Electrochemical reactions of pincer rhodium(I) complexes

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The electrochemical properties of the (PCP)Rh(H2)(1-H)PCP = k1-C6H3–2,6-(CH3P(Bu2))] 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 NaBArF24 in 1,2-difluorobenzene, simple one electron oxidation to [(PCP)Rh(H)2]+ 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) 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] face the challenge of finding a viable alternative to electrocatalysts. 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 = k3-C6H3–2,6-(CH3P(Bu2))] 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)3(CO)/Cl, the related (PCP)Rh(H2) (PCP = k3-C6H3–2,6-(CH3P(Bu2))] complex shows much lower catalytic activity in the cyclooctane/1,2-butylene transfer dehydrogenation with only 0.8 turnovers/h at 150 °C [19]. However, the analogous (PCP)Ir(H2) 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 η6-dehydrogen rhodium(II) 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

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 tetraakis(3,5-bis(trifluoromethyl)phenyl)borate (NaBAr24) was purchased from Polyscience 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...
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/ferrocone (FeCp2^+/C0; Cp = η^5-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 6-31G* 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 was shown to be an inert and non-coordinating replacement [26]. Upon the addition of MeCN to a C6D6 solution of 1-H2, H 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 ppm 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 voltammety (CV) of a 1 mM solution of 1-H2 in 1,2-DFB with 0.05 M NaBu4F4 as supporting electrolyte yields only a reversible RhII^+/I couple (cf. Table 1 and Fig. 2 at E^+/0 = -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^+/0 = -0.74 V vs FeCp2^+/0 which we assign to the RhII^+/I couple. Extending the scan to more positive potentials reveals an irreversible oxidation peak at E^+/0 = +0.18 V vs FeCp2^+/0 which is coupled to a reduction peak at E^0 = -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^+/0, however the peak potentials of E^+/0 and E^0 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^+/0 appears only after anodic scans past the oxidation wave at E^+/0 (see Fig. A1 in Supporting information). Additionally, following the oxidation at E^+/0 a decrease in peak current at E^+/0 of ~40% results. Similar results were observed for 1 mM solutions of 1-solv in DMSO where a reversible one electron couple at E^+/0 appears after anodic scans past the oxidation wave at E^+/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^+/0 is responsible for the irreversibility observed for E^+/0 and E^0.

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 (∆G^0(calc) = -6.7 kcal/mol) and is consistent with the results of the 1H NMR experiments described above in which the 16e square planar RhI acetonitrile complex, 1-solv is the dominant species in solution. A bis-acetonitrile RhI structure was also explored, however geometry optimization resulted in dissociation of both Bu2N arms of the pincer ligand and led to a higher energy (+50.8 kcal/mol) 3-coordinate (s2C-PCP/Rh(NCMe)2) complex. Oxidation of 1-solv in acetonitrile is calculated to occur at E^+/0(calc) = -0.84 V vs FeCp2^+/0 to give 1-solv^+/1 which as a square planar 15e RhII^+/I (S = ½) cation in good agreement with the reversible potentials (E^+/0) reported in Table 1. Subsequent coordination of a second acetonitrile molecule is calculated to be exergonic (∆G^0(calc) = -7.8 kcal/mol) and would produce the square pyramidal 17e RhIII^+/I (S = 0) 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^+/0(calc) = +0.36 V vs FeCp2^+/0 to give a square pyramidal 16e RhIII^+/I (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^+ fragments were investigated computationally, however no stable species were found. Instead, isomerization of cis-2^+ to the trans-bis-acetonitrile dication trans-2^+ in which the PCP carbon is in the apical position of a 16e square pyramidal RhIII complex is calculated to be thermodynamically favorable with ∆G^0(calc) = -14.5 kcal/mol. Coordination of a third molecule of
acetonitrile was also considered, however the resulting RhIII 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+ to subsequent isomerization to trans-2+2 depletes the [1-solv]+ at the electrode surface such that on return scans the reductive peak current at E2+ 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 E2+ to give peak current ratios i/i = ~1. Diffusion is also responsible for decreasing the (trans-2+2) such that the reduction wave at E2+ associated with this species disappears at low scan rates. This reduction, giving rise to trans-2+ as a cationic 17e− d7 RhII (S = ½) species, occurs at more negative potentials (−1.29 V vs FeCp2/[0]) due to localization of the additional electron in an anti-bonding eg* orbital. Isomerization of the resulting trans-bis-acetonitrile RhII complex to cis-2+ is calculated to be highly exergonic with ∆G2(calc) = −28.1 kcal/mol.

In 1,2-DFB oxidation of 1-H2 with 0.05 M NaBArF24 as supporting electrolyte exhibits a single reversible redox event with E2+/1(calc) = −0.77 V vs FeCp2/[0] which is in good agreement with that reported in Table 1. Although the current ratio i/i < 1 and the peak currents of the waves decrease upon cycling the CV, the lack of an irreversible oxidation or reduction similar to E2+ or E2+ indicates 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 NaBArF24 in 1,2-DFB) oxidation of 1-H2 is a reversible one electron process at E2+/1 = −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 E2+/1 (see Table 1 for details) however upon scanning to more positive potentials, an irreversible one
electron oxidation is observed at $E^{\|}$. This is attributed to oxidation of the Rh catalyst to a Rh III species, which then isomerizes to the trans-bis-acetonitrile adduct $\text{trans}^+$. The latter is irreversibly reduced at $E^{\ominus}$ to form trans-bis-acetonitrile $\text{trans}^2^+$. 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.

References


See Supporting information.