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Note

Electrochemical reactions of pincer rhodium(I) complexes

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ABSTRACT

The electrochemical properties of the (PCP)Rh^I(H₂) (**1-H₂**, PCP = κ^3 -C₆H₃-2,6-(CH₂P(^tBu₂))) complex was examined by cyclic voltammetry in acetonitrile (MeCN), dimethylsulfoxide (DMSO) and 1,2-difluorobenzene (1,2-DFB). Upon oxidation in weakly or non-coordinating media such as 0.05 M NaBAR_F₂₄ in 1,2-difluorobenzene, simple one electron oxidation to [(PCP)Rh^{II}(H₂)]⁺ is observed. Conversely, in coordinating solvents (e.g. acetonitrile and dimethylsulfoxide) the reactivity is dominated by solvent coordinated species with a slight variation in the Rh^{III/II} oxidation potentials as a function of the supporting electrolyte conductivity. A computational analysis of these reactions in support of the proposed mechanism is presented.

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1. Introduction

Success of direct organic polymer electrolyte membrane (PEM) fuel cells in which oxidation of an organic fuel, such as an alcohol or hydrocarbon provides the protons and electrons necessary to drive oxygen reduction, relies upon the development of efficient and selective electrocatalysts [1–7]. Traditional PEM fuel cells utilizing platinum group metals or alloys as electrocatalysts [8–10] for the oxidation of hydrogen [4,5] often struggle to effectively electro-dehydrogenate organic fuels. An alternative approach involves the use of a molecular dehydrogenation catalyst [11,12] immobilized on the electrode surface to effect the partial oxidative dehydrogenation of an organic fuel to a stable hydrogen depleted product.

One particular class of dehydrogenation catalysts of interest is derived from PCP (PCP = κ^3 -C₆H₃-2,6-(CH₂P(^tBu₂))) pincer coordinated iridium and rhodium complexes originally reported by Moulton and Shaw [13]. Despite reports of robust photochemical dehydrogenation [14–16] and thermochemical transfer dehydrogenation [17,18] catalysis by Rh(PMe₃)₂(CO)Cl, the related (PCP)RhH₂ (PCP = κ^3 -C₆H₃-2,6-(CH₂P(^tBu₂))) complex shows much lower catalytic activity in the cyclooctane/*tert*-butylethylene transfer dehydrogenation with only 0.8 turnovers/h at 150 °C [19]. However, the analogous (PCP)IrH₂ complex exhibited higher activity (82 turnovers/h at 150 °C) while further structural

modifications to the ligand framework improved turnover numbers to as many as 7000 for γ -alumina supported catalysts [20].

Recent studies have shown that a non-classical η^2 -dihydrogen rhodium(I) is the most stable form of the (PCP)RhH₂ complex described above [21]. Although the utility of this complex as an electrocatalyst is limited by the lability of the H₂ ligand in coordinating solvents (*vide infra*), the cyclic voltammetry data presented here demonstrates responses in the current that vary as a function of solvent, supporting electrolyte and scan rate. We discuss the results of our theoretical and electrochemical studies and propose a mechanism explaining the electrochemical reactivity of the (PCP)Rh(H₂) complex under a variety of conditions.

2. Experimental and computational methods

Acetonitrile (MeCN) was dried by passing through a steel column containing alumina using a Pure Solv solvent purification system and degassed prior to use. Anhydrous dimethylsulfoxide (DMSO), 1,2-difluorobenzene (1,2-DFB) and lithium trifluoromethanesulfonate (LiOTf) were used as received. Electrochemical grade tetrabutylammonium tetrafluoroborate (TBAT), tetrabutylammonium perchlorate (TBAP) and tetrabutylammonium hexafluorophosphate (TBAH) were purchased from Aldrich and used as received. Sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (NaBAR_F₂₄) was purchased from Boulder Scientific Co. and used as received. All ¹H NMR spectra were recorded on a Bruker 400 MHz Avance spectrometer and referenced to residual C₆D₅H (δ 7.16). Electrochemical measurements were conducted on an IviumStat Electrochemical Interface & Impedance Analyzer from Ivium

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Technologies and were carried out in a glovebox under an Ar atmosphere. Cyclic voltammetry experiments were performed in a beaker type cell with a working volume of 5 mL using a standard three-electrode cell with a glassy carbon disk ($d = 3$ mm) working electrode, platinum wire counter electrode and an Ag/AgNO₃ (10 mM) reference electrode in MeCN with 0.1 M TBAT (+0.54 V vs SHE [22]). All potentials are reported vs. the ferrocenium/ferrocene (FeCp₂^{+/0}; Cp = η⁵-cyclopentadienyl) couple in the solvent indicated (+0.08 V vs Ag/AgNO₃ in MeCN; +0.03 V vs Ag/AgNO₃ in DMSO; +0.24 V vs Ag/AgNO₃ in 1,2-DFB).

All electronic structure calculations for the analysis of redox potentials and changes in free energy were performed using the Jaguar electronic structure program [23] and the B3LYP exchange-correlation functional with unrestricted Kohn-Sham wave functions (UB3LYP). Minimum energy configurations were obtained using a mixed basis with the LACVP basis set, which provides a nonrelativistic description of the electron-core potentials (ECPs), for Rh and the 6-311G* basis set for all other atoms. Solvation energies were calculated using the Poisson–Boltzmann self-consistent reaction field method (PBF) [24,25] to represent the solvent with a dielectric constants of 37.5 and 13.8 and an effective radii of 2.19 and 2.69 Å for MeCN and 1,2-DFB, respectively. Values for 1,2-DFB are based on data reported in Ref. [26]. Redox potentials were calculated vs. the [Ru(bpy)₃]^{2+/3+} couple to reduce computational sources of systematic error [27] and then converted to V vs. FeCp₂^{0/+} based on potentials measured under identical experimental conditions as those reported in this work. This methodology and level of theory was demonstrated on a series of transition metal complexes with a standard deviation of 64 mV between experimental and computational data [27].

3. Results & discussion

3.1. Synthesis & reactivity

The rhodium(I) dihydrogen complex **1-H₂** shown in Fig. 1 was prepared as described previously [28,29] and could be stored in an Ar glovebox at –30 °C for a few weeks without any observable decomposition. While typical solvents used in organic electrochemistry (e.g. MeCN) can act as coordinating ligands, 1,2-DFB has been shown to be an inert and non-coordinating replacement [26]. Upon the addition of MeCN to a C₆D₆ solution of **1-H₂** ¹H NMR spectroscopic analysis clearly shows displacement of H₂ by MeCN as indicated by the disappearance of the H₂ signal and the appearance of a signal corresponding to the coordinated MeCN at δ 0.8 ppm (see Fig. A4; uncoordinated MeCN typically appears at 0.58 in C₆D₆) [30]. Conversely, the addition of 1,2 DFB to a separate solution of **1-H₂** in C₆D₆ did not result in the disappearance of the H₂ signal in the ¹H NMR spectrum.

3.2. Electrochemical measurements

The results of the electrochemical measurements are summarized in Table 1. Cyclic voltammetry (CV) of a 1 mM solution of

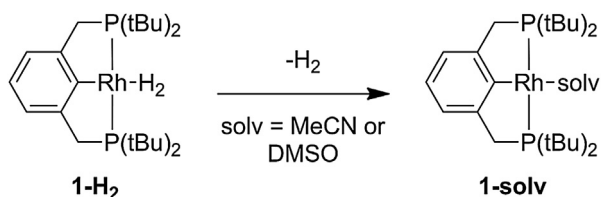


Fig. 1. Solvation of **1-H₂** in coordinating solvents.

1-H₂ in 1,2-DFB with 0.05 M NaBar₂₄ as supporting electrolyte yields only a reversible Rh^{III/I} couple (cf. Table 1 and Fig. 2 at E_{1/2}^{III/I} = –0.74 V vs FeCp₂^{+/0} in the potential window scanned (–1.5 to +1.0 V vs FeCp₂^{+/0}). A CV of a 1 mM solution of **1-solv** in acetonitrile containing 0.1 M TBAT at a scan rate of 0.1 V s^{–1} exhibits a reversible [31] one electron redox wave at E_{1/2}^{III/I} = –0.74 V vs FeCp₂^{+/0} which we assign to the Rh^{III/I} couple. Extending the scan to more positive potentials reveals an irreversible oxidation peak at E_p^{III} = +0.18 V vs FeCp₂^{+/0} which is coupled to a reduction peak at E_p^{IV} = –1.38 V vs FeCp₂^{+/0} as shown in Fig. 3. Increasing the scan rates up to 1.6 V s^{–1} shows no change in the peak potentials associated with E_{1/2}^{III/I}, however the peak potentials of E_p^{III} and E_p^{IV} shift to more anodic and cathodic potentials, respectively. In addition, at the highest scan rates investigated, no reverse reduction or oxidation waves were detected for these processes. Reversing the initial scan direction and cycling the CV clearly shows the irreversible reduction E_p^{IV} appears only after anodic scans past the oxidation wave at E_p^{III} (see Fig. A1 in Supporting information). Additionally, following the oxidation at E_p^{III} a decrease in peak current at E_p^{III} of ~40% results. Similar results were observed for 1 mM solutions of **1-solv** in DMSO where a reversible one electron couple at E_{1/2}^{III/I} = –0.62 V vs FeCp₂^{+/0} is observed followed by an irreversible oxidation at E_p^{III} = +0.24 V vs FeCp₂^{+/0} coupled to an irreversible reduction at E_p^{IV} = –1.97 V vs FeCp₂^{+/0} (see Fig. A2 in Supporting information). In light of the CV results obtained in the non-coordinating solvent 1,2-DFB and given the coordinating ability of MeCN and DMSO, it seems likely that further solvent coordination following oxidation of **1-solv** at E_{1/2}^{III/I} is responsible for the irreversibility observed for E_p^{III} and E_p^{IV}.

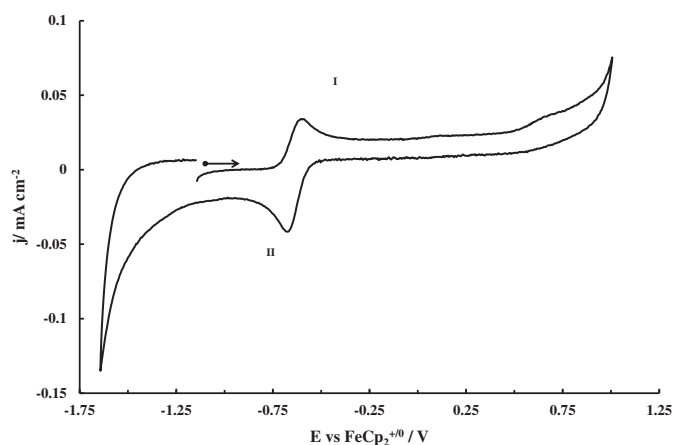
3.3. Mechanistic considerations

Based on this data and DFT calculations with MeCN as solvent [31], Fig. 5 shows a proposed mechanism for the reactions occurring during these electrochemical experiments. Displacement of dihydrogen by MeCN in **1-H₂** is calculated to be spontaneous ($\Delta G_1(\text{calc}) = -6.7$ kcal/mol) and is consistent with the results of the ¹H NMR experiments described above in which the 16e[–] square planar Rh^I acetonitrile complex, **1-solv** is the dominant species in solution. A bis-acetonitrile Rh^I structure was also explored, however geometry optimization resulted in dissociation of both P^t(Bu)₂ arms of the pincer ligand and led to a higher energy (+50.8 kcal/mol) 3-coordinate ($\kappa^1\text{C-PCP}$)Rh^I(NCMe)₂ complex. Oxidation of **1-solv** in acetonitrile is calculated to occur at E_{1/2}^{III/I}(calc) = –0.84 V vs FeCp₂^{+/0} to give **1-solv**⁺ as a square planar 15e[–] Rh^{II} (S = ½) cation in good agreement with the reversible potentials (E_{1/2}^{III/I}) reported in Table 1. Subsequent coordination of a second acetonitrile molecule is calculated to be exergonic ($\Delta G_2(\text{calc}) = -7.8$ kcal/mol) and would produce the square pyramidal 17e[–] Rh^{II} (S = ½) *cis*-bis-acetonitrile cation *cis*-**2**⁺ with an apical MeCN ligand.

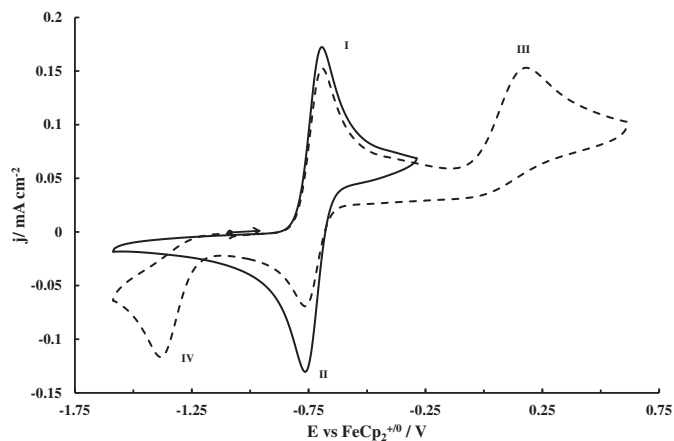
Further oxidation of *cis*-**2**⁺ is irreversible and is observed between +0.09 and +0.24 V vs FeCp₂^{+/0} (Table 1) depending on the supporting electrolyte and solvent used. In acetonitrile, this oxidation is calculated to occur at E_p^{III}(calc) = +0.36 V vs FeCp₂^{+/0} to give a square pyramidal 16e[–] Rh^{III} (S = 0) *cis*-bis-acetonitrile dication. The electrochemical irreversibility for this oxidation observed in cyclic voltammetry experiments is indicative of a rapid chemical reaction following oxidation. Possible adducts containing the BF₄[–] and *cis*-**2**²⁺ fragments were investigated computationally, however no stable species were found. Instead, isomerization of *cis*-**2**²⁺ to the *trans*-bis-acetonitrile dication *trans*-**2**²⁺ in which the PCP carbon is in the apical position of a 16e[–] square pyramidal Rh^{III} complex is calculated to be thermodynamically favorable with $\Delta G_3(\text{calc}) = -14.6$ kcal/mol. Coordination of a third molecule of

Table 1
Redox potentials of 1 mM solutions of **1-solv** at 0.1 V s⁻¹ in the solvent indicated at 298 ± 5 K in V vs FeCp₂⁺⁰.^a

| Solvent | Electrolyte ^b | E _p ^I | E _p ^{II} | E _p ^{III} | E _p ^{IV} | E _{1/2} ^{III/II} | ΔE _p ^{III/II} | i _p ^{III} /i _p ^{II} | i _p ^{III} /i _p ^{IV} |
|----------------------|----------------------------------|-----------------------------|------------------------------|-------------------------------|------------------------------|------------------------------------|-----------------------------------|---|---|
| MeCN | TBAT | -0.69 | -0.77 | +0.18 | -1.38 | -0.73 | 0.075 | 1.0 | 1.0 |
| DMSO | TBAT | -0.58 | -0.66 | +0.24 | -1.97 | -0.62 | 0.080 | 1.0 | 2.4 |
| MeCN | LiOTf | -0.68 | -0.76 | +0.17 | -1.29 | -0.72 | 0.075 | 0.9 | 1.1 |
| MeCN | TBAH | -0.68 | -0.75 | +0.12 | -1.35 | -0.71 | 0.070 | 0.9 | 1.4 |
| MeCN | TBAP | -0.68 | -0.75 | +0.09 | -1.36 | -0.71 | 0.070 | 0.9 | 1.0 |
| MeCN | NaBAR ₂₄ ^F | -0.70 | -0.77 | +0.24 | -1.30 | -0.74 | 0.070 | 0.9 | 1.0 |
| 1,2-DFB ^c | NaBAR ₂₄ ^F | -0.70 | -0.77 | N/A | N/A | -0.74 | 0.070 | 0.8 | N/A |

^a Glassy carbon 3 mm disk working electrode.^b 0.1 M supporting electrolyte except for NaBAR₂₄^F which is 0.05 M.^c Data for **1-H₂** based on ¹H NMR data (see text).**Fig. 2.** CV of **1-H₂** in 1,2-DFB containing 0.05 M NaBAR₂₄^F as supporting electrolyte at a scan rate of 0.1 V s⁻¹.

acetonitrile was also considered, however the resulting Rh^{III} tris-acetonitrile dication is calculated to be 11.4 kcal/mol higher in energy than *trans-2*⁺². At a scan rate of 0.1 V s⁻¹ the oxidation of *cis-2*⁺ and subsequent isomerization to *trans-2*⁺² depletes the [**1-solv**⁺] at the electrode surface enough such that on return scans the reductive peak current at E_p^{II} is diminished by ~40% (see Fig. A3 in Supporting information). Reducing the scan rate to 0.025 V s⁻¹ (Fig. 4) provides enough time for diffusion to replenish [**1-solv**⁺] at the electrode surface, as evidenced by the recovery of reductive peak current at E_p^{II} to give peak current ratios i_p^{III}/i_p^{II} = ~1. Diffusion is also responsible for decreasing the [*trans-2*⁺²] such that the

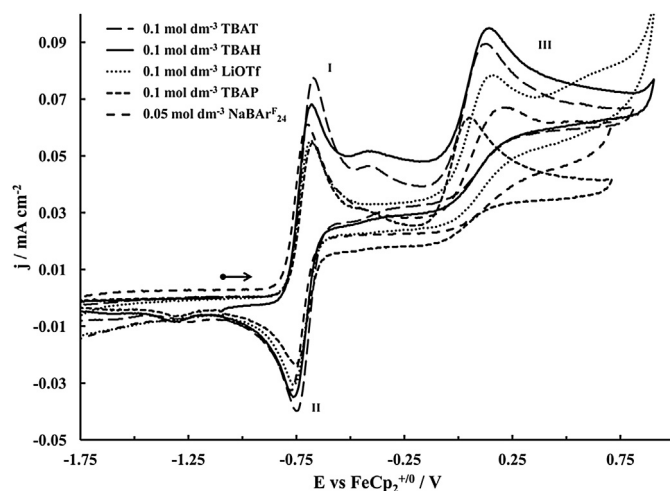
**Fig. 3.** CVs of **1-solv** in MeCN with 0.1 M TBAT as supporting electrolyte at a scan rate of 0.1 V s⁻¹.

reduction wave at E_p^{IV} associated with this species disappears at low scan rates. This reduction, giving rise to *trans-2*⁺ as a cationic 17e⁻ d⁷ Rh^{II} (S = 1/2) species, occurs at more negative potentials (-1.29 V to -1.38 V vs FeCp₂⁺⁰ in acetonitrile; E_p^{IV}(calc) = -1.50 V vs FeCp₂⁺⁰) due to localization of the additional electron in an anti-bonding e_g^{*} orbital. Isomerization of the resulting *trans*-bis-acetonitrile Rh^{II} complex to *cis-2*⁺ is calculated to be highly exergonic with ΔG₄(calc) = -28.1 kcal/mol.

In 1,2-DFB oxidation of **1-H₂** with 0.05 M NaBAR₂₄^F as supporting electrolyte exhibits a single reversible redox event with E_{1/2}^{III/II}(calc) = -0.77 V vs FeCp₂⁺⁰ which is in good agreement with that reported in Table 1. Although the current ratio i_p^{III}/i_p^{II} < 1 and the peak currents of the waves decrease upon cycling the CV, the lack of an irreversible oxidation or reduction similar to E_p^{III} or E_p^{IV} indicate that while **1-H₂**/**1-H₂⁺** may not be stable in solution, there is no evidence of solvent coordination to either of these species.

4. Conclusions

A combination of cyclic voltammetry and DFT calculations have been used to explore the electrochemical reactivity of **1-H₂** in both strongly (MeCN and DMSO) and weakly or non-coordinating (1,2-DFB) solvents. In the least coordinating medium examined (0.05 M NaBAR₂₄^F in 1,2-DFB) oxidation of **1-H₂** is a reversible one electron process at E_{1/2}^{III/II} = -0.74 V vs FeCp₂⁺⁰ yielding **1-H₂⁺**. The situation becomes more complicated in coordinating solvents such as MeCN or DMSO. Again, a reversible one electron oxidation of **1-solv** to **1-solv**⁺ is observed at E_{1/2}^{III/II} (see Table 1 for details) however upon scanning to more positive potentials, an irreversible one

**Fig. 4.** CVs of **1-solv** in MeCN containing the electrolyte indicated at a scan rate of 0.025 V s⁻¹.

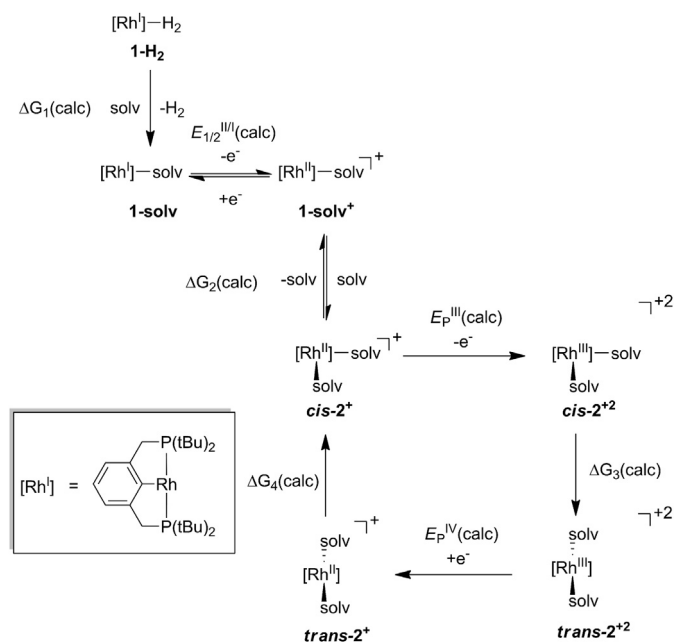


Fig. 5. Proposed mechanism for the electrochemical reactions of **1-H₂** in MeCN and DMSO.

electron oxidation is observed at $E_{1/2}^{\text{III}}$. This is attributed to oxidation of the Rh^{II} *cis*-bis-acetonitrile *cis-2*⁺ to a Rh^{III} species *cis-2*²⁺, which then isomerizes to the *trans*-bis-acetonitrile adduct *trans-2*²⁺. The latter is irreversibly reduced at E_{p}^{IV} to form *trans*-bis-acetonitrile *trans-2*⁺ which subsequently isomerizes to *cis-2*⁺. These results highlight the importance of solvent coordinating ability and its impact on the electrochemical reactivity exhibited by transition metal complexes.

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Appendix A. Supporting information

Supporting information related to this article can be found at <http://dx.doi.org/10.1016/j.jorganchem.2013.10.045>.

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