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# Bimetallic Pt/Ru Complexes as Catalysts for the Electrooxidation of Methanol

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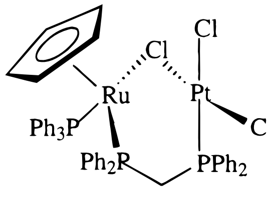
## Introduction

Potential applications of direct methanol fuel cells have led to interest in the electrooxidation of methanol.[1−3] Studies on platinum anodes have established that overpotentials tend to be high and the anode performance degrades over time.[4−6] Addition of a second metal such as Ru to the anode material[7−10] or formulation of more complex alloys[11,12] can ameliorate these problems. On the basis of the optimum percentage of Ru for methanol oxidation, the active site of an Pt/Ru anode was postulated to be a $Pt_3Ru$ ensemble.[13] The $Pt_3$ portion was suggested to be the site of methanol binding and dehydrogenation and Ru to serve as a source of "active oxygen" for the formation of $CO_2$. Evidence that the practical Pt/Ru catalysts are composed of Pt metal and Ru oxides supports this postulate.[14,15] In situ spectroscopic studies on Pt-rich Pt/Ru anodes implicate either oxidation of Pt-bound CO by Ru-bound oxygen species[16,17] or formation of Ru−OH species[18] as the rate-determining step of methanol oxidation. Since C−H activation reactions have been demonstrated for simple Pt complexes[19−22] and Ru compounds are known to be chemical oxidants[23−25] of alcohols and catalysts for their electrooxidation,[26−33] we recently prepared the bimetallic Pt/Ru compound $RuCp(PPh_3)(\mu\text{-}Cl)(\mu\text{-}dppm)PtCl_2$ (**1**) as a possible electrocatalyst for methanol oxidation.[34] The electrochemical oxidation of **1** has now been examined in the absence and presence of methanol. The current increases observed in the cyclic voltammogram in the presence of methanol are consistent with a catalytic oxidation process.



**1**

## Experimental Section

**General Considerations.** Standard Schlenk/vacuum techniques were used throughout. Hexane, methylene chloride, and 1,2-dichloroethane were distilled from $CaH_2$, and diethyl ether was distilled from $Na/Ph_2CO$. All NMR solvents were degassed via freeze−pump−thaw cycles and stored over molecular sieves. All other starting materials were purchased in reagent grade purity and used without further purification.

**Equipment and Instrumental Methods.** Electrochemical experiments were performed under nitrogen using an EG&G PAR model 263A potentiostat/galvanostat. Cyclic voltammograms were recorded in 2.5 mL of 0.7 M $Bu_4NSO_3CF_3/ClCH_2CH_2Cl$ at room temperature under nitrogen in a standard three-electrode cell at a scan rate of 50 mV/s. All potentials are reported vs NHE and referenced to $Ag/Ag^+$. Bulk electrolysis was performed in an H-cell in 2.5 mL of 0.7 M $Bu_4NSO_3CF_3/ClCH_2CH_2Cl$ at room temperature under nitrogen using a vitreous carbon working electrode, a platinum foil counter electrode, and an $Ag/Ag^+$ reference electrode. Cyclic voltammetry was performed with a glassy carbon working electrode (3 mm diameter). GC was performed on an HP5980A chromatograph containing a 15 m × 0.32 mm column of AT-WAX (Alltech, 0.5 $\mu$m film) on fused silica with heptane as the internal standard. $^1H$ and $^{31}P$ NMR spectra were recorded

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**Table 1.** Crystallographic Data for **1**

empirical formula: $C_{51}H_{48}Cl_9P_3PtRu$
$a = 13.296(2)$ Å
$b = 22.363(3)$ Å
$c = 18.625(3)$ Å
$\alpha = 90°$
$\beta = 107.654(2)°$
$\gamma = 90°$
$V = 5277(1)$ Å$^3$
$Z = 4$

fw = 1369.01
space group: $P2_1/n$
$T = -100$ °C
$\lambda = 0.710\ 73$ Å
$\rho_{calc} = 1.723$ g/cm$^3$
$\mu = 3.516$ mm$^{-1}$
R1$^a$ = 0.0233
wR2$^b$ = 0.0480

$^a$ $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b$ $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ $[I > 2\sigma(I)]$.

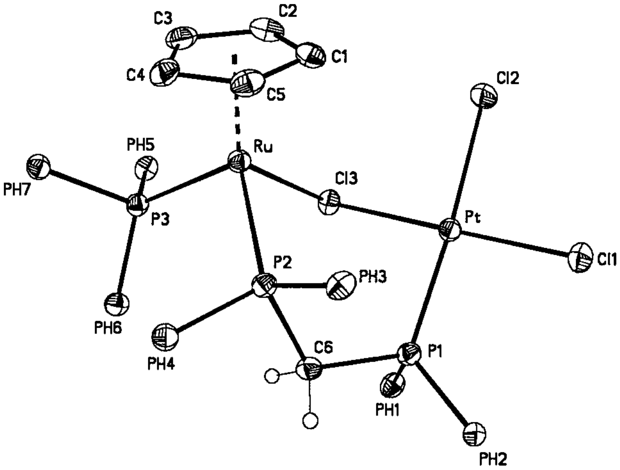

**Figure 1.** Thermal ellipsoid diagram of **1** showing the crystallographic numbering scheme. Thermal ellipsoids are drawn at the 40% probability level. Phenyl rings and most hydrogens are omitted for clarity. Selected distances (Å) and angles (deg): Pt−Cl3 2.3179(7), Pt−Cl1 2.2882(7), Pt−Cl2 2.3717(7), Ru−Cl3 2.4438(7); Pt−Cl3−Ru 105.21(3), P2−Ru−Cl3 89.84(2), P1−Pt−Cl3 87.02(2).

on a Varian VXR-300 NMR spectrometer. $^1$H and $^{31}$P NMR spectra are referenced to the residual proton in the deuterated solvent and to 85% $H_3PO_4$, respectively. The $^{31}$P spectra were proton-decoupled. High-resolution mass spectrometry was performed by the University of Florida analytical service.

**Synthesis of Cp(PPh$_3$)Ru($\mu$-Cl)($\mu$-dppm)PtCl$_2$ (1).** Complex **1** was prepared as described previously.[34]

**Synthesis of [Cp(PPh$_3$)Ru($\mu$-dppm)PtCl$_2$]PF$_6$ (2).** A Schlenk flask was charged with CpRu(PPh$_3$)Cl($\mu$-dppm)PtCl$_2$ (0.050 g, 0.045 mmol) and $CH_2Cl_2$ (20 mL). A solution of $TlPF_6$ (0.031 g, 0.09 mmol) in $CH_2Cl_2$ (20 mL) was then added via cannula to give an orange-yellow solution. The solution was stirred for 30 min at room temperature and was then filtered through Celite. Removal of the solvent afforded a yellow-orange solid, which was recrystallized from $CH_2Cl_2/Et_2O$. The isolated yield of **2** was 0.026 g (54% yield). $^1$H NMR ($CDCl_3$): $\delta$ 8.0−5.8 (m, 35H, *Ph*$_2$PCH$_2$P*Ph*$_2$ + P*Ph*$_3$), 4.81 (s, 5H, Cp), 3.22 and 2.71 (m, 1H each, Ph$_2$P*CH*$_2$PPh$_2$). $^{31}$P NMR ($CDCl_3$): $\delta$ 53.40 (dd, Ru−*P*Ph$_2$−CH$_2$PPh$_2$, $J_{PP} = 19$ Hz, 35 Hz), 37.30 (d, Ru−*P*Ph$_3$, $J_{PP} = 37$ Hz), −3.44 (d, PPh$_2$CH$_2$*P*Ph$_2$−Pt, $J_{PP} = 19$ Hz, $J_{PPt} = 4330$ Hz), −144.1 (septet, PF$_6$). IR ($CH_2Cl_2$): $\nu_{PF_6} = 838$ cm$^{-1}$. MS (electrospray; MeOH): *m/z* 1078.6 ([**2** − PF$_6$]$^+$).

## Results and Discussion

At the time complex **1** was originally reported,[34] structural data were unavailable and there was ambiguity as to whether the complex contained a chloride bridge between the metal centers. To clarify the structure, crystallographic data have been obtained (Table 1). As shown in Figure 1, the complex does indeed exhibit a bridging chloride ligand. The bond lengths and bond angles of the structure are standard, with the expected square planar geometry at Pt and three-legged piano stool configuration at Ru.

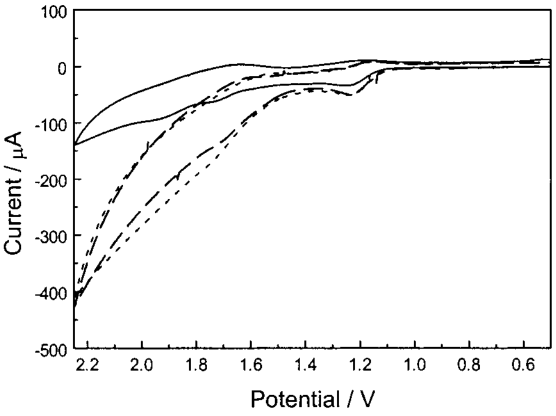

**Figure 2.** Cyclic voltammograms of **1** under nitrogen in 2.5 mL of $C_2H_4Cl_2$/0.7 M $Bu_4NSO_3CF_3$ (glassy carbon working electrode; Ag/Ag$^+$ reference electrode; 50 mV/s): (—) for 10 mM **1**; (- - -) after addition of 50 $\mu$L of methanol; (— —) after addition of 5 $\mu$L of $H_2O$.

The cyclic voltammogram of **1** in $CH_2Cl_2$ exhibits a wave at 1.13 V vs NHE that is fully reversible if the switching potential of the scan is <1.6 V. This wave is assigned to the Ru(II/III) couple, while an irreversible oxidation wave at 1.78 V is assigned to the Pt(II/IV) oxidation.[34] When the voltammetry is performed in $ClCH_2CH_2Cl$ with $Bu_4NSO_3CF_3$ as the electrolyte, another irreversible wave at 1.87 V can be detected. This additional wave is assigned to the Ru(III/IV) couple. Upon addition of methanol to a solution of **1**, the current at the first irreversible oxidative wave is substantially increased over that of a degassed, anhydrous solution of **1** in the absence of methanol (Figure 2). This result is consistent with the catalytic electrooxidation of methanol in conjunction with the Pt(II/IV) oxidative wave. Addition of water to the samples results in further current increases.

The higher currents in the presence of water (Figure 2) suggested the intermediacy of an Ru oxo complex, consistent with earlier reports on the electrooxidation of alcohols by mononuclear ruthenium oxo complexes.[26−28,30−32] Since opening an empty coordination site could be expected to facilitate oxo formation, a chloride ligand was removed from **1** with $TlPF_6$ to form the cationic complex [RuCp(PPh$_3$)($\mu$-dppm)PtCl$_2$]PF$_6$ (**2**). No structural information on the cation of **2** is available at present. However, a chloride-bridged structure similar to that of **1** is a reasonable possibility. Cyclic voltammetry of **2** in the presence of wet methanol produced results similar to those obtained for **1** (data not shown), suggesting that related species are electrochemically generated from **1** and **2** under the conditions of the experiment.

The organic products of bulk electrolyses have been analyzed by a combination of GC and GC/MS. When bulk electrolysis (1.7 V vs NHE) of **1** and dry methanol under nitrogen is carried out for 30 min in 0.7 M $Bu_4NSO_3CF_3/ClCH_2CH_2Cl$, GC analysis of the vacuum-transferred volatile components of the solution indicates that the major product is $CH_2(OCH_3)_2$, the dimethyl acetal of formaldehyde. On the basis of IR and GC comparisons to an authentic sample, the minor product was identified as methyl formate. Observation of $CH_2(OCH_3)_2$ as the major product is consistent with electrooxidation of dry methanol on Pt/Ru anodes, which yields the acetal after acid-catalyzed condensation of the formaldehyde product with excess methanol.[35]

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**Table 2.** Product Distributions for the Electrolyses of Methanol by **1**[a]

| | $\mu$mol of $CH_2(OCH_3)_2$/$\mu$mol of $CHOOCH_3$ (product ratio)[b] | |
|---|---|---|
| charge, C | **1** | **1** + 5 $\mu$L of $H_2O$ |
| 25 | 26.9/11.0 (2.45) | 21.4/12.7 (1.68) |
| 50 | 69.2/29.5 (2.35) | 48.9/36.4 (1.34) |
| 75 | 105.8/69.9 (1.51) | 101.7/86.4 (1.17) |

[a] Electrolyses were performed at 1.7 V vs NHE. A catalyst concentration of 10 mM was used; the methanol concentration was 0.5 M. [b] Determined by GC with respect to heptane as an internal standard and reported as an average of duplicate runs.

Bulk electrolyses of **1** and wet methanol (5 $\mu$L of $H_2O$ added to the cell) under the same conditions as those for the dry methanol experiment result in the same two organic products according to GC analysis. However, the ratio of $CH_2(OCH_3)_2$ to methyl formate is significantly lower (Table 2). Formation of more of the more highly oxidized species in the presence of water is also consistent with the behavior of methanol oxidation on Pt/Ru anodes although water induces $CO_2$ formation in that case.[35] No oxidation products were found when the electrolysis was performed at 1.7 V in the absence of a catalyst.

Condensation of electrochemically generated formaldehyde with excess methanol yields water as a product;[35] therefore, prolonged electrolysis with the catalysts was carried out to determine how the increasing concentration of water affects the distribution of the oxidation products. As shown by the data in Table 2, the presence of water (either added directly or formed in situ by condensation) shifts the distribution toward the more highly oxidized methyl formate. The shift in oxidation products to methyl formate in the presence of water is consistent with participation of Ru oxo species formed by oxidation of **1** with water as the oxygen source.

In contrast to the extensive literature regarding alcohol oxidation by Ru oxo complexes, the onset of catalysis by **1** appears to coincide with oxidation at Pt. Experiments were thus carried out to address the role of the Pt center. Voltammetry of the Pt model compound $Cl_2Pt(\eta^2\text{-dppm})$ (**3**)[36] exhibited an irreversible oxidation wave at 2.21 V with a catalytic increase in the current upon addition of methanol. The voltammetry of the Ru model compound $RuCpCl(\eta^2\text{-dppm})$ (**4**)[37] exhibited a reversible wave at 0.66 V and an irreversible wave at 1.38 V with current increases at the latter upon addition of methanol. Coulombic efficiencies of the electrolyses were calculated from the charges predicted to generate the oxidation products relative to the actual charges passed (after 50 C). Efficiencies of 49%, 49%, and 42% were calculated for the electrolyses of methanol with **1**, **1** + 5 $\mu$L of $H_2O$, and a mixture of **3** and **4**, respectively, at catalyst concentrations of 10 mM. However, the bulk electrolyses occur more rapidly with **1** than with the model complexes. For example, times of 1.7 and 2.8 h were required for the passage of 50 C using **1** and the mixture of **3** and **4**, respectively. The data suggest that the bimetallic structure of **1** is responsible for the increased efficiency; however, direct comparisons are complicated by the greater oxidation potential of **4** relative to that of **1**.

Analysis of the metal-containing compounds by $^{31}P$ NMR spectroscopy after short periods of bulk electrolysis reveals the presence of several bimetallic species with Ru($\mu$-dppm)Pt moieties, as well as the presence of $Cl_2Pt(\eta^2\text{-dppm})$. After exhaustive bulk electrolysis, $Cl_2Pt(\eta^2\text{-dppm})$ is the only identifiable metal species. Since $Cl_2Pt(\eta^2\text{-dppm})$ is inactive for methanol electrooxidation at potentials associated with the electrocatalytic oxidation of methanol with **1**, its formation is undoubtedly related to deactivation of the catalyst.

In conclusion, electrochemical oxidations of complexes **1** and **2** in the presence of MeOH lead to considerable enhancement of the oxidative currents, consistent with the catalytic oxidation of methanol. In the presence of dry methanol, the major organic product from the bulk electrolysis of **1** is $CH_2(OCH_3)_2$. Subsequent addition of water is found to further enhance the currents, consistent with the formation of an Ru oxo intermediate. The organic product from the oxidation of **1** in solutions containing wet methanol is the more highly oxidized methyl formate. Further investigations of the electrocatalysis using **1** and related complexes are underway.

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**Supporting Information Available:** An X-ray crystallographic file, in CIF format, for the structure determination of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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