As redox non-innocent ligand, the bipyridine ligand is generally involved in the reduction mechanisms. It is thus tempting to replace it by other redox non-innocent ligands such as vacant polyoxometalates (POMs). We have thus prepared \([\kappa^2\text{H}_2\text{PW}_{11}\text{O}_{39}\{\text{Rh}^{III}\text{Cp}^*(\text{OH}_2)\}]^{3-}\) which is closely related to \([\text{Cp}^*\text{Rh}^{III}(\text{bpy})\text{Cl}]^+\) by substitution of the monovacant \([\text{PW}_{11}\text{O}_{39}]^{7-}\) Keggin-type POM for the bipyridine ligand. Its activity towards CO2 reduction has been assessed in acetonitrile in the presence of water. Compared to \([\text{Cp}^*\text{Rh}^{III}(\text{bpy})\text{Cl}]^+\) that produces formate selectively over CO and H2, the POM derived catalyst favors proton reduction over CO2 reduction.

### Abstract
Storage of electricity produced intermittently by renewable energy sources is a societal issue. Besides the use of batteries and supercapacitors, conversion of excess electricity into chemical energy is also actively investigated. The conversion of CO2 to fuel or fuel precursors is an option that requires the use of a catalyst to overcome the high activation energy barrier. Of molecular catalysts, metal complexes with polypyridyl ligands are well represented, among which the \([\text{Cp}^*\text{Rh}^{III}(\text{bpy})\text{Cl}]^+\) and \([\text{M}(\text{bpy})(\text{CO})_3\text{X}]\) (M = Re, Mn) complexes. As redox non-innocent ligand, the bipyridine ligand is generally available on the WWW under https://doi.org/10.1002/ejic.201800454.

### Introduction

While fossil energy still remains predominant, its impact on the environment, especially due to the emission of the greenhouse gas CO2, has led to the development of alternative approaches (solar, wind,…) and their increase in the energy mix.[1] However, renewable energy sources is a societal issue. Besides the use of a catalyst to overcome the high activation energy barrier. Of molecular catalysts, metal complexes with polypyridyl ligands are well represented, among which the \([\text{Cp}^*\text{Rh}^{III}(\text{bpy})\text{Cl}]^+\) and \([\text{M}(\text{bpy})(\text{CO})_3\text{X}]\) (M = Re, Mn) complexes. As redox non-innocent ligand, the bipyridine ligand is generally available on the WWW under https://doi.org/10.1002/ejic.201800454.

The reduction of CO2 is a multiproton/multielectron process that can lead to a variety of products, with dihydrogen being the main side product.[7] Molecular catalysts that produce CO are by far the most abundant.[6,8] Careful analysis of the reaction pathways has led to molecular tuning of these catalysts for improved performances. For example, increasing the steric hindrance around the catalyst enhanced the catalytic rate by two orders of magnitude in the \([\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]\) family,[9,10] while dimeric Pd-triphosphine complexes allowed for cooperativity between the metal centers.[11] Tuning the second sphere interactions (protons relays,[12,13] electrostatic stabilization,[14]…) in iron porphyrin complexes has recently led to a water soluble catalyst with high turnover frequency (TOF) and low overpotential,[15] allowing the coupling of a model electrolyzer to a photovoltaic panel.[16] However, the use of CO as a fuel source requires further transformation, and usually its combination with H2 to generate hydrocarbons via the Fisher–Tropsch process is proposed. Reduction of CO2 to formic acid/formate represents an appealing alternative.[17] Formic acid is a liquid that can be either thought of as a source of protons and electrons for a fuel cell or as a high density hydrogen storage unit,[18] but is also a commodity chemical. While early on the selectivity of some molecular catalysts has been reported to be partially shifted from CO to HCOOH,[19–21] recent reports of catalyst truly selective for formate have appeared in the literature.[22,23] Molecular catalysts that go beyond the two electron reduction of CO2 are even scarcer.[24,25]

Polyoxometalates (POMs) are oxo clusters of early transition metals in high oxidation states (typically WVI, MoVI, etc.) often thought of as molecular oxides. They display a great diversity in shape, size, charge and properties and have thus found numerous applications, from catalysis[26] to material science[27–30] or biochemical applications.[31–33] Most relevant here, some POMs display remarkable redox properties, and have in particular been shown to promote the electrocatalytic reduction of protons,[34,35] and even the multielectron/multiproton reduction of nitrite, or more seldom nitrate, to ammonia.[36–40] Surprisingly, only a few reports of CO2 reduction with POMs exists:
while in 1990 Yamase proposed the photoreduction in water of CO₂ to CH₄ catalyzed by [PTi₂W₁₀O₄₀]⁷⁻.[41] Neumann published more recently that [RuSiW₁₁O₃₉]⁵⁻ promotes the photoreduction of CO₂ to CO in toluene.[42] Following Kozik’s work,[43,44] we have reported that [CoSiW₁₁O₃₉]⁶⁻ is an electrocatalyst in dichloromethane for the two electron reduction of carbon dioxide to CO, but also, in the presence of acid, to a very seldom observed four electron reduction product, formaldehyde.[45] Besides being the catalytic species,[46] another role for the POM as an electron/proton relay has also been recently proposed.[47–49]

Besides the necessity to work in a non-coordinating apolar solvent such as dichloromethane, another drawback of [CoSiW₁₁O₃₉]⁶⁻ as an electrocatalyst for CO₂ reduction is its low activity.[45] To move forward, we aimed at investigating the association of the POM properties with those of a known catalyst, preferably in more “classical” solvents like acetonitrile or even water. Numerous examples of organometallic derivatives of POMs were described in the literature.[50–56] For example, some of us have discussed the reaction between [Ru(arene)Cl₂]²⁺ and the monovacant POM [PW₁₁O₃₉]⁷⁻ and described the [PW₁₁O₃₉[Ru(arene)(H₂O)]⁵⁻ and ([PW₁₁O₃₉[Ru(arene)]⁵⁻[WO₃]⁵⁻ derivatives.[57] Interestingly, in these complexes, the monovacant POM acts only as a bidentate ligand, leaving an exchangeable coordination site on the Ru center. Reasoning that the [Cp*RhCl(μ-Cl)]²⁺ precursor should have a quite similar reactivity, we have thus investigated the grafting of a {Cp*Rh(III)}²⁺ fragment on the monovacant [PW₁₁O₃₉]⁷⁻ anion, in order to compare the reactivity of the so formed organometallic derivative with that of [Cp*Rh(μ-Cl)]²⁺, a known CO₂ reduction catalyst that produces formate selectively over CO and H₂.[19,58,59] Indeed, addition of TBANO₃ in an NMR tube containing a solution of (TBA)₃[H₂PW₁₁O₃₉[Rh(III)CP*(OH₂))] in d³-MeCN leads to a variation of the chemical shift of the methyl of the Cp* ligand (from 1.77 ppm to 1.82 ppm), likely resulting from the exchange of a water molecule for NO₃⁻ on the Rh(III) center (see Figure 2).

Figure 1. Part of the FTIR spectra of (TBA)₃[H₂PW₁₁O₃₉[Rh(III)CP*(OH₂)]) (curve I, black), monovacant POM precursor (curve II, blue) and (RhCp*Cl₂)₂ precursor (curve III, green).

Results and Discussion

Synthesis and Characterization of (TBA)₃[H₂PW₁₁O₃₉[Rh(III)CP*(OH₂)])

Addition under inert atmosphere of a freshly prepared yellow solution of [Cp*Rh(CHR=CHR)₃][BF₄]₂ in dichloromethane to a solution of (TBA)₃[H₂PW₁₁O₃₉] in dichloromethane in the presence of triethylamine yields an orange solution (TBA stands for the tetra-n-butylammonium cation and Cp* for the pentamethyl-cyclopentadienyl anion). After one night, its ³¹P NMR spectrum shows a single new peak at δ = –12.24 ppm, with complete consumption of the starting vacant POM at δ = –11.50 ppm (Figure S1). Upon treatment, (TBA)₃[H₂PW₁₁O₃₉[Rh(III)CP*(OH₂)])·H₂O is recovered as an orange powder (Scheme 1), as confirmed by its elemental analysis and mass spectrometry (Figure S4). The number of water molecules was determined by thermogravimetric analysis (Figure S5), while the ratio of TBA/Cp* is confirmed by the relative integration of the methyl protons of the Cp* ligand compared to those of the TBA⁺ cation on the ¹H NMR spectrum (Figure S2). Indeed, this study will also allow the comparison between the POM and bipyridine as redox non-innocent ligands.

Scheme 1. Synthesis of the organometallic derivative [α-H₂PW₁₁O₃₉[RhCp*(OH₂)]][BF₄]_2. (the POM skeleton is displayed in polyhedral representation).
Figure 2. Part of the $^1$H NMR spectrum of (TBA)$_3$[H$_2$PW$_{11}$O$_{39}${RhIIICp*(OH$_2$)}] in d$_3$-MeCN (top) and its evolution upon TBANO$_3$ addition (bottom).

Electrochemical Experiments

The redox properties of (TBA)$_3$[α-H$_2$PW$_{11}$O$_{39}${RhIIICp*(OH$_2$)}] have been assessed by cyclic voltammetry in acetonitrile, using TBABF$_4$ as a supporting electrolyte. All potentials are given vs. a calomel electrode in 1M LiCl solution (0.28 V/NHE) as a reference.

The electrochemical behavior of (TBA)$_3$[α-H$_2$PW$_{11}$O$_{39}$−{RhIIICp*(OH$_2$)}] under argon is rather complex, as displayed on Figure 3 (curve I). Several reduction processes are observed between –0.5 V and –2 V, some of them being irreversible. This is however not surprising, as we can expect the superposition of both POM-based and [Cp*Rh$^{III}$]$^{2+}$ reduction processes. Indeed, electrochemical studies of transition metal substituted POMs [MPW$_{11}$O$_{39}$]$^{5-}$ (M = Ni$^{II}$, Co$^{III}$) in acetonitrile have shown a first W-based reduction process around –1.15 V and a second around –1.8 V,$^{[61]}$ while those of [Cp*Rh$^{III}$(bpy)Cl]$^{+}$ led to pseudo-reversible redox processes at –0.82 V and –2.23 V (Figure S7).$^{[19]}$ Moreover, the cyclic voltammograms of both [MPW$_{11}$O$_{39}$]$^{5-}$ and [Cp*Rh$^{III}$(bpy)Cl]$^{+}$ are modified in the presence of added protons, the latter with irreversible processes due to the formation of a Cp*Rh-hydride intermediate.$^{[19]}$ As the [H$_2$PW$_{11}$O$_{39}${RhIIICp*(OH$_2$)}]$^{3-}$ species is itself a potential source of protons, it does further complicate the redox signature. Thus, the complete attribution of the electrochemical response appears quite challenging and is beyond the scope of this study. More relevant here is the evolution of the electrochemical signature in the presence of water, CO$_2$ or both.

Upon addition of 0 to 10 % of water (w/v CH$_3$CN) under argon, there is an overall shift of the wave’s potentials toward less negative values, together with an increase of intensity (Figure 3 curves II–IV). In particular, there is a large increase of the intensity of the most negative waves (below –1.25 V), which could either originate from a facilitation of the POM skeleton reduction upon protonation, or from catalytic proton reduction. Controlled potential electrolysis of a 0.5 mM solution of (TBA)$_3$[H$_2$PW$_{11}$O$_{39}${RhIIICp*(OH$_2$)}] in acetonitrile performed at –1.8 V in the presence of 5 % of water led to the detection, after 90 min of electrolysis, of an amount of H$_2$ corresponding to 0.33 TON (3.3 10$^{-6}$ mol of H$_2$), however with a low faradic yield (10 %). During the course of electrolysis, the solution progressively turned blue: this color is characteristic of partially reduced POMs, originating from intervalence charge-transfer bands between W$^V$ and W$^VI$,$^{[62]}$ thus confirming that part of the electrons are indeed used to reduce the POMs.

Replacing Ar with CO$_2$ essentially leads to an increase in the electrochemical response below –1.5 V, suggesting an interaction between CO$_2$ and the reduced complex. Upon addition of up to 5 % water, the redox processes below –1.25 V again gain in intensity and appear to be shifted toward less reducing potentials (Figure 4). We thus performed an electrolysis at –1.6 V (performing the electrolysis at –1.4 V resulted in very weak activity, while at –1.8 V only H$_2$ could be detected) in the presence of 5 % water under a CO$_2$ atmosphere. The experiment led, after 5 h electrolysis, to the detection of H$_2$ as a major product (120 10$^{-6}$ mol, 12 TON, 68 % faradic yield) with HCOO$^-$ as a very minor reduction product (8 10$^{-6}$ mol, 0.8 TON, 4.5 % faradic yield). Again, upon reduction, the solution turned blue, indicating that some of electrical charge is used to reduce the POM skeleton, which can partly explain the lower global faradic yield, together with the formation of other, still unidentified, reduction products. As a point of comparison, we performed the same experiment with [Cp*Rh$^{III}$(bpy)Cl]$^{+}$. In our conditions, the latter led to the generation of HCOO$^-$ (180 10$^{-6}$ mol, 18 TON, 60 % faradic yield) as a major product, together with H$_2$ (90 10$^{-6}$ mol, 9 TON, 30 % faradic yield). Thus, replacing the bidentate bipyridine with a bidentate POM allows for a large...
reversal of the selectivity of the [Cp*RhL2(L-L)Cl]+ molecular catalyst (L-L = bpy, n = 2, or L-L = POM, n = 5) in favor of proton reduction over CO2.

Figure 4. Comparison of cyclic voltammograms at a glassy carbon electrode at a scan rate of 100 mV s−1 in acetonitrile +0.1 M TBAF4 of a 1 mM solution of (TBA)3 α-H2PW11O39{RhIIICp*(H2O)} under argon (curve I) and CO2 (curve II), after addition of 1 % volume of water (curve III) and 5 % volume of water (curve IV); E(V vs. Hg2Cl2/Hg, 1 M LiCl).

The active species proposed in the electro-assisted reduction of CO2 by [Cp*RhL2(bpy)Cl]+ is a hydride obtained after the two-electron reduction of the RhIII center and subsequent protonation,[19,63] the following step being the reduction of the bpy ligand, preceding the incorporation of CO2. In the case of [H2PW11O39L(RhIIICp*(OH2))]3–, the protonation will also occur at the reduced POM, which could explain the change in selectivity of the reaction.

Metal complexes with poly(pyridyl) ligands are with complexes of macrocyclic ligands among the most studied molecular electrocatalysts for CO2 reduction.[64] Since the early reports on [Mbpy](CO)3X (M = Re)[65] Mn[9]) many variations on the bpy ligand have been devised to assess steric effects[10,66] or the effects on the catalytic activity of a phenolic proton.[67,68] a charge[69] or a pendant Lewis base[70] in close proximity of the CO2 binding site. Enhancement of the catalytic efficiency is generally observed, significant for bulky ligands that hinder dimerization, often modest in the other cases. The electronic effects of electron-donating or electron-withdrawing substituents on the bpy ligand are still unclear.[66,71] In an example closely related to this study, complexes [Cp*Ir(bpy-R,R)Cl]+ prepared with various unsymmetrically substituted bipyridine ligands were found to have a moderate electrocatalytic activity in CO2 reduction[72] but with no direct correlation between the redox potentials and the catalytic activity. Regarding the replacement of the bpy ligand by another redox non-innocent ligand, rationalization is still missing: none of the [Re(N′N)(CO)3X] complexes with N′N being 2-pyridyl-1,2,3-triazole ligand was found to outperform the benchmark catalyst [Re(bpy)(CO)3X][73] whereas a Re-pyridyl-NHC species displays a slightly higher faradic efficiency[74] and some Re-pyridine-oxazolines higher TOF but decreased faradic efficiency[75] [Mn(N′N)(CO)3X] where N′N stands for iminopyridines[76] or cyclics[77] do catalyze the conversion of CO2 to CO and CO2 but at the cost of an increased overpotential. These examples underline that more structure-activity relationships studies are needed to improve our understanding of the relevant parameters and to find a good balance between decreasing the overpotential and keeping sufficient reducing power in the redox non-innocent ligand.[78] From this point of view, vacant POMs with tunable redox properties still deserve attention as unconventional redox non-innocent ligands.

Conclusions

In this paper, we have described the synthesis of a new organometallic derivative of POMs, (TBA)3[α-H2PW11O39 {RhIIICp*(OH2)}], presenting an accessible coordination site on the RhIII center. The electrochemical response in acetonitrile of [α-H2PW11O39{RhIIICp*(OH2)}]3– is complex, exhibiting several reduction processes. This electrochemical behavior was modified in the presence of CO2, strongly suggesting some interaction with the POM derivative despite the presence of a coordinating solvent, a clear improvement compared to [CoSiW11O39]6–. However, electro-assisted reduction of CO2 in the presence of water as a proton source mainly led to the catalytic formation of dihydrogen, with formate being a minor product.

Experimental Section

Chemicals: Analytical grade solvents were purchased from Sigma–Aldrich. Dichloromethane and acetonitrile were distilled from calcium hydride under argon. Tetrabutylammonium hydrogensulfate (TBAH2SO4, 97 %) and trifluoroacetic acid (TFA) were purchased from Sigma–Aldrich, Tetrabutylammonium hydroxide (TBAOH/MeOH, 40 wt-%), Tetrabutylammonium bromide (TBABr), Tetrabutylammonium nitrate (TBAONO3 and sodium tetrafluoroborate (NaBF4, 97 %) were supplied by Alpha-Aesar. 1,2,3,4,5-Pentamethylcyclopentadiene was provided by Acros Laboratories. [RhCp*Cl(μ-Cl)]2 and [RhCp*Cl(bpy)Cl]+ were synthesized according to literature procedures.[79,80] Tetrabutylammonium tetrafluoroborate (TBAF4) was prepared by mixing 200 mL of 1.3 M NaBF3 with 200 mL of 1 M TBAH2SO4 in water under vigorous stirring. A white precipitate was formed and additional water (about 400 mL) was added. The precipitate was filtered through a frit and washed until wastewater reached a pH of ca. 5. The white powder was redissolved in dichloromethane and dried with MgSO4. The organic phase was filtered and finally evaporated under vacuum to get a white powder stored under argon.

Analytical Methods: FTIR spectra were recorded from KBr pellets on a JASCO FTIR 4100 spectrometer. The spectra were recorded with 16 scans with an accuracy of 4 cm−1. UV/Visible spectra were recorded on Jasco V-670, using quartz cell. $^1$H, $^{13}$C, and $^{31}$P NMR spectra were recorded on a Bruker Advance II 300 MHz. $^1$H and $^{13}$C NMR signals were referenced to the residual solvent signals and
are given relative to (CH₃)₃Si. ³¹P NMR is referenced relative to H₃PO₄ (85 %). Elemental analyses were performed at ICSN-CNRS (Gif-sur-Yvette, France). Thermogravimetric analyses were performed on a TA-Instrument SDT Q600 under dry air. The high resolution ESI mass spectra were recorded using an LTQ Orbitrap hybrid mass spectrometer (Thermofisher Scientific, Bremen, Germany) equipped with an external ESI source operated in the negative ion mode.

**Synthesis of (TBA)₃[α-H₂PW₁₄O₃₉]**: (TBA)₄[α-H₂PW₁₄O₃₉] was prepared according to the literature²¹ and the synthesis of (TBA)₄[α-H₂PW₁₄O₃₉] was adapted from literature as follows:²² (TBA)₄[α-H₂PW₁₄O₃₉] (2.45 g; 0.636 mmol) was dissolved in acetonitrile (50 mL) (any insoluble product was filtered off) and 363 μL of TBAOH/MeOH (40 wt.-%, 0.636 mmol, 1 equiv.) was added dropwise with vigorous stirring. The resulting solution was concentrated to 20 mL and 30 mL of diethyl ether were added. A first white precipitate, containing (TBA)₄[α-H₂PW₁₄O₃₉] was recovered by centrifugation and discarded. An additional 100 mL of diethyl ether was added to the solution, leading to precipitation of a white powder, which was recovered by filtration, rinsed thoroughly with diethyl ether and dried under vacuum. Yield: 1.80 g (69 %) ³¹P NMR (300 MHz, CD₃CN, 20 °C): δ = -11.50 ppm.

**Synthesis of (TBA)₄[α-H₂PW₁₄O₃₉][RhIIICp*(H₂O)]·H₂O**: 103 mg (166 μmol, 0.66 equiv.) of [(RhCp*Cl₂)₂] and 129 mg (662 μmol, 2.1 equiv.) in 250 mL of dichloromethane. The resulting orange solution was stirred under argon overnight. A diluted solution of TFA in dichloromethane (2.1 equiv., 6 mL in the anodic compartment) was added to the solution, leading to precipitation of a white powder, which was recovered by filtration, rinsed thoroughly with diethyl ether and dried under vacuum. Yellow: 1.80 g (69 %) ³¹P NMR (300 MHz, CD₃CN, 20 °C): δ = -11.50 ppm.

**Electrochemical Experiments**: Analytical experiments were carried out with a Princeton Applied Research Potentiostat (Model 263A). The studies were performed using a classical three-electrodes cell. Acetonitrile containing TBAFB₄ (0.1M) was used as electrolytic solution. All studied solutions were purged prior measurements by bubbling inert gas or CO₂ for 10 min for cyclic voltammetry (CV) or 20 min for electrolysis prior measurements, the gas being before-hand bubbled in acetonitrile so as to limit solvent evaporation. Cyclic voltammetry was performed at a scan rate of 100 mV/s. A glassy carbon electrode (3 mm diameter) was used as working electrode, polished with a 1/4μm diamond suspension. The counter electrode was a platinum wire and a Calomel (1 M LiCl) electrode separated by a Vycor tip was used as reference (Radiometer Analytical, France).

Bulk electrolysis experiments were carried out in a custom made two-compartment cell. A glassy carbon electrode (13 mm diameter, Oragyl) was used as the working electrode and a Calomel 1M LiCl reference electrode (Radiometer Analytical, France) was separated by a Vycor tip. The counter electrode used was a platinum wire separated from the working electrode by a frit (porosity 4). The volume of the solution used in the cathodic compartment was 20 mL (6 mL in the anodic compartment) and the typical headspace volume was 46 mL. Saint-Gobain Performance Plastics France natural rubber folding skirt stoppers were used to close the cell. A BioLogic SP 300 potentiostat connected to a booster card was used. Solutions were constantly stirred throughout bulk electrolysis experiments.

**Analysis of Electrolysis Products**: H₂ measurements were performed by gas chromatography on a Shimadzu GC-2014 equipped with a Quadrex column, a Thermal Conductivity Detector and using N₂ as a carrier gas. Other gases (CO, CH₄) were measured using a Shimadzu GC-2010 Plus gas chromatography, fitted with a Restek Shin Carbon column, helium carrier gas, a methanizer and a Flame Ionization Detector. Gas chromatography calibrations were made by sampling known volumes of the various gases. The typical volume of gas injected was 50 μL.

Formate and oxalate concentrations were determined by ion chromatography using a Metrohm 883 Basic IC plus ionic exchange chromatography instrument, a Metrosep A Supp 5 column and a conductivity detector. A typical measurement required the sampling of 1 mL of solution, followed by a 100 fold dilution in deionized 18 MΩ cm⁻¹ water and direct injection of 20 μL into the instrument.

Methanol was assessed using a Shimadzu GC-2010 Plus gas chromatography fitted with a ZB-WAX Plus column, helium as a carrier gas and a flame ionization detector.

Formaldehyde concentration was assessed using the Nash colorimetric test using a V-670 Jasco Spectrophotometer instrument.

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