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## Assessing the Electrocatalytic Properties of the Cp\*Rh III 2+ -Polyoxometalate Derivative [H 2 PW 11 O 39 Rh III Cp\*(OH 2 )] 3- towards CO 2 Reduction

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## Accepted Article

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# Assessing the electrocatalytic properties of the $\{\text{Cp}^*\text{Rh(III)}\}^{2+}$ -Polyoxometalate derivative $[\text{H}_2\text{PW}_{11}\text{O}_{39}\{\text{Rh(III)Cp}^*(\text{OH}_2)\}]^{3-}$ towards $\text{CO}_2$ reduction

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**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  $\text{CO}_2$  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  $[\text{Cp}^*\text{Rh}(\text{bpy})\text{Cl}]^+$  and  $[\text{M}(\text{bpy})(\text{CO})_3\text{X}]$  ( $\text{M} = \text{Re}, \text{Mn}$ ) complexes. 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  $[\alpha\text{-H}_2\text{PW}_{11}\text{O}_{39}\{\text{Rh(III)Cp}^*(\text{OH}_2)\}]^{3-}$  which is closely related to  $[\text{Cp}^*\text{Rh(III)(bpy)Cl}]^+$  by substitution of the monovacant  $[\text{PW}_{11}\text{O}_{39}]^{7-}$  Keggin-type POM for the bipyridine ligand. Its activity towards  $\text{CO}_2$  reduction has been assessed in acetonitrile in the presence of water. Compared to  $[\text{Cp}^*\text{Rh}(\text{bpy})\text{Cl}]^+$  that produces formate selectively over  $\text{CO}$  and  $\text{H}_2$ , the POM derived catalyst favours proton reduction over  $\text{CO}_2$  reduction.

## Introduction

While fossil energy still remains predominant, its impact on the environment, especially due to the emission of the greenhouse gas  $\text{CO}_2$ , has led to the development of alternative approaches (solar, wind,..) and their increase in the energy mix.<sup>[1]</sup> However, a main drawback of these energy sources is their intermittence, and a significant challenge is the storage of the so produced electricity.<sup>[2]</sup> While electrochemical storage into batteries is an option,<sup>[3]</sup> storage within chemical bonds, offering much higher gravimetric densities, is appealing, notably for transportation purposes. Besides a possible hydrogen economy,<sup>[4]</sup> there has been a renewed interest towards  $\text{CO}_2$  reduction over the last years.<sup>[5,6]</sup>

The reduction of  $\text{CO}_2$  is a multiproton/multielectron process that can lead to a variety of

products, with dihydrogen being the main side product.<sup>[7]</sup> Molecular catalysts that produce CO are by far the most abundant.<sup>[6,8]</sup> 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 [Mn(bpy)(CO)<sub>3</sub>Br] family,<sup>[9,10]</sup> while dimeric Pd-triphosphine complexes allowed for cooperativity between the metal centers.<sup>[11]</sup> Tuning the second sphere interactions (protons relays,<sup>[12,13]</sup> electrostatic stabilization,<sup>[14]</sup> ...) in iron porphyrin complexes has recently led to a water soluble catalyst with high turnover frequency (TOF) and low overpotential,<sup>[15]</sup> allowing the coupling of a model electrolyzer to a photovoltaic panel.<sup>[16]</sup> However, the use of CO as a fuel source requires further transformation, and usually its combination with H<sub>2</sub> to generate hydrocarbons via the Fisher-Tropsch process is proposed. Reduction of CO<sub>2</sub> to formic acid/formate represents an appealing alternative.<sup>[17]</sup> 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,<sup>[18]</sup> 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,<sup>[19–21]</sup> recent reports of catalyst truly selective for formate have appeared in the literature.<sup>[22,23]</sup> Molecular catalysts that go beyond the two electron reduction of CO<sub>2</sub> are even scarcer.<sup>[24,25]</sup>

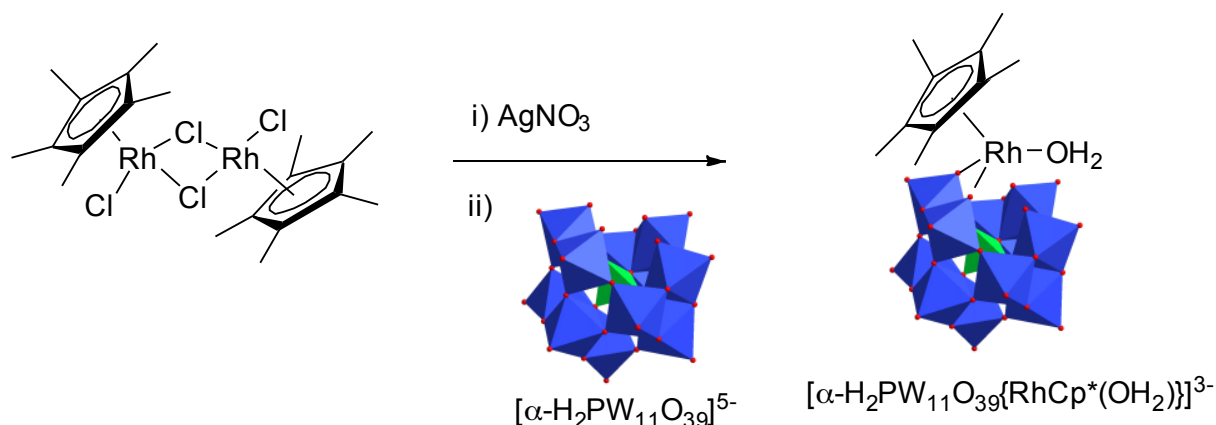
Polyoxometalates (POMs) are oxoclusters of early transition metals in high oxidation states (typically W<sup>VI</sup>, Mo<sup>VI</sup>, ...) often thought of as molecular oxides. They display a great diversity in shape, size, charge and properties and have thus found numerous applications, from catalysis<sup>[26]</sup> to material science<sup>[27–30]</sup> or biochemical applications.<sup>[31–33]</sup> Most relevant here, some POMs display remarkable redox properties, and have in particular been shown to promote the electrocatalytic reduction of protons,<sup>[34,35]</sup> and even the multielectron/multiproton reduction of nitrite, or more seldom nitrate, to ammonia.<sup>[36–40]</sup> Surprisingly, only a few reports of CO<sub>2</sub> reduction with POMs exists: while in 1990 Yamase proposed the photoreduction in water of CO<sub>2</sub> to CH<sub>4</sub> catalyzed by [PTi<sub>2</sub>W<sub>10</sub>O<sub>40</sub>]<sup>7-</sup>,<sup>[41]</sup> Neumann published more recently that [RuSiW<sub>11</sub>O<sub>39</sub>]<sup>5-</sup> promotes the photoreduction of CO<sub>2</sub> to CO in toluene.<sup>[42]</sup> Following Kozik's work,<sup>[43,44]</sup> we have reported that [CoSiW<sub>11</sub>O<sub>39</sub>]<sup>6-</sup> 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.<sup>[45]</sup> Besides being the catalytic species,<sup>[46]</sup> another role for the POM as an electron/proton relay has also been recently proposed.<sup>[47–49]</sup>

Besides the necessity to work in a non-coordinating apolar solvent such as dichloromethane, another drawback of [CoSiW<sub>11</sub>O<sub>39</sub>]<sup>6-</sup> as an electrocatalyst for CO<sub>2</sub> reduction is its low activity.<sup>[45]</sup> 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.<sup>[50–56]</sup> For example, some of us have discussed the reaction between  $[\text{Ru}(\text{arene})\text{Cl}_2]_2$  and the monovacant POM  $[\text{PW}_{11}\text{O}_{39}]^{7-}$  and described the  $[\text{PW}_{11}\text{O}_{39}\{\text{Ru}(\text{arene})(\text{H}_2\text{O})\}]^{5-}$  and  $[\{\text{PW}_{11}\text{O}_{39}\{\text{Ru}(\text{arene})\}\}_2\{\text{WO}_2\}]^{8-}$  derivatives.<sup>[57]</sup> 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  $[\text{Cp}^*\text{RhCl}(\mu\text{-Cl})_2]_2$  precursor should have a quite similar reactivity, we have thus investigated the grafting of a  $\{\text{Cp}^*\text{Rh}(\text{III})\}^{2+}$  fragment on the monovacant  $[\text{PW}_{11}\text{O}_{39}]^{7-}$  anion, in order to compare the reactivity of the so formed organometallic derivative with that of  $[\text{Cp}^*\text{Rh}(\text{III})(\text{bpy})\text{Cl}]^+$ , a known  $\text{CO}_2$  reduction catalyst that produces formate selectively over  $\text{CO}$  and  $\text{H}_2$ .<sup>[19,58,59]</sup> Indeed, this study will also allow the comparison between the POM and bipyridine as redox non-innocent ligands.

## Results and discussion

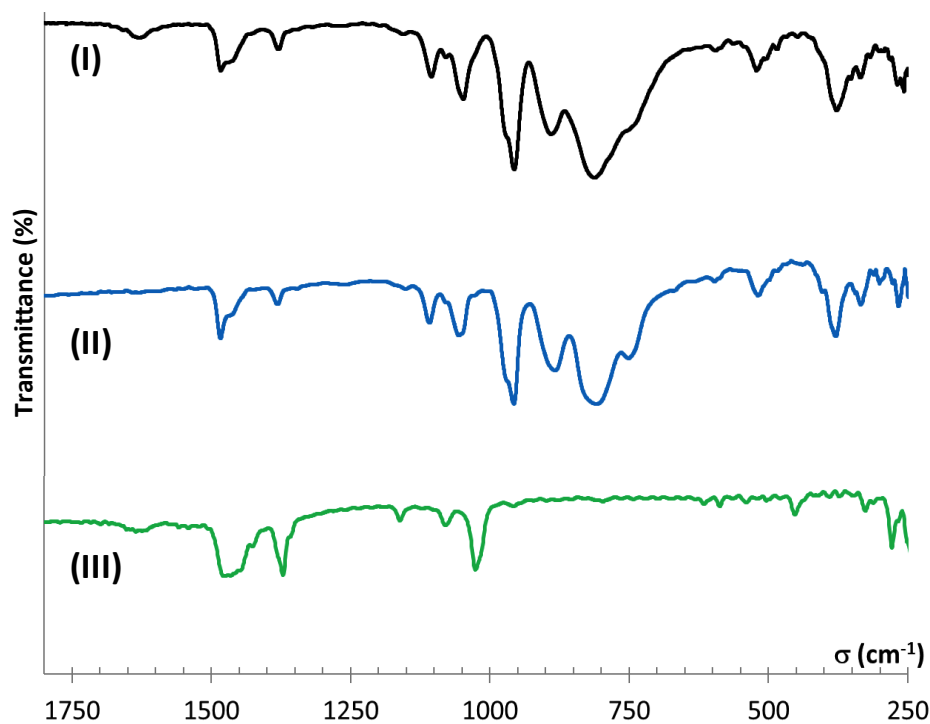
### Synthesis and characterization of $(\text{TBA})_3[\alpha\text{-H}_2\text{PW}_{11}\text{O}_{39}\{\text{Rh}(\text{III})\text{Cp}^*(\text{OH}_2)\}]^{3-}$



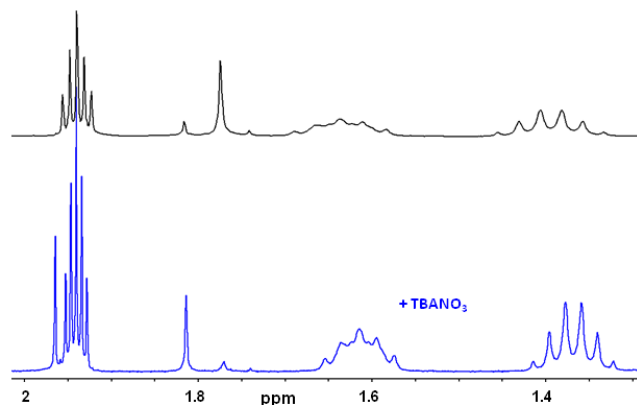
**Scheme 1.** Synthesis of the organometallic derivative  $[\alpha\text{-H}_2\text{PW}_{11}\text{O}_{39}\{\text{Rh}(\text{III})\text{Cp}^*(\text{OH}_2)\}]^{3-}$ . (the POM skeleton is displayed in polyhedral representation)

Addition under inert atmosphere of a freshly prepared yellow solution of  $[\text{Cp}^*\text{Rh}(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$  in dichloromethane to a solution of  $(\text{TBA})_5[\alpha\text{-H}_2\text{PW}_{11}\text{O}_{39}]$  in dichloromethane in the presence of triethylamine yields an orange solution (TBA stands for the tetra-*n*-butylammonium cation and  $\text{Cp}^*$  for the pentamethyl-cyclopentadienyl anion). After one night, its  $^{31}\text{P}$  NMR spectrum shows a single new peak at  $\delta = -12.24$  ppm, with complete consumption of the starting vacant POM at  $\delta = -11.50$  ppm (Figure S1). Upon treatment,  $(\text{TBA})_3[\alpha\text{-H}_2\text{PW}_{11}\text{O}_{39}\{\text{Rh}(\text{III})\text{Cp}^*(\text{OH}_2)\}]\cdot\text{H}_2\text{O}$  is recovered as an orange powder, 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/ $\text{Cp}^*$  is confirmed by the relative integration of the methyl protons of the

Cp\* ligand compared to those of the TBA<sup>+</sup> cation on the <sup>1</sup>H NMR spectrum (Figure S2). The IR spectrum of (TBA)<sub>3</sub>[α-H<sub>2</sub>PW<sub>11</sub>O<sub>39</sub>{Rh(III)Cp\*(OH<sub>2</sub>)}.H<sub>2</sub>O displays the characteristic signature of the Keggin structure. Most notably, the ν(P-O) band is still split into two components (Δσ=59 cm<sup>-1</sup>), which is quite similar to that of the starting [PW<sub>11</sub>O<sub>39</sub>]<sup>7-</sup> anion (Δσ=52 cm<sup>-1</sup>) (see Figure 1). This splitting is diagnostic of a cation partially incorporated into the lacuna of the POM.<sup>[60]</sup> We thus propose that the vacant POM acts as a bidentate ligand on the {Cp\*Rh(III)}<sup>2+</sup> moiety, leaving an accessible coordination site on the metal ion, as was previously observed for the {Ru-arene}<sup>2+</sup> derivatives.<sup>[57]</sup> Indeed, addition of TBANO<sub>3</sub> in an NMR tube containing a solution of (TBA)<sub>3</sub>[H<sub>2</sub>PW<sub>11</sub>O<sub>39</sub>{Rh(III)Cp\*(OH<sub>2</sub>)}] in d<sup>3</sup>-MeCN leads to a variation of the chemical shift of the methyl of the Cp\* ligand (from 1.77ppm to 1.82 ppm), likely resulting from the exchange of a water molecule for NO<sub>3</sub><sup>-</sup> on the Rh<sup>III</sup> center (see Figure 2).



**Figure 1.** Part of the FT-IR spectra of (TBA)<sub>3</sub>[H<sub>2</sub>PW<sub>11</sub>O<sub>39</sub>{Rh(III)Cp\*(OH<sub>2</sub>)}] (black), monovacant POM precursor (blue) and (RhCp\*Cl<sub>2</sub>)<sub>2</sub> precursor (green)

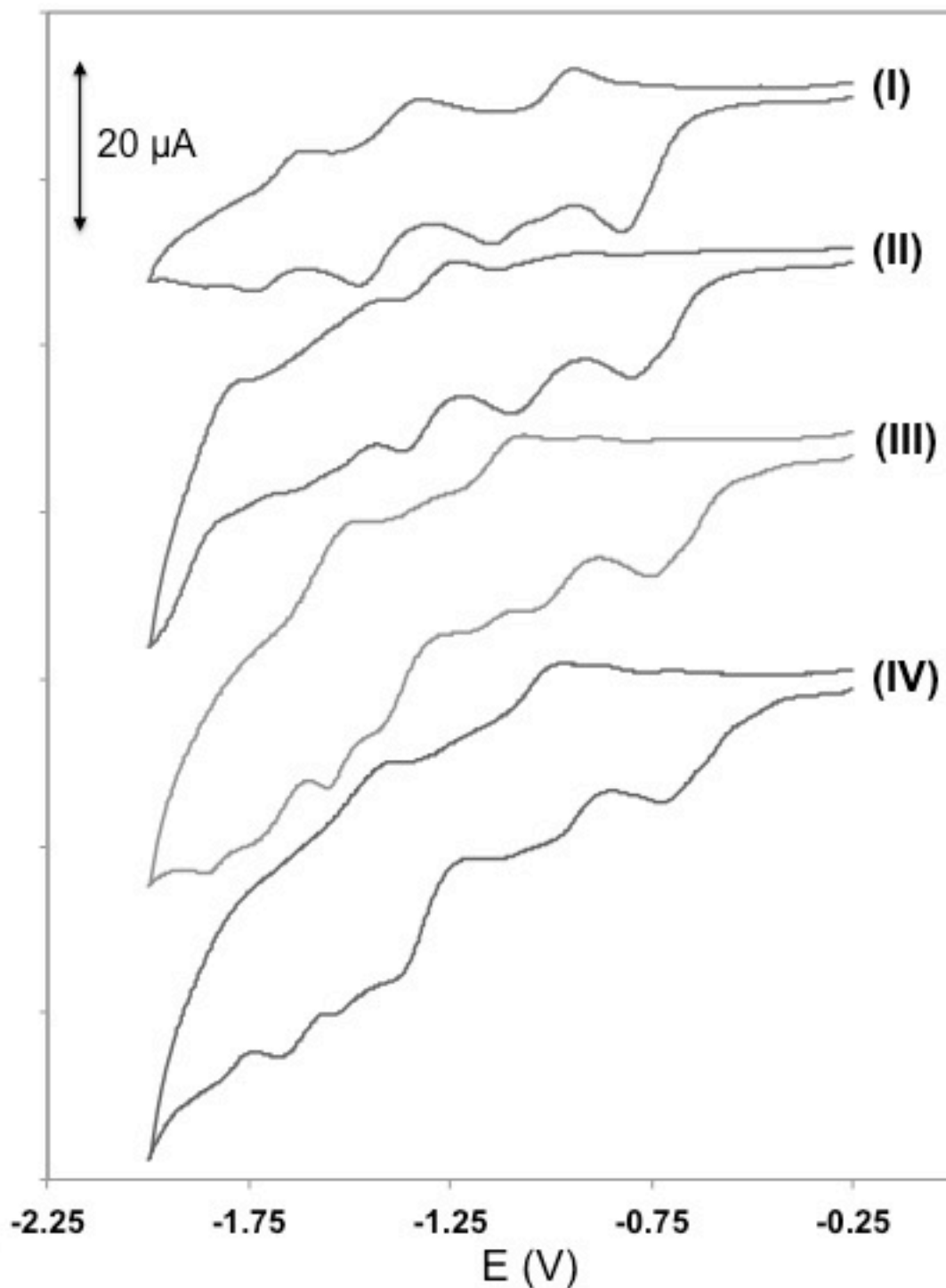


**Figure 2.** Part of the <sup>1</sup>H NMR spectrum of (TBA)<sub>3</sub>[H<sub>2</sub>PW<sub>11</sub>O<sub>39</sub>{Rh(III)Cp\*(OH<sub>2</sub>)}] in d<sup>3</sup>-MeCN (top) and its evolution upon TBANO<sub>3</sub> addition (bottom).

### Electrochemical experiments

The redox properties of (TBA)<sub>3</sub>[α-H<sub>2</sub>PW<sub>11</sub>O<sub>39</sub>{Rh(III)Cp\*(OH<sub>2</sub>)}] have been assessed by cyclic voltammetry in acetonitrile, using TBABF<sub>4</sub> as a supporting electrolyte. All potentials are given versus a calomel electrode in 1M LiCl solution (0.28V/ NHE) as a reference.

The electrochemical behavior of (TBA)<sub>3</sub>[α-H<sub>2</sub>PW<sub>11</sub>O<sub>39</sub>{Rh(III)Cp\*(OH<sub>2</sub>)}] under argon is rather complex, as displayed on Figure 3 (curve I). Several reduction processes are observed between -0.5V and -2V, some of them being irreversible. This is however not surprising, as we can expect the superposition of both POM-based and {Cp\*Rh(III)}<sup>2+</sup> reduction processes. Indeed, electrochemical studies of transition metal substituted POMs [MPW<sub>11</sub>O<sub>39</sub>]<sup>5-</sup> (M=Ni<sup>II</sup>, Co<sup>II</sup>) in acetonitrile have shown a first W-based reduction process around -1.15V and a second around -1.8V,<sup>[61]</sup> while those of [Cp\*Rh(III)(bpy)Cl]<sup>+</sup> led to pseudo-reversible redox processes at -0.82V and -2.23V (Figure S7).<sup>[19]</sup> Moreover, the cyclic voltammograms of both [MPW<sub>11</sub>O<sub>39</sub>]<sup>5-</sup> and [Cp\*Rh(III)(bpy)Cl]<sup>+</sup> are modified in the presence of added protons, the latter with irreversible processes due to the formation of a Cp\*Rh-hydride intermediate.<sup>[19]</sup> As the [H<sub>2</sub>PW<sub>11</sub>O<sub>39</sub>{Rh(III)Cp\*(OH<sub>2</sub>)}]<sup>3-</sup> 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<sub>2</sub> or both.

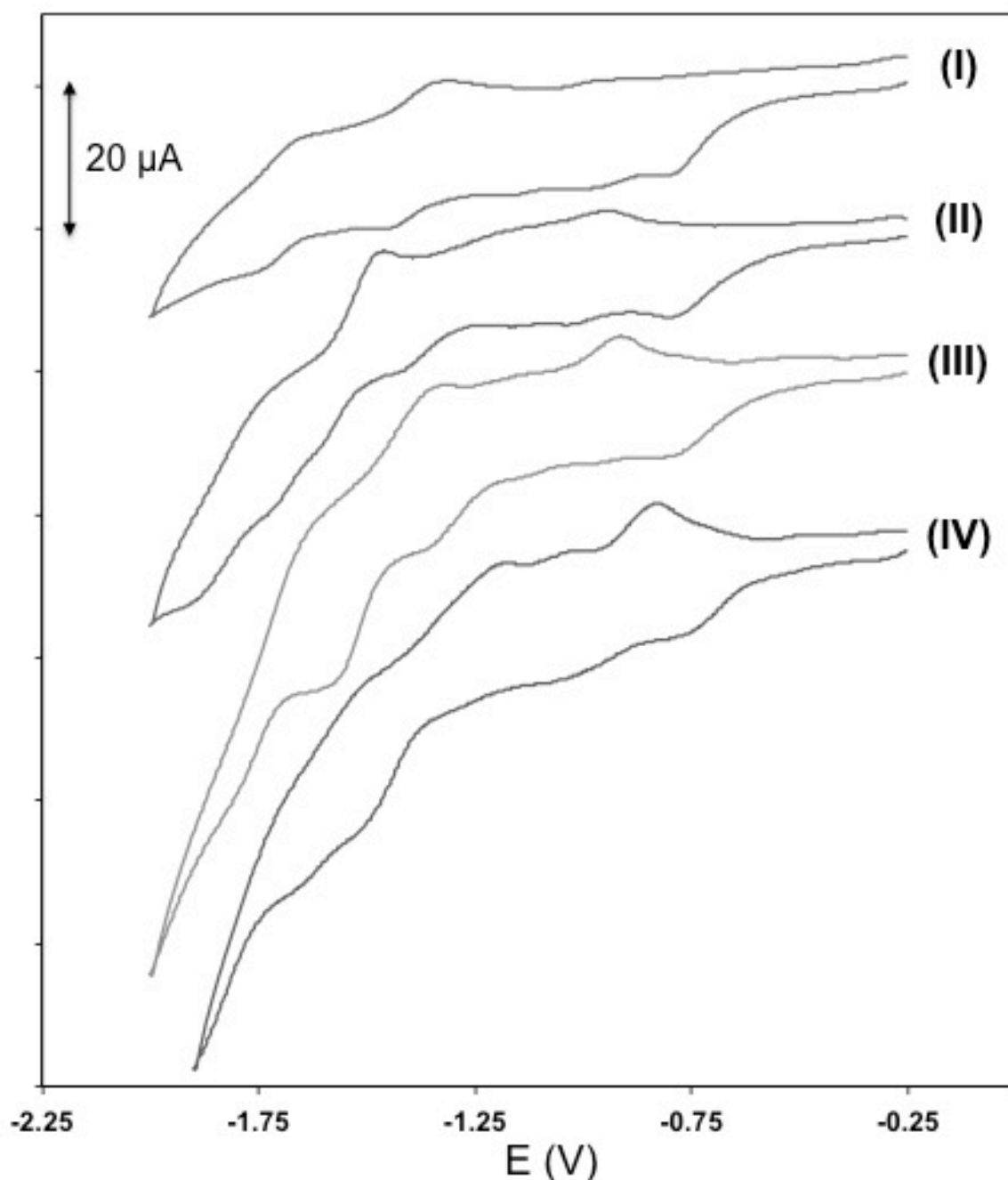


**Figure 3.** Comparison of cyclic voltammograms at a glassy carbon electrode at a scan rate of  $100 \text{ mV}\cdot\text{s}^{-1}$  in acetonitrile + 0.1 M TBABF<sub>4</sub> under argon of a 1 mM solution of (TBA)<sub>3</sub>[H<sub>2</sub>PW<sub>11</sub>O<sub>39</sub>{Rh(III)Cp\*(H<sub>2</sub>O)}] (curve I), after addition of 1% volume of water (curve II), 5% volume of water (curve III) and 10% volume of water (curve IV); E(V vs Hg<sub>2</sub>Cl<sub>2</sub>/Hg, 1M LiCl).

Upon addition of 0 to 10 % of water (v/v CH<sub>3</sub>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 -1.25V), which could either originates 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  $(\text{TBA})_3[\text{H}_2\text{PW}_{11}\text{O}_{39}\{\text{Rh}(\text{III})\text{Cp}^*(\text{OH}_2)\}]$  in acetonitrile performed at -1.8V in the presence of 5% of water led to the detection, after 90 minutes of electrolysis, of an amount of  $\text{H}_2$  corresponding to 0.33 TON ( $3.3 \cdot 10^{-6}$  mol of  $\text{H}_2$ ), 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  $\text{W}^{\text{V}}$  and  $\text{W}^{\text{VI}}$ ,<sup>[62]</sup> thus confirming that part of the electrons are indeed used to reduce the POMs.



**Figure 4.** Comparison of cyclic voltammograms at a glassy carbon electrode at a scan rate of  $100 \text{ mV}\cdot\text{s}^{-1}$  in acetonitrile + 0.1 M  $\text{TBABF}_4$  of a 1 mM solution of  $(\text{TBA})_3[\text{H}_2\text{PW}_{11}\text{O}_{39}\{\text{Rh}(\text{III})\text{Cp}^*(\text{H}_2\text{O})\}]$  under argon (curve I) and  $\text{CO}_2$  (curve II), after addition of 1% volume of water (curve III) and 5% volume of water (curve IV); E(V vs  $\text{Hg}_2\text{Cl}_2/\text{Hg}$ , 1M LiCl).

Replacing Ar with CO<sub>2</sub> essentially leads to an increase in the electrochemical response below -1.5V, suggesting an interaction between CO<sub>2</sub> and the reduced complex. Upon addition of up to 5% water, the redox processes below -1.25V again gain in intensity and appear to be shifted toward less reducing potentials (Figure 4). We thus performed an electrolysis at -1.6V\*(\* footnote: performing the electrolysis at -1.4V resulted in very weak activity, while at -1.8V only H<sub>2</sub> could be detected) in the presence of 5% water under a CO<sub>2</sub> atmosphere. The experiment led, after 5h electrolysis, to the detection of H<sub>2</sub> as a major product (120 10<sup>-6</sup> mol, 12 TON, 68 % faradic yield) with HCOO<sup>-</sup> as a very minor reduction product (8 10<sup>-6</sup> 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]<sup>+</sup>. In our conditions, the latter led to the generation of HCOO<sup>-</sup> (180 10<sup>-6</sup> mol, 18 TON, 60% faradic yield) as a major product, together with H<sub>2</sub> (90 10<sup>-6</sup> 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\*Rh(III)(L-L)]<sup>n+</sup> molecular catalyst (L-L= bpy, n=2, or L-L= POM, n=5) in favor of proton reduction over CO<sub>2</sub> reduction.

The active species proposed in the electro-assisted reduction of CO<sub>2</sub> by [Cp\*Rh(III)(bpy)Cl]<sup>+</sup> is a hydride obtained after the two-electron reduction of the Rh(III) center and subsequent protonation,<sup>[19,63]</sup> the following step being the reduction of the bpy ligand, preceding the incorporation of CO<sub>2</sub>. In the case of [H<sub>2</sub>PW<sub>11</sub>O<sub>39</sub>{Rh(III)Cp\*(OH<sub>2</sub>)}]<sup>3-</sup>, the protonation will also likely occur at the reduced POM, which could explain the change in selectivity of the reaction.

Metal complexes with polypyridyl ligands are with complexes of macrocyclic ligands among the most studied molecular electrocatalysts for CO<sub>2</sub> reduction.<sup>[64]</sup> Since the early reports on [M(bpy)(CO)<sub>3</sub>X] (M= Re,<sup>[65]</sup> Mn<sup>[9]</sup>) many variations on the bpy ligand have been devised to assess steric effects<sup>[10,66]</sup> or the effects on the catalytic activity of a phenolic proton,<sup>[67,68]</sup> a charge<sup>[69]</sup> or a pendant Lewis base<sup>[70]</sup> in close proximity of the CO<sub>2</sub> 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.<sup>[66,71]</sup> In an example closely related to this study, complexes [Cp\*Ir(bpy-R,R')Cl]<sup>+</sup> prepared with various unsymmetrically substituted bipyridine ligands were found to have a moderate electrocatalytic activity in CO<sub>2</sub> reduction<sup>[72]</sup> 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  $[\text{Re}(\text{N}^{\wedge}\text{N})(\text{CO})_3\text{X}]$  complexes with  $\text{N}^{\wedge}\text{N}$  being 2-pyridyl-1,2,3-triazole ligand was found to outperform the benchmark catalyst  $[\text{Re}(\text{bpy})(\text{CO})_3\text{X}]$ ,<sup>[73]</sup> whereas a Re-pyridyl-NHC species displays a slightly higher faradic efficiency<sup>[74]</sup> and some Re-pyridine-oxazolines higher TOF but decreased faradic efficiency,<sup>[75]</sup>  $[\text{Mn}(\text{N}^{\wedge}\text{N})(\text{CO})_3\text{X}]$  where  $\text{N}^{\wedge}\text{N}$  stands for iminopyridines<sup>[76]</sup> or  $\alpha$ -diimines<sup>[77]</sup> do catalyze the conversion of  $\text{CO}_2$  to  $\text{CO}$  and  $\text{CO}_3^{2-}$  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.<sup>[78]</sup> 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,  $(\text{TBA})_3[\alpha\text{-H}_2\text{PW}_{11}\text{O}_{39}\{\text{Rh}(\text{III})\text{Cp}^*(\text{OH}_2)\}]$ , presenting an accessible coordination site on the  $\text{Rh}^{\text{III}}$  center. The electrochemical response in acetonitrile of  $[\alpha\text{-H}_2\text{PW}_{11}\text{O}_{39}\{\text{Rh}(\text{III})\text{Cp}^*(\text{OH}_2)\}]^{3-}$  is complex, exhibiting several reduction processes. This electrochemical behavior was modified in the presence of  $\text{CO}_2$ , strongly suggesting some interaction with the POM derivative despite the presence of a coordinating solvent, a clear improvement compared to  $[\text{CoSiW}_{11}\text{O}_{39}]^{6-}$ . However, electro-assisted reduction of  $\text{CO}_2$  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 over calcium hydride under argon. Tetrabutylammonium hydrogensulfate ( $\text{TBAHSO}_4$ , 97%) and trifluoroacetic acid (TFA) were purchased from Sigma-Aldrich, Tetrabutylammonium hydroxide ( $\text{TBAOH}/\text{MeOH}$ , 40 wt%), Tetrabutylammonium bromide (TBABr), Tetrabutylammonium nitrate ( $\text{TBANO}_3$ ) and sodium tetrafluoroborate ( $\text{NaBF}_4$ , 97%) were supplied by Alpha-Aesar. 1,2,3,4,5-Pentamethylcyclopentadiene was provided by Acros Laboratories.  $[(\text{RhCp}^*\text{Cl}(\mu\text{-Cl}))_2]$  and  $[\text{RhCp}^*(\text{bpy})\text{Cl}]\cdot\text{Cl}$  were synthesized according to literature procedures.<sup>[79,80]</sup>

Tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>) was prepared by mixing 200 mL of 1.3 M NaBF<sub>4</sub> with 200 mL of 1M TBAHSO<sub>4</sub> in water under vigorous stirring. A white precipitate was formed and additional water (about 400 mL) was added. The precipitate was filtered on a frit and washed until wastewater reached a pH of ca. 5. The white powder was redissolved in dichloromethane and dried with MgSO<sub>4</sub>. The organic phase was filtered and finally evaporated under vacuum to get a white powder stored under argon.

### Analytical methods

FT-IR 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<sup>-1</sup>. UV-visible spectra were recorded on Jasco V-670, using quartz cell. <sup>1</sup>H, {<sup>1</sup>H} -<sup>13</sup>C and <sup>31</sup>P NMR spectrums were recorded on a Bruker Advance II 300 MHz. <sup>1</sup>H and <sup>13</sup>C NMR signals were referenced to the residual solvent signals and are given relative to (CH<sub>3</sub>)<sub>4</sub>Si. <sup>31</sup>P NMR is referenced relative to H<sub>3</sub>PO<sub>4</sub> (85%). Elemental analyses were performed at ICSN-CNRS (Gif-sur-Yvette, France). Thermogravimetric analyses were performed on 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)<sub>5</sub>[α-H<sub>2</sub>PW<sub>11</sub>O<sub>39</sub>].

(TBA)<sub>4</sub>[α-H<sub>3</sub>PW<sub>11</sub>O<sub>39</sub>] was prepared according to the literature<sup>[81]</sup> and the synthesis of (TBA)<sub>5</sub>[α-H<sub>2</sub>PW<sub>11</sub>O<sub>39</sub>] was adapted from literature as follows:<sup>[82]</sup> (TBA)<sub>4</sub>[α-H<sub>3</sub>PW<sub>11</sub>O<sub>39</sub>] (2.45 g; 0.636 mmol) was dissolved in acetonitrile (50 mL) (any insoluble product was filtered off) and 636 μL of TBAOH/MeOH (40 wt%, 0.636 mmol, 1 eq.) was added drop-wise 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)<sub>4</sub>[α-H<sub>3</sub>PW<sub>11</sub>O<sub>39</sub>], 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%) <sup>31</sup>P NMR (300 MHz, CD<sub>3</sub>CN, 20°C): δ=-11.50 ppm.

### Synthesis of (TBA)<sub>3</sub>[α-H<sub>2</sub>PW<sub>11</sub>O<sub>39</sub>{Rh(III)Cp\*(H<sub>2</sub>O)}].H<sub>2</sub>O.

103 mg (166 μmol, 0.66 eq.) of [(RhCp\*Cl<sub>2</sub>)<sub>2</sub>] and 129 mg (662 μmol, 2.6 eq.) of AgBF<sub>4</sub> were added into a septum closed 15mL Falcon® tube purged with argon. Then, 2 ml of dry distilled acetonitrile was added and the mixture was sonicated for 15 minutes. The initially red cloudy solution turned quickly bright yellow while a white powder precipitated. It was removed by centrifugation, and washed twice with 3mL of dichloromethane. The yellow organic phases were evaporated under vacuum at 55°C to remove excess solvent. The yellow crystalline product was then redissolved under

argon in 20 mL of dry distilled dichloromethane and added drop-wise with vigorous stirring under argon to a solution of 974 mg (250  $\mu\text{mol}$ , 1 eq.) of  $(\text{TBA})_5[\text{H}_2\text{PW}_{11}\text{O}_{39}]$  with 51.5 mg of  $\text{Et}_3\text{N}$  (510  $\mu\text{mol}$ , 2.1 eq.) in 250 mL of dichloromethane. The resulting orange solution was stirred under argon overnight.

A diluted solution of TFA in dichloromethane (510  $\mu\text{mol}$ , 2.1 eq., 0.1g TFA / 100mL) was added slowly with vigorous stirring to the previous orange solution. An orange precipitate was formed and filtered on a frit (porosity 4), rinsed with dichloromethane, then with diethyl ether and dried under vacuum. A fine yellow-orange powder was obtained ( $m = 600$  mg Yield: 65%).

The crude product was then dissolved in 35 mL of  $\text{MeNO}_2$ , and washed with 10 mL of water and separated by decantation. The operation was repeated until the wash water retains its initial pH. (Brown impurities that appear after the first washing are filtered off). The organic phase was then concentrated to 10 mL under vacuum at 55°C then poured dropwise in 90 mL of diethyl ether with vigorous stirring. The orange powder was recovered by centrifugation, washed with diethyl ether and dried under vacuum ( $m = 500$ mg, final yield: 55 %). All our attempts to grow single crystal of this compound were unsuccessful.

$^{31}\text{P}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ , 20 °C)  $\delta = -12.2$  ppm;  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ , 20 °C):  $\delta = 3.13$  (m, 24H,  $\text{NCH}_2$ ), 1.77 (s, 15H,  $\text{Cp}^*\text{-CH}_3$ ), 1.64 (m, 24H,  $\text{NCH}_2\text{CH}_2$ ), 1.40 (sext, 24H,  $\text{NCH}_2\text{CH}_2\text{CH}_2$ ), 0.98 (t, 36H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ) ppm;  $^{13}\text{C}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ , 20 °C):  $\delta = 59.32$  (TBA), 24.37 (TBA), 20.32 (TBA), 13.84 (TBA), 9.37 ( $\text{Cp}^*\text{-CH}_3$ ) ppm; FT-IR (KBr pellet, in  $\text{cm}^{-1}$ ): 2961 (w, C-H, TBA and  $\text{Cp}^*$ ), 2934 (w, C-H, TBA and  $\text{Cp}^*$ ), 2873 (w, C-H, TBA and  $\text{Cp}^*$ ), 1483 (w, TBA and  $\text{Cp}^*$ ), 1381 (w,  $\text{Cp}^*$ ), 1155 (w), 1105 (w), 1079 (w, P-O), 1048 (m, P-O), 970 (sh,  $\text{W}=\text{O}_t$ ), 957 (s,  $\text{W}=\text{O}_t$ ), 890 (m,  $\text{W-O-W}$ ), 813 (s,  $\text{W-O-W}$ ), 751 (sh,  $\text{W-O-W}$ ), 594 (w,  $\text{W-O-W}$ ), 522 (w,  $\text{W-O-W}$ ), 379 (m,  $\text{W-O-W}$ );<sup>[57,60]</sup> UV-vis:  $\epsilon_{(256\text{ nm})} = 42\ 970$   $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ;  $\epsilon_{(400\text{ nm})} = 2\ 924$   $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ; Elemental analysis (calculated for  $\text{C}_{58}\text{H}_{129}\text{N}_3\text{O}_{41}\text{PRhW}_{11}$ ): C: 18.93% (18.93%); H: 3.38% (3.53%); N: 0.96% (1.14 %).

### 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  $\text{TBABF}_4$  (0.1M) was used as electrolytic solution. All studied solutions were purged prior measurements by bubbling inert gas or  $\text{CO}_2$  for 10 min for cyclic voltammetry (CV) or 20 min for electrolysis prior measurements, the gas being beforehand 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  $\frac{1}{4}$   $\mu\text{m}$  diamond suspension. The counter electrode was a platinum wire and a Calomel (1M 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, Orignalys) 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 20mL (6 mL in the anodic compartment) and the typical headspace volume was 46mL. Saint-Gobain Performance Plastics France natural rubber folding skirt stoppers were used to close the cell. A Bio-Logic SP 300 potentiostat connected to a booster card was used. Solutions were constantly stirred throughout bulk electrolysis experiments.

#### **Analysis of electrolysis products**

H<sub>2</sub> measurements were performed by gas chromatography on a Shimadzu GC-2014 equipped with a Quadrex column, a Thermal Conductivity Detector and using N<sub>2</sub> as a carrier gas. Other gases (CO, CH<sub>4</sub>) 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  $\mu\text{L}$ .

Formate and oxalate concentrations were determined by ionic 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 deionised 18 M $\Omega$  cm<sup>-1</sup> water and direct injection of 20  $\mu\text{L}$  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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**Keywords:** Polyoxometalates, organometallic derivative, carbon dioxide reduction, redox non-innocent ligand

## References

- [1] © OECD/IEA, *Key World Energy Statistics*, IEA Publishing, **2016**.
- [2] R. Amirante, E. Cassone, E. Distaso, P. Tamburrano, *Energy Convers. Manag.* **2017**, *132*, 372–387.
- [3] C. P. Grey, J. M. Tarascon, *Nat. Mater.* **2016**, *16*, 45–56.
- [4] N. Armaroli, V. Balzani, *ChemSusChem* **2011**, *4*, 21–36.
- [5] M. Robert, *ACS Energy Lett.* **2016**, *1*, 281–282.
- [6] C. Costentin, M. Robert, J.-M. Savéant, *Chem Soc Rev* **2013**, *42*, 2423–2436.
- [7] A. M. Appel, J. E. Bercaw, A. B. Bocarsly, H. Dobbek, D. L. DuBois, M. Dupuis, J. G. Ferry, E. Fujita, R. Hille, P. J. A. Kenis, C. A. Kerfeld, R. H. Morris, C. H. F. Peden, A. R. Portis, S. W. Ragsdale, T. B. Rauchfuss, J. N. H. Reek, L. C. Seefeldt, R. K. Thauer, G. L. Waldrop, *Chem. Rev.* **2013**, *113*, 6621–6658.
- [8] H. Takeda, C. Cometto, O. Ishitani, M. Robert, *ACS Catal.* **2017**, *7*, 70–88.
- [9] M. Bourrez, F. Molton, S. Chardon-Noblat, A. Deronzier, *Angew. Chem. Int. Ed.* **2011**, *50*, 9903–9906.
- [10] M. D. Sampson, A. D. Nguyen, K. A. Grice, C. E. Moore, A. L. Rheingold, C. P. Kubiak, *J. Am. Chem. Soc.* **2014**, *136*, 5460–5471.
- [11] B. D. Steffey, C. J. Curtis, D. L. DuBois, *Organometallics* **1995**, *14*, 4937–4943.
- [12] C. Costentin, S. Drouet, M. Robert, J.-M. Savéant, *Science* **2012**, *338*, 90–94.
- [13] I. Azcarate, C. Costentin, M. Robert, J.-M. Savéant, *J. Phys. Chem. C* **2016**, *120*, 28951–28960.
- [14] I. Azcarate, C. Costentin, M. Robert, J.-M. Savéant, *J. Am. Chem. Soc.* **2016**, *138*, 16639–16644.
- [15] C. Costentin, M. Robert, J.-M. Savéant, A. Tatin, *Proc. Natl. Acad. Sci.* **2015**, *112*, 6882–6886.
- [16] A. Tatin, C. Comminges, B. Kokoh, C. Costentin, M. Robert, J.-M. Savéant, *Proc. Natl. Acad. Sci.* **2016**, *113*, 5526–5529.
- [17] A. Taheri, L. A. Berben, *Chem Commun* **2016**, *52*, 1768–1777.
- [18] T. C. Johnson, D. J. Morris, M. Wills, *Chem Soc Rev* **2010**, *39*, 81–88.
- [19] C. Caix, S. Chardon-Noblat, A. Deronzier, *J. Electroanal. Chem.* **1997**, *434*, 163–170.
- [20] C. W. Machan, M. D. Sampson, C. P. Kubiak, *J. Am. Chem. Soc.* **2015**, *137*, 8564–8571.
- [21] J.-M. Savéant, *Chem. Rev.* **2008**, *108*, 2348–2378.
- [22] P. Kang, T. J. Meyer, M. Brookhart, *Chem. Sci.* **2013**, *4*, 3497.
- [23] S. Roy, B. Sharma, J. Pécaut, P. Simon, M. Fontecave, P. D. Tran, E. Derat, V. Artero, *J. Am. Chem. Soc.* **2017**, *139*, 3685–3696.
- [24] K. Kobayashi, K. Tanaka, *Phys. Chem. Chem. Phys.* **2014**, *16*, 2240.
- [25] H. Rao, L. C. Schmidt, J. Bonin, M. Robert, *Nature* **2017**, *548*, 74–77.
- [26] C. L. Hill, in *Compr. Coord. Chem. II* (Eds.: J.A. McCleverty, T.J. Meyer), Pergamon, Oxford, **2003**, pp. 679–759.
- [27] J. M. Clemente-Juan, E. Coronado, A. Gaita-Arino, *Chem Soc Rev* **2012**, *41*, 7464–7478.
- [28] H. N. Miras, J. Yan, D.-L. Long, L. Cronin, *Chem Soc Rev* **2012**, *41*, 7403–7430.
- [29] Y.-F. Song, R. Tsunashima, *Chem Soc Rev* **2012**, *41*, 7384–7402.
- [30] G. Izzet, F. Volatron, A. Proust, *Chem. Rec.* **2016**, *17*, 250–266.
- [31] B. Hasenknopf, *Front. Biosci. J. Virtual Libr.* **2005**, *10*, 275–287.
- [32] M. Aureliano, G. Fraqueza, C. A. Ohlin, *Dalton Trans.* **2013**, *42*, 11770–11777.
- [33] N. Gao, H. Sun, K. Dong, J. Ren, T. Duan, C. Xu, X. Qu, *Nat. Commun.* **2014**, *5*, 3422.
- [34] M. Sadakane, E. Steckhan, *Chem. Rev.* **1998**, *98*, 219–238.
- [35] R. Liu, G. Zhang, H. Cao, S. Zhang, Y. Xie, A. Haider, U. Kortz, B. Chen, N. S. Dalal, Y. Zhao, L. Zhi, C.-X. Wu, L.-K. Yan, Z. Su, B. Keita, *Energy Env. Sci* **2016**, *9*, 1012–1023.
- [36] J. E. Toth, F. C. Anson, *J. Am. Chem. Soc.* **1989**, *111*, 2444–2451.
- [37] S. Dong, M. Liu, *J. Electroanal. Chem.* **1994**, *372*, 95–100.
- [38] B. Keita, E. Abdeljalil, L. Nadjo, R. Contant, R. Belgiche, *Electrochem. Commun.* **2001**, *3*, 56–62.
- [39] B. Keita, L. Nadjo, *J. Mol. Catal. Chem.* **2007**, *262*, 190–215.



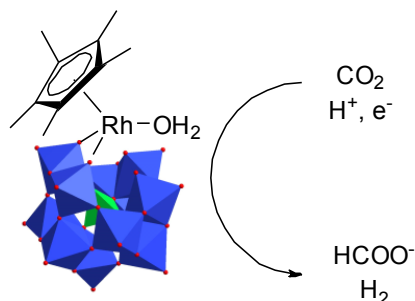
- [40] S. Imar, C. Maccato, C. Dickinson, F. Laffir, M. Vagin, T. McCormac, *Langmuir* **2015**, *31*, 2584–2592.
- [41] T. Yamase, M. Sugeta, *Inorg. Chim. Acta* **1990**, *172*, 131–134.
- [42] A. M. Khenkin, I. Efremenko, L. Weiner, J. M. L. Martin, R. Neumann, *Chem. - Eur. J.* **2010**, *16*, 1356–1364.
- [43] S. H. Szczepankiewicz, C. M. Ippolito, B. P. Santora, T. J. Van de Ven, G. A. Ippolito, L. Fronckowiak, F. Wiatrowski, T. Power, M. Kozik, *Inorg. Chem.* **1998**, *37*, 4344–4352.
- [44] J. Paul, M. Page, P. Sauers, K. Ertel, C. Pasternak, W. Lin, M. Kozik, in *Polyoxometalate Chem. Nano-Compos. Des.*, T. Yamase, M. Pope, USA, **2002**, pp. 205–215.
- [45] M. Girardi, S. Blanchard, S. Griveau, P. Simon, M. Fontecave, F. Bedioui, A. Proust, *Eur. J. Inorg. Chem.* **2015**, *22*, 3642–3648.
- [46] S. Das, S. Biswas, T. Balaraju, S. Barman, R. Pochamoni, S. Roy, *J. Mater. Chem. A* **2016**, *4*, 8875–8887.
- [47] J. Etedgui, Y. Diskin-Posner, L. Weiner, R. Neumann, *J. Am. Chem. Soc.* **2011**, *133*, 188–190.
- [48] E. Haviv, L. J. W. Shimon, R. Neumann, *Chem. - Eur. J.* **2017**, *23*, 92–95.
- [49] S.-X. Guo, D. R. MacFarlane, J. Zhang, *ChemSusChem* **2016**, *9*, 80–87.
- [50] J. F. W. Keana, M. D. Ogan, *J. Am. Chem. Soc.* **1986**, *108*, 7951–7957.
- [51] P. Gouzerh, A. Proust, *Chem. Rev.* **1998**, *98*, 77–112.
- [52] P. Gouzerh, R. Villanneau, R. Delmont, A. Proust, *Chem. - Eur. J.* **2000**, *6*, 1184–1192.
- [53] L.-H. Bi, G. Al-Kadamany, E. V. Chubarova, M. H. Dickman, L. Chen, D. S. Gopala, R. M. Richards, B. Keita, L. Nadjo, H. Jaensch, G. Mathys, U. Kortz, *Inorg. Chem.* **2009**, *48*, 10068–10077.
- [54] N. H. Nsouli, E. V. Chubarova, R. Al-Oweini, B. S. Bassil, M. Sadakane, U. Kortz, *Eur. J. Inorg. Chem.* **2013**, *2013*, 1742–1747.
- [55] P. A. Abramov, M. N. Sokolov, S. Floquet, M. Haouas, F. Taulelle, E. Cadot, E. V. Peresyphkina, A. V. Virovets, C. Vicent, N. B. Kompankov, A. A. Zhdanov, O. V. Shuvaeva, V. P. Fedin, *Inorg. Chem.* **2014**, *53*, 12791–12798.
- [56] P. A. Abramov, M. N. Sokolov, A. V. Virovets, S. Floquet, M. Haouas, F. Taulelle, E. Cadot, C. Vicent, V. P. Fedin, *Dalton Trans.* **2015**, *44*, 2234–2239.
- [57] V. Artero, D. Laurencin, R. Villanneau, R. Thouvenot, P. Herson, P. Gouzerh, A. Proust, *Inorg. Chem.* **2005**, *44*, 2826–2835.
- [58] C. Caix, S. Chardon-Noblat, A. Deronzier, J.-C. Moutet, S. Tingry, *J. Organomet. Chem.* **1997**, *540*, 105–111.
- [59] M. B. Chambers, X. Wang, N. Elgrishi, C. H. Hendon, A. Walsh, J. Bonnefoy, J. Canivet, E. A. Quadrelli, D. Farrusseng, C. Mellot-Draznieks, M. Fontecave, *ChemSusChem* **2015**, *8*, 603–608.
- [60] C. Rocchiccioli-Deltcheff, R. Thouvenot, *J. Chem. Res. M* **1977**, 0549–0571.
- [61] M. S. Balula, J. A. Gamelas, H. M. Carapuça, A. M. V. Cavaleiro, W. Schlindwein, *Eur. J. Inorg. Chem.* **2004**, *2004*, 619–628.
- [62] N. Casan-Pastor, L. C. W. Baker, in *Polyoxometalates Platonic Solids Anti-Retroviral Act.*, M. T. Pope and A. Müller Eds., **1994**, pp. 203–217.
- [63] C. L. Pitman, O. N. L. Finster, A. J. M. Miller, *Chem. Commun.* **2016**, *52*, 9105–9108.
- [64] N. Elgrishi, M. B. Chambers, X. Wang, M. Fontecave, *Chem. Soc. Rev.* **2017**, DOI 10.1039/C5CS00391A.
- [65] J. Hawecker, J.-M. Lehn, R. Ziessel, *J. Chem. Soc. Chem. Commun.* **1984**, *0*, 328–330.
- [66] J. M. Smieja, C. P. Kubiak, *Inorg. Chem.* **2010**, *49*, 9283–9289.
- [67] F. Franco, C. Cometto, F. F. Vallana, F. Sordello, E. Priola, C. Minero, C. Nervi, R. Gobetto, *Chem. Commun.* **2014**, *50*, 14670–14673.
- [68] J. Agarwal, T. W. Shaw, H. F. Schaefer, A. B. Bocarsly, *Inorg. Chem.* **2015**, *54*, 5285–5294.
- [69] S. Sung, D. Kumar, M. Gil-Sepulcre, M. Nippe, *J. Am. Chem. Soc.* **2017**, *139*, 13993–13996.
- [70] K. T. Ngo, M. McKinnon, B. Mahanti, R. Narayanan, D. C. Grills, M. Z. Ertem, J. Rochford, *J. Am. Chem. Soc.* **2017**, *139*, 2604–2618.
- [71] E. E. Benson, K. A. Grice, J. M. Smieja, C. P. Kubiak, *Polyhedron* **2013**, *58*, 229–234.

- [72] F. D. Sypaseuth, C. Matlachowski, M. Weber, M. Schwalbe, C. C. Tzschucke, *Chem. – Eur. J.* **2015**, *21*, 6564–6571.
- [73] H. Y. V. Ching, X. Wang, M. He, N. Perujo Holland, R. Guillot, C. Slim, S. Griveau, H. C. Bertrand, C. Policar, F. Bedioui, M. Fontecave, *Inorg. Chem.* **2017**, *56*, 2966–2976.
- [74] N. P. Liyanage, H. A. Dulaney, A. J. Huckaba, J. W. Jurss, J. H. Delcamp, *Inorg. Chem.* **2016**, *55*, 6085–6094.
- [75] J. K. Nganga, C. R. Samanamu, J. M. Tanski, C. Pacheco, C. Saucedo, V. S. Batista, K. A. Grice, M. Z. Ertem, A. M. Angeles-Boza, *Inorg. Chem.* **2017**, *56*, 3214–3226.
- [76] S. J. P. Spall, T. Keane, J. Tory, D. C. Cocker, H. Adams, H. Fowler, A. J. H. M. Meijer, F. Hartl, J. A. Weinstein, *Inorg. Chem.* **2016**, *55*, 12568–12582.
- [77] M. V. Vollmer, C. W. Machan, M. L. Clark, W. E. Antholine, J. Agarwal, H. F. Schaefer, C. P. Kubiak, J. R. Walensky, *Organometallics* **2015**, *34*, 3–12.
- [78] C. Riplinger, M. D. Sampson, A. M. Ritzmann, C. P. Kubiak, E. A. Carter, *J. Am. Chem. Soc.* **2014**, *136*, 16285–16298.
- [79] C. White, A. Yates, P. M. Maitlis, D. M. Heinekey, in *Inorg. Synth.*, John Wiley & Sons, Inc., **2007**, pp. 228–234.
- [80] U. Kölle, M. Grätzel, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 567–570.
- [81] E. Radkov, R. H. Beer, *Polyhedron* **1995**, *14*, 2139–2143.
- [82] C. Dablemont, *Fonctionnalisation de Polyoxometallates à Structure de Keggin*: Introduction de Liaisons Métal-Azote Multiples, PhD Thesis, Paris 06, **2003**.

## Entry for the Table of Contents

## FULL PAPER

$[\alpha\text{-H}_2\text{PW}_{11}\text{O}_{39}\{\text{Rh(III)Cp}^*(\text{OH}_2)\}]^{3-}$  was prepared by reaction between the monovacant Keggin-type  $[\alpha\text{-H}_2\text{PW}_{11}\text{O}_{39}]^{5-}$  and  $[\text{Cp}^*\text{Rh}(\text{CH}_3\text{CN})_3]^{2+}$ . It is closely related to the  $\text{CO}_2$  reduction electrocatalyst  $[\text{Cp}^*\text{Rh(III)}(\text{bpy})\text{Cl}]^+$  by changing the bpy ligand by the polyoxometalate, both acting as redox non-innocent bidentate ligands. The selectivity of the  $\text{CO}_2$  reduction was altered from the production of formate to dihydrogen.



## Polyoxometalate electrocatalysis

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Assessing the electrocatalytic properties of the  $\{\text{Cp}^*\text{Rh(III)}\}^{2+}$ -Polyoxometalate derivative  $[\text{H}_2\text{PW}_{11}\text{O}_{39}\{\text{Rh(III)Cp}^*(\text{OH}_2)\}]^{3-}$  towards  $\text{CO}_2$  reduction

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