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# A (Nitrido)chromium(V) Function Incorporated in a Keggin-Type Polyoxometalate: $[PW_{11}O_{39}CrN]^{5-}$ – Synthesis, Characterization and Elements of Reactivity

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The (nitrido)chromium(V) derivative $[PW_{11}O_{39}\{CrN\}]^{5-}$ (**1a**) was synthesized by the reaction of the monolacunary $[H_3PW_{11}O_{39}]^{4-}$ polyanion with a $\{CrN\}^{2+}$ function generated in situ. The EPR spectrum of the formed polyoxometalate confirmed the presence of a paramagnetic $Cr^V$ complex, and the presence of the nitrido bond was inferred by IR spectroscopy. The reactivity of $[PW_{11}O_{39}\{CrN\}]^{5-}$ was investigated and evidence of nucleophilic behaviour towards trifluoroacetic anhydride, forming the acylimido derivative $[PW_{11}O_{39}\{Cr^VNCOCF_3\}]^{4-}$ (**2a**), is also reported.

## Introduction

The formation of C–N bonds, particularly in heterocyclic chemistry, is fundamental to organic synthesis.[1] The most desirable source of an N atom would obviously be molecular nitrogen itself, notwithstanding its inertness. Although some examples have been reported of the elaboration of Chatt-type $N_2$ complexes in the synthesis of heterocycles,[2] alternative nitrene sources are generally used. These have been highlighted recently.[3] Two complementary approaches have been considered in the literature: the one-pot reaction of an appropriate nitrene source (e.g., phenyliminoiodinane,[4–9] organic azides,[10,11] sulfonamides,[3,12,13] chloramine-T, etc.)[14–17] in the presence of a metallic cation catalyst, or the use of preformed (nitrido)metal or (imido)-metal complexes.[18–26] Building on our long standing interest in nitrogeneous derivatives of polyoxometalates (POMs),[27–40] we have chosen to study the formation and reactivity of nitrido–POM derivatives[41,42] for several reasons: (i) POMs form a unique class of compounds due to their structural diversity and tunable electronic properties; many examples of mono- or polylacunary species are known, which behave as all-inorganic ligands towards metallic cations.[43–47] (ii) As is the case for porphyrin or corrole ligands, for which nitrido derivatives are known, POMs are able to stabilize metallic cations in high oxidation states.[48–51] (iii) We favoured nitrido over organoimido (or nitrene) derivatives, as the reactivity of some nitrido derivatives encompasses the formation of metal–imido functions, provided that the metal–nitrido function is nucleophilic.[52] Moreover, by varying the POM structural type, and the identity or oxidation state of the metallic cation incorporated, one can expect to tune the reactivity of the metal–nitrido function from nucleophilic to electrophilic. We recently reported osmium–, rhenium– and (nitrido)ruthenium derivatives of POMs[53–55] and we describe herein the syn-

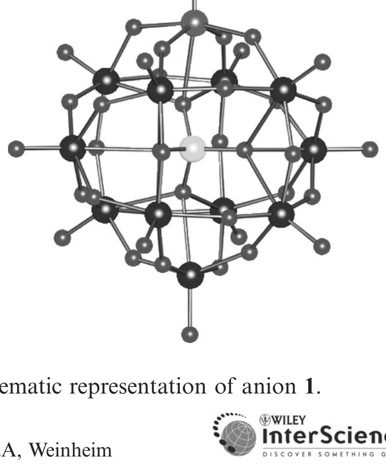

Figure 1. Schematic representation of anion **1**.

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thesis and characterization of $[PW_{11}O_{39}\{Cr^VN\}]^{5-}$ (Figure 1), together with the preliminary results of its reactivity, from which we inferred nucleophilic behaviour.

## Results and Discussion

### Synthesis of $(tba)_4H[PW_{11}O_{39}\{CrN\}]$ (1)

Although numerous examples of nitrogenous derivatives of the Lindqvist anion $[Mo_6O_{19}]^{2-}$, including nitrosyl, organoimido and organodiazenido species, have been described,[56] few examples are known in the Keggin family. Indeed, the higher reducibility of $[PMo_{12}O_{40}]^{3-}$ in comparison to $[Mo_6O_{19}]^{2-}$ precludes the direct functionalization of the latter by the amines or hydrazines commonly used in the functionalization of the former,[31,57] whereas the corresponding polyoxotungstates are not reactive under such conditions. As a result, functionalized Keggin-type anions described up to date have been obtained by complexation of a preformed {metal–nitrogenous ligand} function with a lacunary polyanion, which acts as an all-inorganic multidentate ligand. We thus recently described the synthesis of $[PW_{11}O_{39}\{OsN\}]^{4-}$, $[PW_{11}O_{39}\{ReN\}]^{n-}$ ($n$ = 4, 3) and $[PW_{11}O_{39}\{RuN\}]^{4-}$,[53–55] by reaction between $[PW_{11}O_{39}]^{7-}$ and $[OsNCl_5]^{2-}$, $[ReNCl_2(PPh_3)_2]$ and $[RuNCl_4]^-$, respectively. The synthesis of the recently reported organoimido derivatives $[PW_{11}O_{39}\{ReNPh\}]^{4-}$ and $[PW_{11}O_{39}\{WNPh\}]^{4-}$ follows the same procedure.[31,58]

Early and recent reports on intermetallic N-atom transfers have drawn our attention as a potential alternative route to nitrido derivatives of POMs. Recently, Gross et al. showed that $[(tpfc)Cr^VN]^-$ can be prepared by N-atom transfer from [(saloph)MnN] [saloph = *N*,*N′*-bis(salicylidene)*o*-phenyl dianion] to $[(tpfc)Cr^{III}(py)_2]$ [$H_3tpfc$ = 5,10,15-tris(pentafluorophenyl)corrole].[21] This prompted us to explore the reaction between [(saloph)MnN] and $(tba)_4[PW_{11}O_{39}\{Cr^{III}(H_2O)\}]$,[59] (tba = tetrabutylammonium cation) but we could not evidence the formation of the desired product. The mechanism proposed for the intermetallic N-transfer relies on three steps: (i) formation of a bimetallic μ-nitrido-bridged precursor, (ii) bielectronic transfer and (iii) dissociation of the resulting complex.[60–62] As $Cr^{III}$ is known to be inert, the first step could prove to be problematic in this case,[60] but we were also not successful in employing this route with the more labile $Mn^{III}$ centre in $(tba)_4H[SiW_{11}O_{39}\{Mn^{III}(H_2O)\}]$.[63] We conclude that, in order to favour the second step, more study of the electronic properties of the chosen POM systems will be required by analogy to previous studies on porphyrin systems.[64,65]

Fortunately, we were more successful with the synthetic route devised by Bendix et al.,[24] who showed that a variety of (nitrido)chromium complexes can be easily synthesized by the reaction of $[CrCl_3(thf)_3]$ with [(salen)MnN], which generates a source of the $\{CrN\}^{2+}$ function in situ,[66] and subsequent complexation with a polydentate ligand. By using a similar procedure, $(tba)_4[H_3PW_{11}O_{39}]$ was treated with this $\{CrN\}^{2+}$ source to yield $(tba)_4H[PW_{11}O_{39}\{CrN\}]$ (**1**). Elemental analysis confirmed the incorporation of a chromium–nitrido function into the lacunary polyanion. We should however note here that the sample was always contaminated with a small percentage of $(tba)_3[PW_{12}O_{40}]$ (10%) even after several recrystallization steps in acetonitrile.

### Characterization of $(tba)_4H[PW_{11}O_{39}CrN]$ (1)

#### *IR Spectroscopy*

The IR spectrum of **1** shows, as expected, the characteristic features of a Keggin-type structure, with strong vibrational bands at 810, 885 and 954 cm$^{-1}$, corresponding to the ν(W–O–W) and ν(W=O$_t$) stretching frequencies. Incorporation of the {CrN} function into the lacunary $[PW_{11}O_{39}]^{7-}$ framework results in a lowering of the ν(P=O) splitting from 53 to 36 cm$^{-1}$. Similar behaviour has already been noted for derivatives containing other first-row transition metals.[67] A notable feature in the IR spectrum of **1** is the presence of a new weak band at 997 cm$^{-1}$, assignable as the ν(CrN) stretching frequency, in agreement with the literature.[24]

#### *$^{31}P$ NMR Spectroscopy*

The $^{31}P$ NMR spectrum of **1** was recorded in $CD_3CN$ and, as expected for a paramagnetic $Cr^V$ derivative, a relatively broad peak ($\Delta_{1/2}$ = 20 Hz) was observed at –11.5 ppm. A second minor peak observed at –14.1 ppm is assigned to $[PW_{12}O_{40}]^{3-}$ often present as an impurity (10%) in our samples. Attempts at purification by recrystallization were unfruitful. Because of the presence of the paramagnetic centre, we did not try to record the $^{183}W$ NMR spectrum.

#### *X-Band EPR Spectroscopy*

Spectra of **1** in solution in acetonitrile were recorded at ambient and low temperature (77 K, frozen solution). At ambient temperature, the spectrum of **1** exhibits a sharp isotropic signal at $g_{iso} \approx 1.96$ as depicted in Figure 2, characteristic of a $Cr^V$ ($S$ = 1/2) centre with $3d^1$ electronic configuration.[24,60,64] A similar spectrum was reported for the oxido analogue $[PW_{11}O_{39}\{Cr^VO\}]^{4-}$.[59,68] The hyperfine structure expected for the coupling of the unpaired electron with the nuclear spin of the less abundant $^{53}Cr$ isotope (9.5% $^{53}Cr$; $I$ = 3/2)[24] is also observed though the signal is quite large and asymmetric. Our conditions did not, however, allow the detection of the superhyperfine coupling to the nitrido ligand. This is not unprecedented in the literature.[69] In the case of the $d^1$ system $[PW_{11}O_{39}\{Re^{VI}N\}]^{4-}$, the lack of nitrogen superhyperfine coupling was ascribed to an odd electron primarily localized on the rhenium 5d $x^2–y^2(d_\pi)$ orbital overlapping with $2p_\pi$ orbitals of the in-plane oxygen ligands.[54] The spectrum of **1** recorded at 77 K in a frozen solution revealed an axial system with $g_\perp$ = 1.98 and $g_\parallel$ = 1.91.

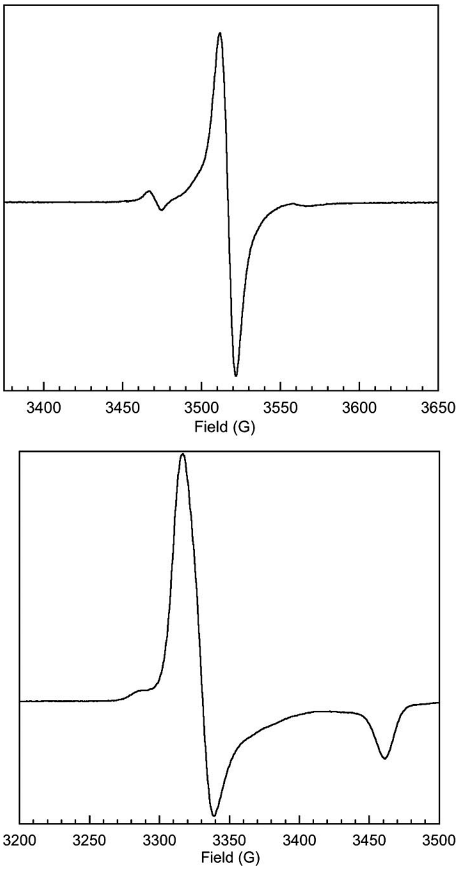

Figure 2. EPR spectrum of $(tba)_4H[PW_{11}O_{39}\{Cr^VN\}]$ in $CH_3CN$ ($5\times10^{-3}$ м) at room temperature (top) and at 77 K (bottom).

### *UV/Vis Spectroscopy*

To a first approximation, the coordination sphere around the chromium centre in $[PW_{11}O_{39}\{CrN\}]^{5-}$ possesses $C_{4v}$ symmetry. This symmetry could lead to three electronic d–d transitions, $^2B_2\rightarrow{}^2B_1$, $^2B_2\rightarrow{}^2E$ and $^2B_2\rightarrow{}^2A_1$. In the case of the nitridobis(pyrrolidinedithiocarbamate)chromium(V) complex described by Bendix et al.,[24] the first two transitions were observed at 548 and 440 nm. Given the similar Cr environment within **1**, i.e., four oxido ligands in the *xy* plane and the nitrido ligand along the *z* axis, we would expect a similar spectrum for **1**. However, the UV/Vis spectrum, recorded in acetonitrile and depicted in Figure 3 displays only a single band at 467 nm (log $\varepsilon$ = 2.1) that we ascribe to the $^2B_2\rightarrow{}^2E$ transition; the $^2B_2\rightarrow{}^2B_1$ transition is expected to be weak because of its electrical dipole forbidden character.[24] The highest energy d–d transition $^2B_2\rightarrow{}^2A_1$ is probably hidden by the ligand-to-metal charge transfers characteristic of the polyanion. Other pseudooctahedral (nitrido)chromium complexes have been shown to display a single d–d transition of low intensity in the range 405–450 nm.[69]

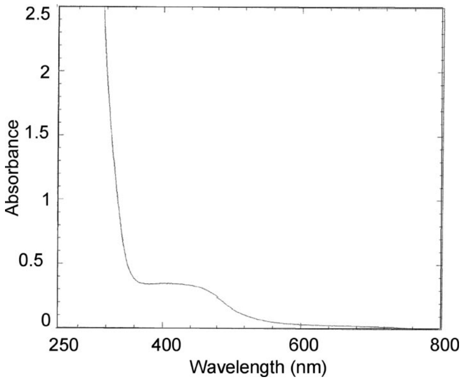

Figure 3. UV/Vis spectrum of $(tba)_4H[PW_{11}O_{39}\{Cr^VN\}]$ showing an absorption band at $\lambda_{max}$ = 467 nm (log $\varepsilon_{max}$ = 2.1) in $CH_3CN$ ($5\times10^{-3}$ м).

### *Cyclic Voltammetry*

Characterization of **1** by cyclic voltammetry, in acetonitrile and at a carbon electrode, showed a reversible wave at 0.87 V (vs. SCE). The latter was assigned to the oxidation of a $Cr^V$ centre to $Cr^{VI}$ (see Figure 4). As previously noticed for corrole complexes,[21] the $\{Cr^VN\}$ function is easier to oxidize than the isoelectronic $\{Cr^VO\}$ function.[68] The stabilization of the $\{Cr^VN\}$ function within the $PW_{11}$ framework relative to that provided by porphyrinato or corrole ligands can be inferred by the following comparisons. Although the oxidation potentials of the corrole complexes $[(tpfc)Cr^VN]^-$ and $[(tpfc)Mn^VN]^-$ are very similar at 0.56 and 0.59 V, respectively,[21,65] the latter value is significantly lower than that of the $\{Mn^VN\}$ function in a porphyrin environment: $[(oep)Mn^VN]$ (oep = octaethylporphyrinato dianion) and $[(tpfpp)Mn^VN]$ [tpfpp = tetrakis(pentafluorophenyl)porphyrinato] are oxidized at 0.90 and 1.37 V, respectively.[65] The stabilization of the $\{Cr^VN\}$ function by the $[PW_{11}O_{39}]^{7-}$ polyanion would thus be similar to that of the octaethylporphyrinato ligand. The attribution of the other redox processes is much more complex. Four reduction waves are observed out of which three are reversible at –0.795, –1.519 and –1.962 V. These waves are linked to the reduction of the $Cr^V$ centre together with the $W^{VI}$ centres but we cannot differentiate them at this stage.

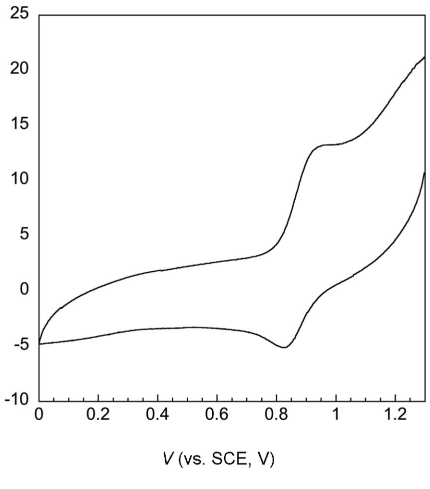

Figure 4. Cyclic voltammogram of $(tba)_4H[PW_{11}O_{39}\{Cr^VN\}]$ in $CH_3CN$ ($10^{-3}$ м) at a carbon electrode (100 mV/s).

### Reactivity of $(tba)_4H[PW_{11}O_{39}CrN]$ (1)

The reactivity at nitrogen in the metal–nitrido function depends on the nature of the metal, its oxidation state and the character of the ancillary ligands: whereas the nitrido ligand is expected to be nucleophilic when bonded to an early transition metal, its electrophilicity increases when moving to late transition metals.[52] With all other parameters kept constant, the electrophilicity of the nitrido ligand will increase with the oxidation state of the transition metal. Although the rhenium derivative $[PW_{11}O_{39}\{ReN\}]^{n-}$ appeared to be nonreactive, whether as $Re^{V}$, $Re^{VI}$ or $Re^{VII}$, the ruthenium analogue $[PW_{11}O_{39}\{Ru^{VI}N\}]^{4-}$ was electrophilic: the ultimate release of $PPh_3NPPh_3^+$ upon reaction with $PPh_3$ demonstrated for the first time the feasibility of N-atom transfer from POM–nitrido derivatives.[55] Employing first-row transition metals should enable the nitrido ligand to become more nucleophilic.

The reactivity of $(tba)_4H[PW_{11}O_{39}CrN]$ (**1**) towards an alkene was thus investigated in its reaction with cyclooctene, in the presence of trifluoroacetic anhydride (tfaa) at low temperature, following the conditions of Groves et al.[18] The resulting mother liquor was evaporated to dryness, and the organic compounds were extracted into dichloromethane. The organic phase was analyzed by different spectroscopic methods in search of the aziridine 9-(trifluoroacetyl)-9-azabicyclo[6.1.0]nonane. IR and $^1H$ NMR spectroscopy and GC–MS analysis showed that no aziridine was formed during the reaction. Polyoxometallic product **2** was also studied after washing with dichloromethane and recrystallization in acetonitrile. Various spectroscopic methods support the formation of the acylimido $Cr^V$ derivative $(tba)_4[PW_{11}O_{39}\{CrNC(O)CF_3\}]$, as in the case of (nitrido)(porphyrinato)chromium complexes:[70] (i) The infrared spectrum of **2** shows the presence of two new bands at 1203 and 1682 $cm^{-1}$, which can be assigned to the ν(C–F) and ν(C=O) vibrational frequencies respectively, whereas the band at 997 $cm^{-1}$ previously assigned to the ν(Cr=N) stretching frequency in **1** has disappeared. (ii) The $^{19}F$ NMR spectrum of **2** recorded in a $CH_3CN/CDCl_3$ mixture at room temperature reveals two peaks: a broad peak at –76.3 ($\Delta_{1/2}$ = 40 Hz) and a sharp peak at –77.4 ppm, which was assigned to tfaa present as 5% impurity. The presence of the broad peak is consistent with a "$COCF_3$" group bound to a paramagnetic chromium centre. A broad peak at –11.7 ppm ($\Delta_{1/2}$ = 20 Hz) is also observed in the $^{31}P$ NMR spectrum of **2**, recorded in $CD_3CN$. This peak is only slightly shifted relative to that found in the spectrum of **1**, indicating that the electronic environment around the chromium centre does not change significantly in the formation of **2**. (iii) The EPR and UV spectra as well as the voltammogram of **2** are very close to those of **1**. The EPR spectrum at room temperature shows an isotropic signal at $g_{iso} = 1.96$, and at 77 K again an axial symmetry is observed with $g_{\perp} = 1.98$ and $g_{\parallel} = 1.91$, whereas a single absorption band was observed at 463 nm (log $\varepsilon = 2.6$) in the UV/Vis spectrum. The voltammogram of **2** is only slightly modified (less than 100 mV) with all the redox processes occurring at higher potential, as expected. (iv) The ESI mass spectrum of **2**, recorded in the negative mode, displays two isotopic clusters centred at $m/z$ = 923 and 1507, corresponding to the $[HPW_{11}O_{39}\{CrNCO\}]^{3-}$ and $[H(tba)PW_{11}O_{39}\{CrNCO\}]^{2-}$ fragments, respectively. Unfortunately, the experimental conditions used for the analysis did not allow the detection of the molecular ion. Other fragments corresponding to the association of $[PW_{11}O_{39}CrN]^{5-}$ with different cations are also observed (see Supporting Information).

Unfortunately, crystals of **2** belong to the cubic crystallographic system (cubic I, $a$ = 17.7 Å, $V$ = 5500 Å$^3$), which precludes any detailed analysis by X-ray diffraction. The asymmetric unit should therefore display only one metallic centre, composed of 11/12 W and 1/12 Cr atoms, one disordered terminal ligand, one doubly bridging oxygen atom and one quadruply bridging oxygen atom linked to the phosphorus atom, as previously observed.[53]

The formation of acylimido species incapable of transfer to olefins was reported in the literature for some (nitrido)(porphyrinato)chromium(V) systems,[70] in contrast to the reactivity of (nitrido)(porphyrinato)manganese(V) complexes.[18,71] The formation of these chromium–acylimido functions was then shown to be reversible upon addition of tetrabutylammonium hydroxide.[18,70] Hence, compound **2** was treated with tetrabutylammonium hydroxide (2 equiv.) in acetonitrile, at room temperature. Slow admission of diethyl ether vapour into this solution allowed the formation of orange crystals that were then analyzed by IR spectroscopy. The IR spectrum showed the reappearance of the band at 997 $cm^{-1}$, previously assigned to the ν(CrN) stretching frequency. Moreover, the $^{19}F$ NMR spectrum of redissolved crystals displayed only one single peak (narrow) at –78.5 ppm, corresponding to trifluoroacetic acid. The $^{31}P$ NMR spectrum showed a peak at –9.4 ppm, instead of the expected signature of the parent $(tba)_4H[PW_{11}O_{39}CrN]$ (**1**) at –11.7 ppm. This discrepancy could be due to the formation of an unprotonated salt of $[PW_{11}O_{39}CrN]^{5-}$, in the presence of an excess amount of tetrabutylammonium hydroxide. The mass spectrum (ESI) confirmed the formation of $[PW_{11}O_{39}\{CrN\}]^{5-}$, with disappearance of the peak at $m/z$ = 923, previously assigned to the $[HPW_{11}O_{39}\{CrNCO\}]^{3-}$ fragment. Analysis of the product of the reaction between **2** and tetrabutylammonium hydroxide thus further supports its description as the acylimido derivative $(tba)_4[PW_{11}O_{39}\{CrNC(O)CF_3\}]$.

Among the other possible products that could be formed, $[PW_{11}O_{39}\{Cr^{III}OC(O)CF_3\}]^{5-}$ is excluded by EPR and mass spectrometry, whereas the *O*-acylation product $[PW_{11}O_{38}\{OC(O)CF_3\}\{CrN\}]^{4-}$ would not explain the disappearance of the IR stretching vibration at 997 $cm^{-1}$ (and its reappearance upon reaction with tetrabutylammonium hydroxide, see above). The ν(CO) vibration observed at 1682 $cm^{-1}$, below and not above 1700 $cm^{-1}$, also favours *N*-acylation vs. *O*-acylation.[70] There is precedence for *O*-alkylations or *O*-arylations in the chemistry of POMs.[27,72,73] In the present case, however, such an *O*-alkylation, if observed, should also have been observed with other similarly charged species: whereas $[PW_{11}O_{39}\{Cr^{V}N\}]^{5-}$ also reacts, according to $^{31}P$ NMR spectroscopy, with the trityl carbocation $Ph_3C^+$, $[PW_{11}O_{39}\{Re^{V}N\}]^{5-}$, obtained by reduction of $[PW_{11}O_{39}\{Re^{VI}N\}]^{4-}$, does not.[74]

We thus confidently inferred from the above data, taken all together, that the reaction of $(tba)_4H[PW_{11}O_{39}CrN]$ (**1**) with cyclooctene in the presence of tfaa yields $(tba)_4[PW_{11}O_{39}\{CrNC(O)CF_3\}]$ (**2**). We also verified that **2** is formed in the absence of cyclooctene.

## Conclusions

The versatility of POMs as all-inorganic ligands in the coordination of various transition metals, especially in high oxidation states, will allow the synthesis of (nitrido)metal derivatives with tunable electronic properties. We have presented here the synthesis and full characterization of $(tba)_4H[PW_{11}O_{39}\{CrN\}]$ (**1**), which displays a nucleophilic {CrN} function. Reaction with trifluoroacetic anhydride yields the corresponding acylimido derivative, $(tba)_4[PW_{11}O_{39}\{CrNC(O)CF_3\}]$ (**2**). No transfer of the NC(O)-$CF_3$ group from the POM to cyclooctene was evidenced under the reaction conditions we used. This behaviour parallels that of some (nitrido)(porphyrinato)chromium systems.[70]

Further reactions at the nucleophilic {CrN} function will be explored to form alkyl- or arylimido derivatives. Imido derivatives of POMs are indeed mainly restricted to the Lindqvist series, albeit extension to the Keggin or Dawson series would be valuable for POM-based materials.[75–77] We believe that our approach could provide a worthwhile alternative route to the synthesis of Keggin–imido derivatives, of which only two examples are known.[31,58]

## Experimental Section

**Instrumentation and Techniques of Measurement:** IR spectra were recorded as KBr pellets with a Bio-Rad Win-IR FTS 165 FTIR spectrophotometer. UV/Vis spectra were recorded with a Shimadzu UV-2101 spectrophotometer. The $^{31}P$ (121.5 MHz) NMR spectra were obtained at room temperature in 5 mm o.d. tubes with a Bruker AvanceII 300 spectrometer equipped with a QNP probehead. The chemical shifts are given according to IUPAC convention with respect to 85% $H_3PO_4$ and were measured by the substitution method. X-band EPR spectra were recorded with a Bruker ELEXSYS 500 X-band spectrometer. For low-temperature studies, an Oxford Instrument continuous flow liquid cryostat and a temperature control (ITC 503) system were used. The temperatures were calibrated by using a RhFe thermoresistance that was put inside a 5-mm quartz tube. Electrochemical data were recorded in acetonitrile, with sample concentration of $10^{-3}$ M and 0.1 M (tba) $BF_4$ as the supporting electrolyte. Cyclic voltammetry at a carbon electrode was carried out with a PAR model 273 instrument by using a standard three-electrode cell, consisting of the working electrode, an auxiliary platinum electrode and an aqueous saturated calomel electrode (SCE) equipped with a double junction.

**Synthesis:** The reagents $(tba)_4[H_3PW_{11}O_{39}]$,[78] $[CrCl_3(thf)_3]$[79] and [(saloph)Mn(N)] [saloph = *N*,*N′*-bis(salicylidene)*o*-phenyl dianion][22] were synthesized according to published procedures and their purity was confirmed by infrared spectroscopy, and for $(tba)_4[H_3PW_{11}O_{39}]$ by $^{31}P$ NMR spectroscopy. Acetonitrile was freshly distilled from calcium hydride prior to use. Elemental analyses were performed by the Service de Microanalyses (Université Pierre et Marie Curie, Paris, France).

**$(tba)_4H[PW_{11}O_{39}\{Cr^{V}N\}]$ (1):** To the violet solution formed by dissolution of $[CrCl_3(thf)_3]$ (0.11 g, 0.30 mmol) in distilled acetonitrile (15 mL), under argon, was added [(saloph)Mn(N)] (0.12 g, 0.31 mmol). A brown suspension immediately formed. The reaction mixture was stirred for 30 min at room temperature, then filtered through a glass frit and the filtrate containing the (nitrido)-chromium(V) complex was kept. In another round-bottomed flask, $(tba)_4[H_3PW_{11}O_{39}]$ (2.23 g, 0.6 mmol) was dissolved in distilled acetonitrile (20 mL) under argon. Triethylamine (0.13 mL, 0.92 mmol) and the above (nitrido)chromium(V) complex solution were then added, and the reaction mixture was stirred at room temperature overnight. A brownish-orange solution was obtained, which was concentrated by rotary evaporation. Slow diffusion of diethyl ether into this solution yielded 0.85 g (80%) of orange crystals of **1**. IR (KBr): $\tilde{\nu}$ = 391 (w), 520 (w), 670 (w), 737 (sh.), 810 (s), 885 (m), 954 (s), 997 (sh.), 1060 (m), 1098 (w), 1154 (w), 1382 (w), 1484 (m), 1654 (w), 2874 (w), 2938 (sh.), 2964(m) $cm^{-1}$. UV ($CH_3CN$): $\lambda_{max}$ (log $\varepsilon$) = 467 (2.1) nm. $^{31}P$ NMR (121.5 MHz, $CD_3CN$, 25 °C): $\delta = -11.5$ ($\Delta\nu_{1/2}$ = 20 Hz) ppm.$C_{64}H_{145}CrN_5O_{39}PW_{11}$ (3714.2): calcd. C 20.70, H 3.94, N 1.89, P 0.83; found C 21.40, H 4.09, N 1.98, P 0.76.

**$(tba)_4[PW_{11}O_{39}\{Cr^{V}NCOCF_3\}]$ (2):** Compound **1** (0.87 g, 0.24 mmol) was introduced into a 25-mL round-bottomed flask, and the latter was purged with argon. Distilled acetonitrile (10 mL) was then added followed by cyclooctene (32 µL, 0.24 mmol). The resulting solution was cooled to –55 °C and trifluoroacetic anhydride (40 µL, 0.28 mmol) was added. The solution was stirred for 20 min at this temperature and then warmed to room temperature, where it was stirred for another 2 h. The colour of the solution changed from orange-brown to dark brown. The mother liquor was then evaporated to dryness to give a brown solid, which was washed with dichloromethane (10 mL) so as to extract all the organic components. The mixture was then filtered and dried on a glass frit to give a brown powder. The solid obtained was recrystallized from acetonitrile, and by slow diffusion of diethyl ether 0.6 g of brown crystals of **2** were obtained in 66% yield. IR (KBr): $\tilde{\nu}$ = 376 (sh.), 387 (m), 516 (w), 596 (w), 686 (w), 726 (sh.), 808 (s), 886 (m), 962 (s), 1063 (sh.), 1081 (m), 1142 (w), 1203 (w), 1382 (w), 1484 (m), 1682 (m), 2875 (w), 2937 (sh.), 2963 (m) $cm^{-1}$. UV ($CH_3CN$): $\lambda_{max}$ (log $\varepsilon$) = 463 (2.6) nm. $^{31}P$ NMR (121.5 MHz, $CD_3CN$, 25 °C): $\delta = -11.7$ ($\Delta\nu_{1/2}$ = 20 Hz) ppm. $^{19}F$ NMR (282 MHz, $CH_3CN/CDCl_3$, 25 °C): $\delta = -76.3$ ($\Delta\nu_{1/2}$ = 40 Hz) ppm. $C_{66}H_{144}CrF_3N_5O_{40}PW_{11}$ (3810.2): calcd. C 20.70, H 3.94, N 1.80, P 0.81; found C 19.88, H 3.81, N 1.80, P 0.88.

**Supporting Information** (see footnote on the first page of this article): IR spectra of **1** and **2**; $^{19}F$ NMR spectrum of **2**; MS (ESI–) of **2** and of POM formed after reaction of **2** with tetrabutylammonium hydroxide.

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