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Addition of N-Heterocyclic Carbenes to a Ruthenium(VI) Nitrido Polyoxometalate: a New Route to Cyclic Guanidines

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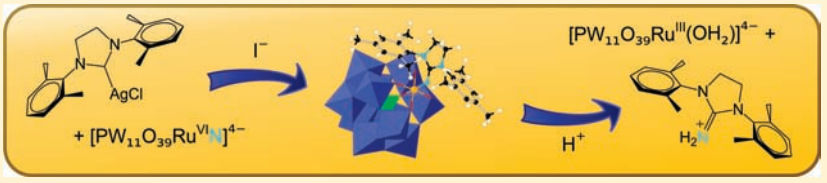
Supporting Information

ABSTRACT:



The scope of N-atom transfer from the electrophilic ruthenium(VI) nitrido containing polyoxometalate $[PW_{11}O_{39}Ru^{VI}N]^{4-}$ has been extended to the N-heterocyclic carbene $\{CH_2(Mes)N\}_2C$ and the coupling product $\{CH_2(Mes)N\}_2CNH_2^+$ characterized by ^1H NMR and high-resolution mass spectrometry. Because guanidines display many fields of applications ranging from biology to supramolecular chemistry, this could afford an original route to the synthesis of cyclic guanidines. This also enlarges the potential of nitrido complexes in the synthesis of heterocycles, mainly illustrated in the literature through the formation of aziridines through N-atom transfer to alkenes. In the course of the reaction, the ruthenium(III)-containing polyoxometallic intermediate $[PW_{11}O_{39}Ru^{III}\{NC\{N(Mes)CH_2\}_2\}]^{5-}$ has been thoroughly characterized by continuous-wave and pulsed electron paramagnetic resonance, which nicely confirms the presence of the organic moiety on the polyoxometallic framework, Ru K-edge X-ray absorption near-edge structure, and electrochemistry.

INTRODUCTION

Heterocyclic chemistry is an essential link between organic chemistry and biochemistry. Indeed, a majority of the bioactive molecules present at least one heterocycle. In particular, many natural marine alkaloids feature polycyclic guanidine motifs.[1,2] Natural guanidine derivatives are found in microorganisms, marine algae, and sponges but also in plants, invertebrates, and terrestrial vertebrates.[3,4] Natural and synthetic guanidines present much interest not only for their pronounced biological activities but also for their use as superbases,[5] organic catalysts,[6−8] building blocks for artificial anion receptors,[9,10] and peptide mimetics.[11] Guanidinium therapeutic agents of special interest include neuramidinase inhibitors, for instance, Glaxo's Zanamivir (Relenza), which exhibits antiviral activity against many viruses such as influenza A and B.[12]

Carbon−heteroatom bond formation has been the subject of intense research in the past century and is still a challenging issue, albeit a large array of synthetic strategies is yet available. However, although many synthetic routes to guanidine derivatives have been reported,[3] the synthesis of cyclic guanidines is often difficult.[13] Recent routes to cyclic guanidines include palladium- and nickel-catalyzed oxidative diamination of alkenes[14] and the addition of N-centered radicals to cyanamide compounds.[15] N-atom transfer to N-heterocyclic carbenes (NHCs)[16,17] also offers a potential route to cyclic guanidines. This parallels the formation of cyclic ureas through oxidation of NHCs.[18] The coupling of NHCs with organic azides indeed affords triazenes,[19,20] which can extrude dinitrogen upon heating. Furthermore, intramolecular imido−carbene coupling has been observed in cobalt(III) imido complexes with tripodal NHC ligands.[21] We thus reasoned that nitrido−NHC coupling could provide an alternative route to cyclic guanidines. A broad range of nitrido transition-metal complexes are known, and their reactivity can be tuned by playing with the metal, its oxidation state, and the ancillary ligands.[22,23] While osmium nitrido complexes are

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generally electrophilic species,[24,25] however allowing extensive redox tuning,[26] the reactivity of ruthenium nitrido complexes is more balanced:[27] nucleophilic porphyrin ruthenium nitrido complexes have been involved in amination reactions after activation by trifluoroacetic anhydride (TFAA),[28] while electrophilic Schiff base ruthenium nitrido complexes that react with amines[29] and phosphines[30] or directly with alkenes have been described.[31] The formation of aziridines through N-atom group transfer to alkenes is much more documented in the case of manganese nitrido species.[32−36] To the best of our knowledge, the previous use of nitrido precursors in heterocyclic synthesis was mainly limited to the formation of aziridines,[37] so that extension to guanidines would significantly enlarge the synthetic scope of nitrido complexes. Of special interest in the present context is the reaction of an osmium(VI) nitrido complex with a bis(1,3-dialkylimidazolidin-2-ylidene)carbene precursor to produce osmium(IV) azavinylidene complexes, which could, in principle, evolve to give cyclic guanidines, although this was not reported.[38] In many cases, however, reactions of NHCs with metal nitrido complexes only result in the substitution of ancillary ligands.[39,40]

Polyoxometalates (POMs) display unique properties as ligands.[41−43] They are able to stabilize both low- and high-oxidation metal states, and like porphyrins[32] and corroles,[44,45] they can accommodate metal nitrido functions, as documented in our recent reports (M = Re,[46] Cr,[47] Ru,[48−50] M = Mn[51]). There is now both experimental and theoretical[52] evidence for the influence of POMs on the reactivity of high-valent metal−nitrido bonds. Among the metal nitrido substituted Keggin-type POMs that we are currently studying, the rhenium(VII), -(VI), and -(V) and manganese(V) nitrido species are almost unreactive, and even if chromium(V) nitrido could be acylated by TFAA, we found no evidence for transfer to alkenes, which indicates that the POM stabilizes the metal nitrido function even more than expected and that the reactivity of metal nitrido substituted POMs cannot simply be anticipated from that of classical coordination complexes with organic multidentate ligands. Among the above-mentioned complexes, the ruthenium(VI) nitrido species stands out. We have thus previously shown that $[PW_{11}O_{39}RuN]^{4-}$ (Figure 1) reacts with triphenylphosphine to give a ruthenium(V) phosphoraniminato complex and, ultimately, the bis(triphenylphosphane)iminium cation.[48,49] These studies have now been extended to NHCs with the aim of synthesizing cyclic guanidine derivatives. Among the wide range of NHCs, very few are easily isolated. NHCs, which are air-sensitive, are often generated in situ in the presence of metallic precursors to form the corresponding metal NHCs.[53,54] Transmetalation with silver(I) NHC complexes has been used as a convenient alternative method. Silver NHCs are air-stable and readily accessible species[55,56] that behave as efficient carbene-transfer agents toward various metals. To our knowledge, the transfer of an NHC from silver NHC complexes to an N atom has not been previously investigated.[57,58]

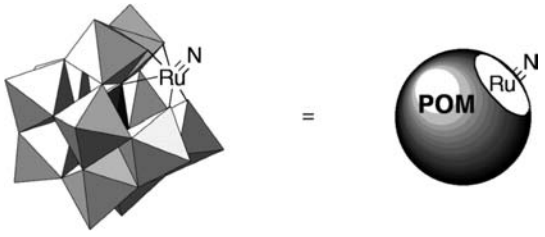


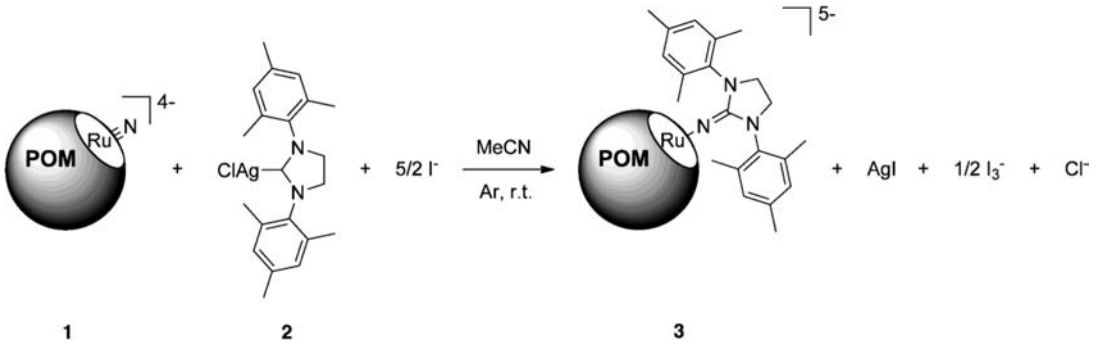
Figure 1. Polyhedral and schematic representation of $[PW_{11}O_{39}Ru^{VI}N]^{4-}$.

RESULTS AND DISCUSSION

In a typical procedure, $(n\text{-}Bu_4N)_4[PW_{11}O_{39}Ru^{VI}N]$ [$(n\text{-}Bu_4N)_4$**1**] was allowed to react, under argon, with 2 equiv of the silver NHC $\{CH_2(Mes)N\}_2CAgCl$ (**2**) and 4 equiv of $(n\text{-}Bu_4N)I$, at room temperature in acetonitrile, for 16 h (Scheme 1). After some workup, $(n\text{-}Bu_4N)_4H[PW_{11}O_{39}Ru^{III}\text{-}\{NC\{N(Mes)CH_2\}_2\}]$ [$(n\text{-}Bu_4N)_4$H**3**] was isolated in 95% yield. Heating of the reaction mixture had no effect on the rate, and no reaction was observed in the absence of $(n\text{-}Bu_4N)I$, which was consequently added to help the elimination of silver. Compound **3** is air- and moisture-stable. The high-frequency region of its Fourier transform (FT-IR) spectrum shows weak bands characteristic of the $(MesN)_2C$ fragment, while the characteristic bands for the Keggin structure in the low-frequency region are only slightly shifted with respect to **1**. However, a splitting of the ν(PO) stretching band is clearly evidenced, as was previously observed in the reaction between **1** and PPh_3.[48] Broad signals in the ^1H, ^{13}C, and ^{31}P NMR spectra (CD_3CN, 300 K, $\delta = -21$ ppm, $\Delta\nu_{1/2} = 150$ Hz) suggest that **3** is paramagnetic, as confirmed by electron paramagnetic resonance (EPR). Although compound $(n\text{-}Bu_4N)_4$H**3** could be crystallized in various conditions and solvents, we failed to obtain suitable crystals for a detailed X-ray crystal structure analysis.

In a frozen MeCN/toluene solution at 77 K, compound $(n\text{-}Bu_4N)_4$H**3** exhibits a rhombic EPR spectrum (Figure 2), characteristic of a metal-centered spin $^1/_2$, with g_1, g_2, and g_3 values of 2.44, 2.25, and 1.66, respectively. These values are very close to those reported for $(n\text{-}Bu_4N)_4[PW_{11}O_{39}Ru^{III}(OH_2)]$[59,60] but also to those of $(n\text{-}Bu_4N)_3[PW_{11}O_{39}Ru^{V}(NPPh_3)]$.[48]

Scheme 1. Reactivity of an Electrophilic Ruthenium(VI) Nitrido POM with Silver NHC, in the Presence of Iodide



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This issue was further addressed by X-ray absorption near-edge spectroscopy (XANES) at Ru K-edge. All spectra (Figure 3) were recorded in transmission mode on solid samples. Because the environment of the ruthenium, a distorted octahedron constituted mainly of O atoms, is similar in all of the species taken as references, the position of the edge is expected to be a function of the oxidation state only. The data indicate that this is actually the case, with the energy of the edge increasing as the oxidation state of the ruthenium increases. The near edge for **3** lies close to the edge of the ruthenium(III) reference and too far away from that of the ruthenium(V). Accordingly, **3** is formulated as $[PW_{11}O_{39}Ru^{III}\{NC\{N(Mes)CH_2\}_2\}]^{5-}$, while the addition of $\{CH_2(Mes)N\}_2C$ to **1** was expected to afford the ruthenium(IV) complex $[PW_{11}O_{39}Ru^{IV}\{NC\{N(Mes)CH_2\}_2\}]^{4-}$. The latter was presumably reduced by iodide added in excess to activate the reaction. No apparent reaction was observed upon the addition of $(n\text{-}Bu_4N)I$ to a solution of $(n\text{-}Bu_4N)_4$**1** in acetonitrile, and the reported value of 0.35 V/NHE (0.11 V/SCE) for the standard potential of I_3^-/I^- in acetonitrile[61] confirms that the reduction of $[PW_{11}O_{39}Ru^{IV}\{NC\{N(Mes)CH_2\}_2\}]^{4-}$, which was not detected, would be at least thermodynamically possible (see below for the redox data for **3**).

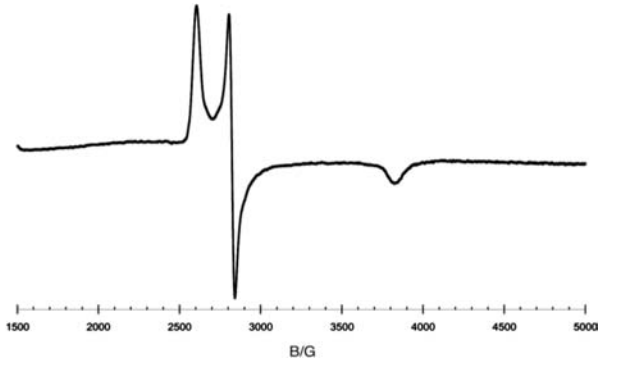

Figure 2. X-band EPR spectrum (ν = 9, 1396 GHz) of compound $(n\text{-}Bu_4N)_4$**H3**, 5×10^{-3} M in a frozen CH_3CN/toluene solution (77 K).

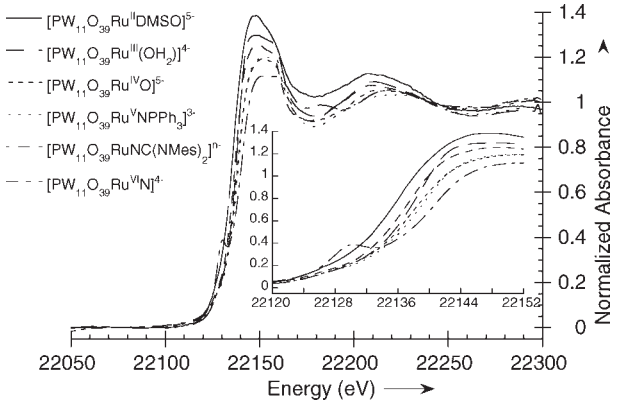

Figure 3. Ru K-edge (22 117 eV) XANES spectra of $(n\text{-}Bu_4N)_4$**H3**, $Cs_5[PW_{11}O_{39}Ru^{II}(DMSO)]$,[62] $(n\text{-}Bu_4N)_4[PW_{11}O_{39}Ru^{III}(H_2O)]$,[59] $(n\text{-}Bu_4N)_4H[PW_{11}O_{39}Ru^{IV}O]$,[63] $(n\text{-}Bu_4N)_3[PW_{11}O_{39}Ru^{V}(NPPh_3)]$[49] and $(n\text{-}Bu_4N)_4$**1**.[48]

To confirm the presence of the organic moiety on ruthenium, pulsed EPR experiments were performed on $(n\text{-}Bu_4N)_4$**H3** for two orientations of the **g** tensor value with respect to the direction of the B_0 static magnetic field. Thus, HYSCORE spectra for g_1 = 2.31 and g_2 = 2.14 have been recorded (Figure 4). Indeed, this two-dimensional pulsed EPR technique allows for measurement of the quadrupolar and hyperfine couplings of the electronic spin with the surrounding nuclei. In the present case, analysis of the two spectra gave evidence for two types of ^{14}N nuclei (I = 1, ν_I = 1.06 MHz),[64,65] one with a small hyperfine interaction and the second with a large hyperfine coupling constant $|A|$ of about 5.5 MHz and a maximum quadrupolar component $|P_{zz}|$ of about 1 MHz. The strong interaction probably results from the N atom directly attached to the ruthenium(III), while the weaker has been associated with the two equivalent N atoms of the guadinine cycle. Moreover, a ^{13}C (I = $^1/_2$; ν_I = 3.77 MHz) hyperfine interaction with a coupling constant of 4 MHz is also detected around 3.6 MHz, together with weak coupling to protons indicated by a small peak

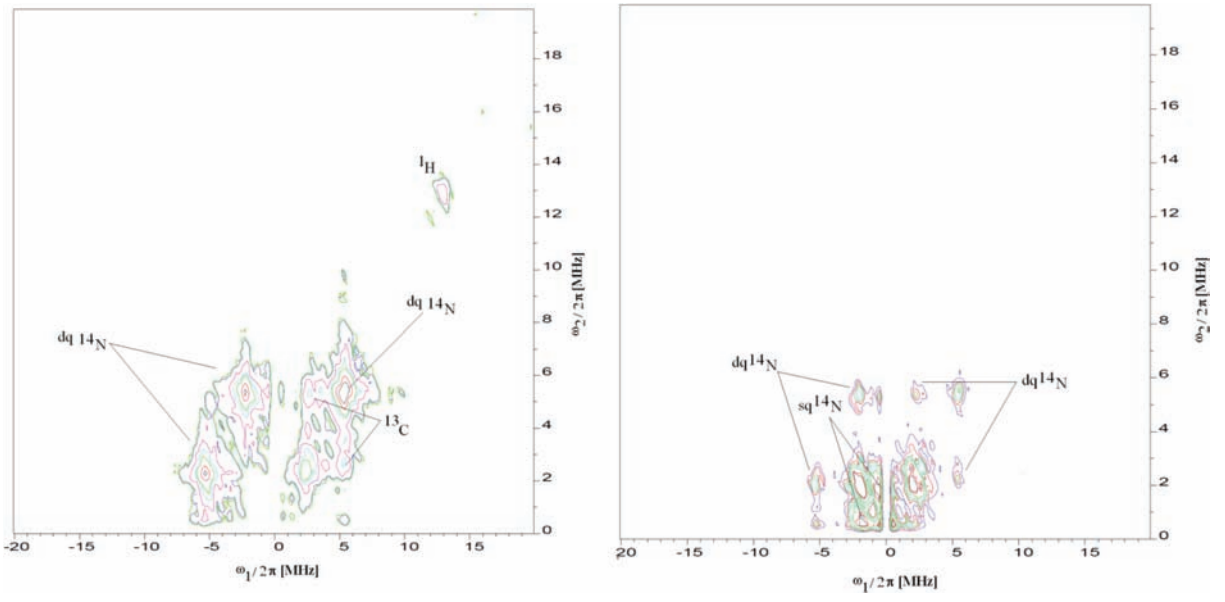

Figure 4. HYSCORE spectra recorded at 4 K for g_1 = 2.31 (left) and g_2 = 2.14 (right) values of the continuous-wave spectrum. The τ value was set to 136 ns with 256 × 256 points along t_1 and t_2 directions.

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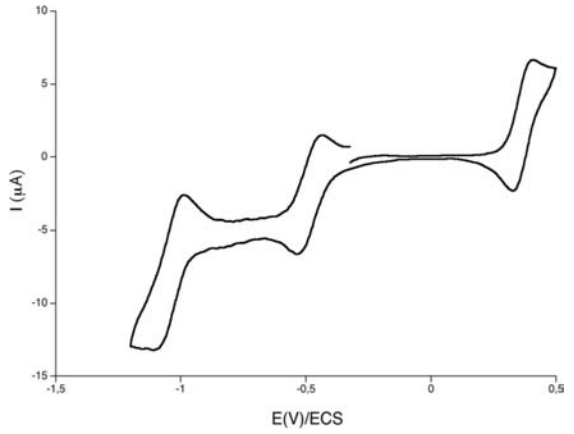
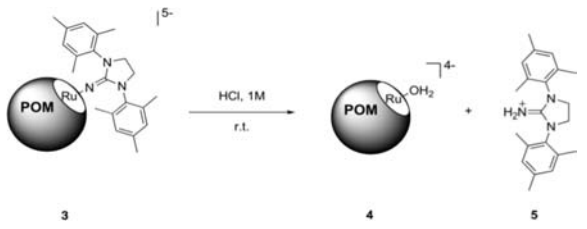


Figure 5. Cyclic voltammogram of $(n\text{-Bu}_4\text{N})_4$**H3** ($10^{-3}$ M) in CH_3CN with 10^{-1} M $(n\text{-Bu}_4\text{N})BF_4$ as the supporting electrolyte, at a carbon electrode and versus SCE (scan rate 20 mV s^{-1}).

Scheme 2. Formation of the Guanidinium Cation via Acid Hydrolysis



centered at the ^{1}H nuclear Larmor frequency of ν_I = 14.5 MHz. All of these data inferred from the HYSCORE spectra demonstrate that the organic group is indeed attached to the ruthenium(III) paramagnetic center in **3** (see the Supporting Information for detailed analysis of the HYSCORE spectra).

According to cyclic voltammetry (CV), oxidation of **3**, presumably to $[PW_{11}O_{39}Ru^{IV}\{NC\{N(Mes)CH_2\}_2\}]^{4-}$, occurs at $E_{1/2}$ = 0.35 V/SCE in acetonitrile. Besides the Ru^{III}/Ru^{IV} oxidation process, the cyclic voltammogram of **3** (Figure 5) shows two quasi-reversible reduction processes at $E_{1/2}$ = −0.49 and −1.04 V/SCE, which are assigned to the Ru^{III}/Ru^{II} and W^{VI}/W^{V} couples, respectively. The three waves are shifted with respect to those of $[PW_{11}O_{39}Ru^{III}(OH_2)]^{4-}$, which are observed at +0.94, −0.32, and −1.62 V/SCE.[59] This change could mainly reflect the difference in the whole charge of the polyanion: the higher the charge, the easier the metal gets oxidized and the harder it gets reduced.

Hydrolysis of complex **3** by the addition of aqueous HCl to a solution of $(n\text{-Bu}_4\text{N})_4$**H3** in dichloromethane yielded $[PW_{11}O_{39}Ru^{III}(OH_2)]^{4-}$ (**4**), unambiguously identified by its ^{31}P NMR spectrum (−70 ppm; $\Delta\nu_{1/2}$ = 1000 Hz; see refs 59 and 63) with liberation of the guanidinium cation $\{CH_2(Mes)N\}_2CNH_2^+$ (**5**; Scheme 2). The latter was isolated as the chloride salt (**5**Cl), which proved to be contaminated with $(n\text{-Bu}_4\text{N})$Cl. Metathetical exchange of Cl^- for PF_6^-, followed by repeated recrystallization from chloroform, afforded **5**PF_6, with minimal contamination by tetrabutylammonium.

CONCLUSION

We have shown that the cyclic guanidinium cation $\{CH_2(Mes)N\}_2CNH_2^+$ can be obtained via the initial coupling of the electrophilic ruthenium(VI) nitrido complex **1** with the $(Mes_2N)_2C$ NHC, opening an original route to more elaborated heterocycles. We are currently exploring the scope of this new route to other cyclic guanidines. The electronic and steric effects driving the reaction will be addressed by investigating a range of silver NHCs.

EXPERIMENTAL SECTION

Instrumentation. Reagents were purchased from commercial sources and used as received. The ruthenium nitrido POM $(n\text{-Bu}_4\text{N})_4[PW_{11}O_{39}Ru^{VI}N]$ $[(n\text{-Bu}_4\text{N})_4$**1**$]$ and silver carbene $\{CH_2(Mes)N\}_2$CAgCl (**2**) were prepared as previously reported.[48,55] Unless otherwise noted, reactions were carried out under an argon atmosphere with magnetic stirring. CH_3CN was dried and distilled from CaH_2. IR spectra were recorded from KBr pellets (dilution of approximately 2% by weight) on a Bio-Rad Win-IR FTS 165 FT-IR spectrophotometer and UV−visible spectra on a Shimadzu UV-2101 spectrophotometer. The ^{31}P (121.5 MHz), ^{13}C (75.6 MHz), and ^{1}H (300 MHz) NMR spectra were obtained at 300 K in 5-mm-o.d. tubes on a Bruker Avance II 300 spectrometer equipped with a QNP probehead. The chemical shifts are given with respect to 85% H_3PO_4 for ^{31}P NMR (measured by the substitution method) and to tetramethylsilane for ^{1}H NMR (using a nondeuterated solvent as an internal secondary reference) and ^{13}C NMR (using the solvent peaks as an internal secondary reference). CV studies were performed in an acetonitrile solution with an EG&G model 273A potentiostat, using a standard three-electrode cell. The working electrode is a glassy carbon electrode (diameter 3 mm), the reference electrode is a calomel electrode filled with a 3 M LiCl solution and equipped with a double junction, and the counter electrode is a platinum wire. The supporting electrolyte is $(n\text{-Bu}_4\text{N})PF_6$ (0.1 M), and the scan rate is 20 mV s^{-1}. All potentials are given relative to SCE. Electrospray ionization mass spectrometry (ESI-MS) spectra were recorded using an ion-trap mass spectrometer (Bruker Esquire 3000) equipped with an orthogonal ESI-MS source. Sample solutions (50 μM in acetonitrile) were injected into the ESI-MS source using a syringe pump with a flow rate of 120 μL min^{-1}. The capillary high voltage was set to 3500 V. The capillary exit and first skimmer were varied between −18.0 and −45.0 V for the former and between −8.0 and −15.0 V for the latter. X-band EPR spectroscopy was performed on a JEOL FA300 spectrometer: a quartz dewar was inserted inside the cavity for liquid-nitrogen-temperature experiments. The microwave power was set at 0.998 mW (nonsaturating conditions). XANES data were obtained at the Soleil synchrotron source, on the SAMBA beamline. The spectra were recorded at Ru K-edge (22 117 eV). Detection in transmission mode at liquid-nitrogen temperature was used for solid samples ground and pressed into a pellet. The experiments were calibrated with a foil of metallic ruthenium. After background correction, the XANES spectra were normalized at 22 230 eV. Pulsed-EPR experiments were performed at 4 K with a Bruker ELEXSYS E580 spectrometer. A spin echo is generated by a series of $\pi/2$ and π microwave pulses ($\pi/2$ and π represent the rotation angles of electron magnetization), with controlled time delays between pulses. By variation of these time delays, the echo intensity exhibits modulations at the frequencies of the hyperfine interactions. We have used the pulse sequence $\pi/2-\tau-\pi/2-t_1-\pi-t_2-\pi/2-\tau-$echo (HYperfine Sublevel CORrelation Spectroscopy, HYSCORE), whereby an echo is generated at time τ after the last $\pi/2$ pulse, with τ representing the delay between the first two $\pi/2$ pulses. The echo intensity is measured at each t_1 and t_2 value, which are varied stepwise at constant τ. This two-dimensional set of echoes gives, after Fourier transformation along t_1 and t_2, a two-dimensional HYSCORE spectrum.[66] The lengths of the $\pi/2$ and π pulses were 12 and 32 ns, respectively. A delay τ = 136 ns between the first two $\pi/2$ pulses gave the best sensitivity and resolution for the detection, with no blind-spot effect.

Synthesis of the Keggin Derivative $(n\text{-}Bu_4N)_4H[PW_{11}O_{39}Ru^{III}\{NC\{N(Mes)CH_2\}_2\}]$ [$(n\text{-}Bu_4N)_4$H3]. A solution of $(n\text{-}Bu_4N)_4$**1** (0.265 mmol, 1 g), **2** (0.530 mmol, 248 mg), and $(n\text{-}Bu_4N)$I (1 mmol, 783 mg) in acetonitrile (20 mL) was stirred under argon at room temperature for 16 h. Solvent was removed under vacuum, and the residue was taken up in chloroform (50 mL). After water (50 mL) was added to the now dark solution, the organic layer was separated and washed two times with 20 mL of water. Evaporation under vacuum afforded $(n\text{-}Bu_4N)_4$H**3** (1.07 g, 95%) as a dark-brown solid. IR (KBr, cm^{-1}): ν_{max} 377 (s), 491 (m), 515 (m), 589 (w), 655 (w), 799 (vs), 879 (s), 955 (s), 1043 (m), 1077 (m), 1104 (w), 1153 (w), 1267 (w), 1269 (w), 1311 (w), 1365 (w), 1382 (m), 1484 (m), 1509 (m), 2874 (s), 2935 (s), 2962 (s). UV−vis (λ_{max}, CH_3CN): 380 nm. ^{31}P NMR (121.5 MHz, CD_3CN, short delay pulse program): δ −21 ($\Delta\nu_{1/2}$ = 150 Hz). ^{1}H NMR (300 MHz, CD_3CN): δ −1.0 ($\delta\nu_{1/2}$ = 40 Hz), 1.0 (t, $(CH_3(CH_2)_3)_4N^+$), 1.4 (m, $(CH_3CH_2\text{-}(CH_2)_2)_4N^+$), 1.7 (m, $(CH_3CH_2CH_2CH_2)_4N^+$), 3.2 (m, $(CH_3\text{-}(CH_2)_2CH_2)_4N^+$), 5.8 ($\delta\nu_{1/2}$ = 100 Hz), 7.3 ($\delta\nu_{1/2}$ = 50 Hz), 10.5 ($\delta\nu_{1/2}$ = 40 Hz) broad peaks due to paramagnetism of the species. ESI-MS: m/z (Da) 1033 ($\{H_2[PW_{11}O_{39}Ru\{NC(NMes)_2\}]\}^{3-}$), 1671 ($\{H_2TBA[PW_{11}O_{39}Ru\{NC(NMes)_2\}]\}^{2-}$). RPE: g_1 = 2.44, g_2 = 2.25, g_3 = 1.66. Anal. Calcd for $C_{85}H_{171}N_7P_1Ru_1W_{11}O_{39}$: C, 25.09; H, 4.24; N, 2.41; P, 0.76; Ru, 2.48; W, 49.68. Found: C, 24.80; H, 4.23; N, 2.45; P, 0.76; Ru, 2.35; W, 51.10.

Synthesis of the Guanidine Derivative $\{CH_2(Mes)N\}_2CNH_2PF_6$ (5PF_6). To a stirred solution of $(n\text{-}Bu_4N)_4$H**3** (0.262 mmol, 1.07 g) in dichloromethane (25 mL) was added 1 M aqueous HCl (25 mL). The mixture was stirred at room temperature for 2 h and then taken to dryness under vacuum. The dark residue was extracted with $CHCl_3$ (25 mL). A remaining brown solid, subsequently identified as $(n\text{-}Bu_4N)_4[PW_{11}O_{39}Ru^{III}(OH_2)]$ by ^{31}P NMR (δ = −70 ppm, $\Delta\nu_{1/2}$ = 1000 Hz; see refs 59 and63), was removed by filtration. Then the filtrate was washed several times with 1 M aqueous NH_4PF_6. After the organic phase had been concentrated down to 2 mL, diethyl ether was added until the mixture had started to become cloudy. This mixture was gently heated at 50 °C until it was limpid, and then it was allowed to crystallize at −14 °C. According to ^{31}P NMR, compound **3** has totally disappeared, but ^{1}H NMR revealed contamination of guanidinium chloride with $(n\text{-}Bu_4N)$Cl. Upon repeated recrystallization from chloroform, 5PF_6 was obtained, almost free of tetrabutylammonium. IR (KBr, cm^{-1}): ν_{max} 349 (w), 398 (w), 427 (m), 500 (w), 554 (vs), 738 (m), 830 (vs), 880 (m), 1036 (w), 1150 (w), 1233 (m), 1264 (m), 1302 (m),1588 (s), 1612 (s), 1635 (m), 1656 (m), 3352(w), 3490(w). ^{1}H NMR (300 MHz, CD_3CN): δ 2.34 (s, 12H), 2.38 (s, 6H), 4.16 (s, 4H), 7.14 (s, 4H), 1.0 (t, $(CH_3(CH_2)_3)_4N^+$), 1.4 (m, $(CH_3CH_2(CH_2)_2)_4N^+$), 1.7 (m, $(CH_3CH_2CH_2CH_2)_4N^+$), 3.2 (m, $(CH_3(CH_2)_2CH_2)_4N^+$) for a $(n\text{-}Bu_4N)^+$ cation. ^{13}C NMR (75.6 MHz, CD_3CN): δ 17.6 (4C), 21.2 (2C), 48.6 (2C), 130.8, 130.8, 138.2, 141.6, 156.8. HR-MS. Calcd for $C_{21}H_{28}N_3^+$: 322.22777. Found: 322.22754. In agreement with the relative intensities on the ^{1}H NMR spectrum, microanalysis was based on the formula 5$PF_6\cdot 0.5(n\text{-}Bu_4N)PF_6$. Anal. Calcd for $C_{29}H_{46}F_9N_{3.5}P_{1.5}$: C, 52.68; H, 7.02; N, 7.42; P, 7.03. Found: C, 53.00; H, 7.24; N, 6.43; P, 7.05.

■ ASSOCIATED CONTENT

Supporting Information. IR and ^{1}H and ^{31}P NMR spectra of $(n\text{-}Bu_4N)_4$H**3** and IR, ^{1}H and ^{13}C NMR, and HR-MS spectra of $\{CH_2(Mes)N\}_2CNH_2PF_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

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