re}^{\text{VI}}\text{N})]$ (**2**) (top) and $(n\text{-Bu}_4\text{N})_4[\text{PW}_{11}\text{O}_{39}(\text{Re}^{\text{V}}\text{O})]$ (bottom) (1 mM in CH_3CN, 0.1 M $(n\text{-Bu}_4\text{N})\text{BF}_4$, E in volts *vs.* SCE at a carbon electrode, 100 mV s^{-1}).

Indeed, $(n\text{-Bu}_4\text{N})_3[\text{PW}_{11}\text{O}_{39}(\text{Re}^{\text{VII}}\text{N})]$ (**3**) can be prepared by the oxidation of **2** (0.405 g; 0.11 mmol) using $(n\text{-Bu}_4\text{N})\text{Br}_3$ (0.051 g; 0.11 mmol)[11] in CH_3CN (10 mL) at room temperature. After stirring overnight, **3** was collected by filtration, and the filtrate was allowed to evaporate slowly to yield a further crop of **3** as green crystals. Crude **3** was recrystallized in CH_3CN (total yield in crystals 0.212 g, 56%). Calc. for $C_{48}H_{108}N_4O_{39}PReW_{11}$: C, 15.99; H, 3.02; N, 1.55. Found: C, 15.89; H, 2.92; N, 1.63%. IR (KBr; cm^{-1}): 1092sh, 1079s, 1069sh, 975vs, 894s, 813vs. ^{31}P NMR (CH_3CN–CD_3COCD_3; 2 : 1 v : v): −13.79 ppm ($\Delta\nu_{1/2}$ = 2 Hz). ^{183}W NMR (CH_3CN–CD_3COCD_3; 7 : 1 v : v): −55.5 (2 W), −83.6 (4 W), −84.2 (2 W), −87.5 (2 W), −92.4 (1 W) ppm. Contrary to the large chemical shift dispersion ($\Delta\delta_{^{183}\text{W}}$ = 132 ppm) observed for **1**, that for **3** (37 ppm) agrees with a d^0 configuration of the Re^{VII} substituting atom.

Apart from their potential utility in nitrogen-atom transfer reactions, the nitrido-Keggin systems described herein offer the possibility of accessing other nitrogenous heteropolyanion derivatives, such as organoimido and phosphorane iminato species. We are pursuing such opportunities with these and other nitrido-POM systems.

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Notes and references

‡ *Cell parameters for* **2**: cubic, space group *Im*3*m*, a = 17.774(9) Å, V = 5615(4) Å^3. The X-ray diffraction studies on a single crystal revealed, as expected, a disorder of the mono-substituted Keggin anion with only one metallic center in the asymmetric unit. These parameters however have been used for the indexing of the powder diffraction pattern.

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