Final Technical Report
"Bimetallic Complexes as Methanol Oxidation Catalysts"
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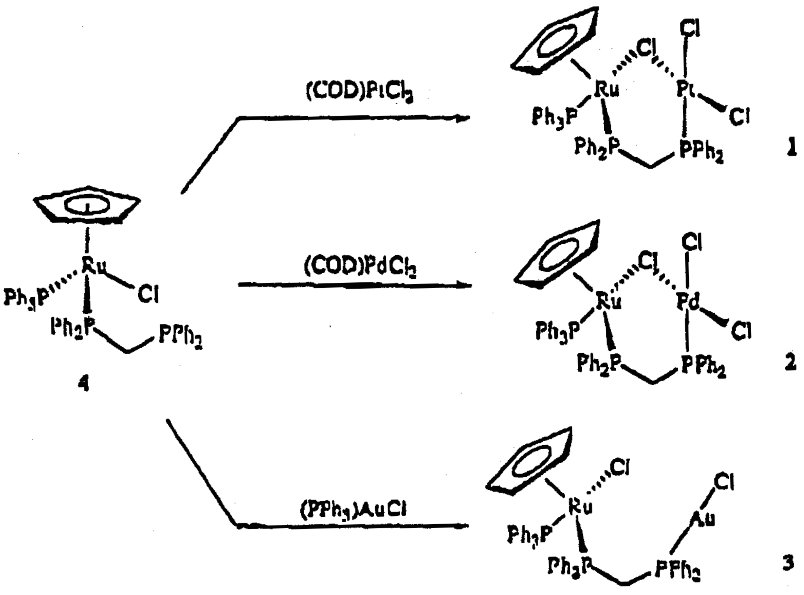
A. STATEMENT OF PROBLEM

Our work on the electrocatalyzed oxidation of methanol was initially motivated by the interest in methanol as an anodic reactant in fuel cells. The literature on electrochemical oxidation of alcohols can be roughly grouped into two sets: fuel cell studies and inorganic chemistry studies. Work on fuel cells primarily focuses on surface-catalyzed oxidation at bulk metal anodes, usually Pt or Pt/Ru alloys. In the surface science/electrochemistry approach to these studies, single molecule catalysts are generally not considered. In contrast, the inorganic community investigates the electrooxidation of alcohols in homogeneous systems. Ruthenium complexes have been the most common catalysts in these studies. The alcohol substrates are typically either secondary alcohols (*e.g.*, isopropanol) such that the reaction stops after 2 e^- oxidation to the ketone or primary alcohols (*e.g.*, benzyl alcohol) so that competition between 2 e^- oxidation to the aldehyde and 4 e^- oxidation to the carboxylic acid can be observed. Methanol, which can also undergo 6 e^- oxidation to CO_2, rarely appears in the homogeneous catalysis studies. Surface studies have shown that two types of metal centers with different functions result in more effective catalysts than a single metal; however, application of this concept to homogenous systems has not been demonstrated. The major thrust of our work is to apply this insight from the surface studies to homogenous catalysis. Even though homogeneous systems would not be appropriate models for active sites on Pt/Ru anodes, it is possible that heterobimetallic catalysts could also utilize two metal centers for different roles. Starting from that perspective, this work involves the preparation and investigation of heterobinuclear catalysts for the electrochemical oxidation of methanol.

B. SUMMARY OF MOST IMPORTANT RESULTS

Preparation and Characterization of Complexes 1-3. $CpRu(Cl)(PPh_3)(\eta^1\text{-dppm})$ (4) was reacted with $Pt(COD)Cl_2$ to afford 77% yield of the Ru/Pt complex $CpRu(PPh_3)(\mu\text{-}Cl)(\mu\text{-dppm})PtCl_2$ (1) (Scheme 1). The Ru/Pd complex $CpRu(PPh_3)(\mu\text{-}Cl)(\mu\text{-dppm})PdCl_2$ (2) was prepared analogously in 71% yield from the reaction of 4 with $(COD)PdCl_2$ at room temperature. Treatment of 4 with $AuPPh_3Cl$ affords the heterobimetallic complex $CpRu(PPh_3)(Cl)(\mu\text{-dppm})AuCl$ (3) in 66% yield.

Scheme 1



Confirmation of the structure of 1 was obtained via X-ray crystallography (Figure 1).[77] The bond lengths and bond angles of 1 are standard, with the expected square planar geometry at Pt and three-legged piano stool configuration at Ru. The crystal structure of 2 was predictably similar to that of 1. Confirmation of the structure of 3 was obtained via X-ray crystallography. As shown in Figure 2, the complex exhibits no interaction between the Ru and Au centers beyond what could be transmitted via through bond interactions involving the dppm ligand. This situation differs from that in 1 and 2, in which the Cl bridge links the metal atoms more closely. The bond lengths and bond angles of the structure are standard, with the expected square planar geometry at Pt and linear configuration at Au.

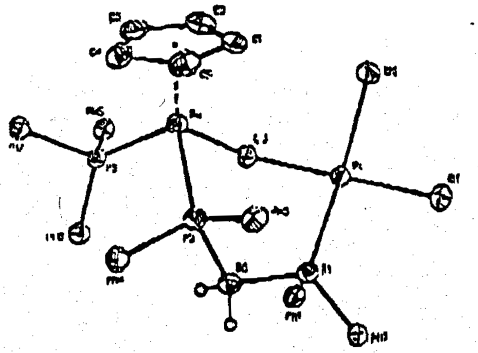


Figure 1. Thermal ellipsoids diagram of 1 showing the crystallographic numbering scheme. Thermal ellipsoids are drawn at the 40% probability level. Phenyl rings and most hydrogens are omitted for clarity. Selected distances (Å) and angles (deg) are as follows: Pt-Cl3 2.3179(7), Pt-Cl1 2.2882(7), Pt-Cl2 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).

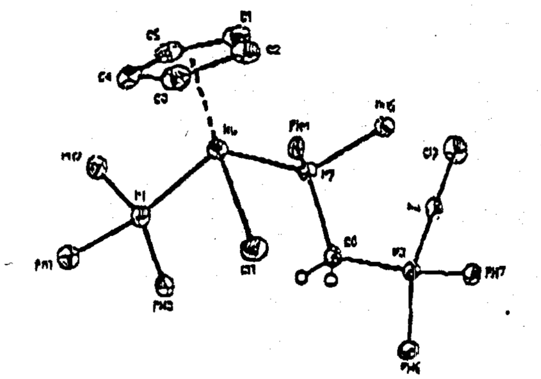


Figure 2. Thermal ellipsoids diagram of 3 showing the crystallographic numbering scheme. Thermal ellipsoids are drawn at the 40% probability level. Phenyl rings and most hydrogens are omitted for clarity. Selected distances (Å) and angles (deg) are as follows: Ru-P2 2.2946(11), Ru-Cl1 2.4598(11), Au-P3 2.2288(12), Au-Cl2 2.2860(13), P2-Ru-P1 98.36(4), P2-Ru-Cl1 88.95(4), P1-Ru-Cl1 92.65(4), P3-Au-Cl2 179.36(5).

Cyclic Voltammetry of Complexes 1-3. Cyclic voltammetry of the Ru/Pt complex 1 in CH_2Cl_2/TBAH exhibits a couple at 1.13 V vs. NHE and an irreversible oxidation wave at 1.78 V. The wave at 1.13 V is fully reversible if the switching potential of the scan is < 1.6 V, and is assigned to the Ru(II/III) couple. In comparison, the Ru(II/III) wave of the mononuclear compound 4 is observed at 0.56 V. The positive shift of nearly 600 mV in the redox potential of 1 indicates a significant loss in electron density at the metal via the chloride bridge to the coordinatively unsaturated Pt center. Further electrochemical evidence of such an interaction comes from the oxidation wave from the platinum center. The irreversible wave at 1.78 V is assigned to the Pt(II/IV) oxidation. The Pt oxidation at 1.78 V contrasts with that of the starting material, Pt(COD)Cl_2, which shows no oxidation wave within the solvent window of CH_2Cl_2 (< 2.0 V). When the voltammetry is performed in DCE/TBAT (DCE = 1,2-dichloroethane, TBAT = tetrabutylammonium trifluoromethanesulfonate), another irreversible wave at 1.87 V can be detected. This additional wave is assigned to the Ru(III/IV) couple.

Cyclic voltammetry of the Ru/Pd system 2 in DCE/TBAT exhibits a quasireversible couple at 1.29 V vs. NHE and an irreversible oxidation wave at 1.45 V. The wave at 1.29 V is assigned to the Ru(II/III) couple. This wave is shifted about 160 mV positive compared to that of the Ru/Pt complex 1. The shift is consistent with electron donation through the Cl bridge to the more electron-deficient Pd center of 2 (the first oxidation wave of the model compound $PdCl_2(\eta^2$-dppm) is approximately 200 mV positive of its Pt analogue). The irreversible wave at 1.45 V is assigned to the Pd(II/IV) oxidation based on comparisons with the cyclic voltammogram of $PdCl_2(\eta^2$-dppm).

The Ru/Au complex 3 exhibits a pair of quasireversible couples at 0.86 V and 1.40 V vs. NHE in DCE/TBAT. The wave at 0.86 V is assigned to the Ru(II/III) couple, while the wave at 1.40 V is attributed to the Au(I/III) oxidation. The latter wave is similar to that of the starting material, $Au(PPh_3)Cl$, which has been reported to oxidize at 1.68 V vs. NHE in CH_2Cl_2. As discussed above, the Ru(II/III) wave of the mononuclear compound 4, is observed at 0.56 V. We have also examined the cyclic voltammetric behavior of the mononuclear Ru model complex, CpRuCl(η^2-dppm) (5). The Ru(II/III) couple of 5 occurs at 0.61 V, while the Ru(III/IV) couple is observed at 1.38 V. Overall, the first two redox potentials of 3 more closely resemble their mononuclear model compounds than do the first two redox potentials of 1 or 2. This is consistent with the crystal structure, which suggests that interactions between the metal centers of 3 are likely to be minimal, while coupling of the metals via the μ-Cl bridges of 1 and 2 is more substantial.

Catalytic Electrooxidation of Methanol By Complexes 1-3. Electrochemical oxidation of $CpRu(PPh_3)(\mu\text{-}Cl)(\mu\text{-}dppm)PtCl_2$ (1) in the presence of MeOH leads to considerable enhancement of the oxidative currents, consistent with the catalytic oxidation of methanol. Upon addition of methanol to a solution of 1, the current at the irreversible oxidative wave at 1.78 V vs. NHE is increased over that of a degassed, anhydrous solution of 1 in the absence of methanol (Figure 3). This result is consistent with the catalytic electrooxidation of methanol in conjunction with the Pt(II/IV) oxidative wave.

The organic products of bulk electrolysis have been analyzed by GC and GC/MS. When bulk electrolysis of 1 with dry methanol (1.7 V vs. NHE, 30 min, 0.7 M DCE/TBAT)

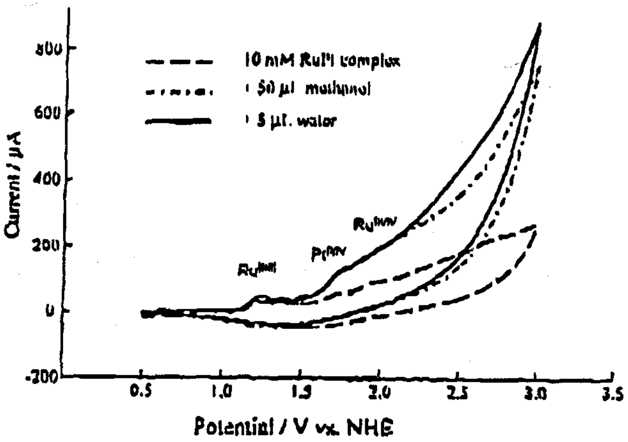


Figure 3. Cyclic voltammograms of 1 under nitrogen in 2.5 mL of DCE/0.7 M TBAT; glassy carbon working electrode; Ag/Ag⁺ reference electrode

Table 1. Product Distributions and Current Efficiencies for the Electrochemical Oxidation of Dry Methanol by 1, 2 and 3[a]

product ratio (μmoles of $CH_2(OCH_3)_2$ / $HCOOCH_3$)[b]

Charge / C	Ru/Pt (1)	Ru/Pd (2)	Ru/Au (3)	Ru (5)[c]
25	2.45	3.18	1.44	n.o.[d]
50	2.35	2.41	1.23	n.o.[d]
75	1.51	1.54	0.98	n.o.[d]
100	1.23	0.94	0.59	n.o.[d]
130	1.20	0.87	0.46	∞[e]
Efficiency	18.6	24.6	25.4	3.2

[a] Electrolyses were performed at 1.7 V vs. NHE. A catalyst concentration of 10 mM was used. Methanol concentration was 0.35 M. [b] Determined by GC with respect to heptane as an internal standard. Each ratio is reported as an average of 2-5 experiments. [c] Ru = $CpRuCl(\eta^2\text{-}dppm)$. [d] No products observed. [e] Only $CH_2(OCH_3)_2$ observed.

is carried out under nitrogen, GC analysis indicates that the major product is $CH_2(OCH_3)_2$, the dimethyl acetal of formaldehyde, while the minor product is methyl formate (Table 1). Bulk electrolysis of **1** and wet methanol (5 μL H_2O added to the cell) under the same conditions results in the same organic products by GC analysis. However, the ratio of $CH_2(OCH_3)_2$ to methyl formate is significantly lower (Table 2). No oxidation products were found when the electrolysis was performed at 1.7 V in the absence of a catalyst.

Formation of $CH_2(OCH_3)_2$ by condensation of formaldehyde with excess methanol yields water. 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 Tables 1 and 2, the presence of water (either directly added or formed *in situ* by condensation) shifts the distribution toward the more highly oxidized methyl formate. This shift in product ratios is consistent with participation of Ru oxo species formed by oxidation of **1** with water as the oxygen source. Interestingly, despite the extensive literature precedent for alcohol oxidation by Ru oxo complexes, the onset of catalysis by **1** appears to coincide with oxidation at Pt.

Table 2. Product Distributions for the Electrochemical Oxidation of Wet Methanol by **1**, **2** and **3**[a,b]

product ratio (μmoles of $CH_2(OCH_3)_2$ / $HCOOCH_3$)[c]

Charge / C	Ru/Pt (3)	Ru/Pd (1)	Ru/Au (2)	Ru (5)[d]
25	1.68	1.38	1.26	n.o.[e]
50	1.34	0.98	1.05	n.o.[e]
75	1.17	0.84	0.97	n.o.[e]
100	0.67	0.70	0.41	n.o.[e]
130	0.41	0.54	0.34	0.33
Efficiency	19.5	20.6	26.1	7.2

[a]Electrolyses were performed at 1.7 V vs. NHE. A catalyst concentration of 10 mM was used. Methanol concentration was 0.35 M. [b]Water (5 μL) was added to the cell. [c]Determined by GC with respect to heptane as an internal standard. Each ratio is reported as an average of 2-5 experiments. [d]Ru = CpRuCl(η^2-dppm). [e]No products observed.

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(μ-dppm)Pt moieties, consistent with ligand exchange during the reaction. After exhaustive bulk electrolysis, $Cl_2Pt(\eta^2$-dppm) is the only identifiable metal species. Since $Cl_2Pt(\eta^2$-dppm) is inactive for methanol electrooxidation at potentials used in the electrocatalytic oxidation of methanol with **1**, its formation is undoubtedly related to deactivation of the catalyst. Interestingly, phosphine oxides derived from the dppm ligands could not be detected in the ^{31}P NMR spectra, suggesting that phosphine oxidation is not a major degradation pathway.

The cyclic voltammogram of the Ru/Pd complex $CpRu(PPh_3)(\mu$-Cl)(μ-dppm)$PdCl_2$ (**2**) after addition of methanol (Figure 4a) shows a minimal current increase at the Ru(II/III) couple followed by a significant increase at the Pd(II/IV) wave. In contrast, methanol oxidation with the Ru/Au complex CpRu(PPh$_3$)Cl(μ-dppm)AuCl (3) occurs at the Ru(III/IV) wave, which is similar to the behavior of simple mononuclear Ru complexes that catalyze alcohol oxidation. Addition of 5 μL of water to the samples results in further current increases for both 2 and 3. Cyclic voltammograms of the model Ru complex CpRuCl(η^2-dppm) (5) under the same conditions as 1-3 exhibit considerable increases in the voltammetric current in the presence of methanol. However, the onset of oxidation occurs at potentials far more positive relative to the Ru(III/IV) wave of the bimetallic complexes.

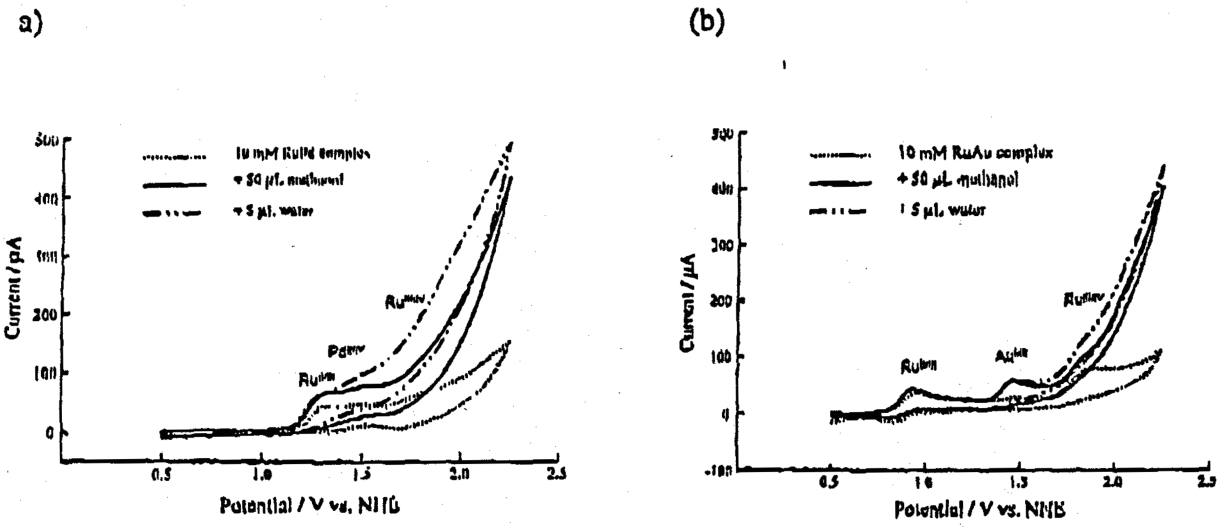


Figure 4. Cyclic voltammograms of 2 and 3 under N$_2$ in 2.5 mL of DCE/0.7 M TBAT; glassy carbon working electrode; Ag/Ag$^+$ reference electrode; 50 mV/s. (a) 2. (b) 3.

Differences among the behavior of 1, 2 and 3 can be seen in the evolution of product distributions shown in Tables 1 and 2, which present the average product ratios of formaldehyde dimethyl acetal to methyl formate formed during bulk electrolysis of dry and wet methanol. The presence of water consistently shifts the product ratios toward the four-electron oxidation product, HCOOCH$_3$. This trend is reflected by all the complexes and can be seen both in the initial product ratios for wet vs. dry samples and in the tendency toward production of more methyl formate in the dry samples as the reaction progresses. The time evolution of product ratios in the dry samples presumably arises from water that is generated *in situ* during the condensation of formaldehyde and formic acid with excess methanol.

The potential for bulk electrolyses (1.7 V vs. NHE) was chosen during the initial studies on Ru/Pt complex 1, which exhibits its rise in catalytic current coincident with the Pt(II/IV) wave at that potential. For comparison purposes, bulk electrolyses with complexes 2, 3, and 5 were performed at the same potential. Thus, for bimetallic complexes 1-3, oxidation was positive of both the Ru(II/III) couple and the first oxidative wave for the second metal. Only in model compound 5 had Ru reached the Ru(IV) oxidation state during the bulk electrolyses. The difference in the identity and oxidation state of the second metal appears to be reflected in the product ratios. At early stages of the reaction, all three bimetallic complexes afford higher proportions of dimethyl acetal. However, in oxidation of dry samples with Ru/Pt complex 1 the acetal continues to predominate even at later stages of the reaction (Tables 1 and 2). The Ru/Pd complex 2 begins to yield HCOOCH$_3$ as the major product as the reaction progresses and similar (but more rapid) changes in behavior are observed for Ru/Au complex 3. In contrast, Ru complex 5 affords only trace amounts of dimethyl acetal under dry conditions. Under wet conditions, 5 favors methyl formate formation but the reaction is very slow.

Current efficiencies are also summarized in Tables 1 and 2. These values are the ratio of the charge necessary to produce the observed yields of $CH_2(OCH_3)_2$ and $HCOOCH_3$ to the total charge passed during bulk electrolysis. Although the current efficiencies for heterobinuclear complexes 1-3 were moderate (19 to 26%), they are significantly higher than the 3.2 and 7.2% current efficiencies obtained from the mononuclear model compound $CpRuCl(\eta^2\text{-dppm})$ (5) under dry and wet conditions, respectively. Although the nature of the metal-metal interaction varies in complexes 1-3, in each case the presence of the second metal center apparently results in enhanced catalytic activity.

C. LIST OF PUBLICATIONS

1. "Synthesis and Electrochemical Oxidation of Bridged Ruthenium/Platinum Complexes of 1,10-Phenanthroline-5,6-diolate," Hill, P.L.; Lee, L.Y.; Younkin, T.R.; Orth, S.D.; McElwee-White, L., *Inorg. Chem.*, **1997**, *36*, 5655-5657.

2. "Bimetallic Pt/Ru Complexes as Catalysts for the Electrooxidation of Methanol," Tess, M.E.; Hill, P.L.; Torraca, K.E.; Kerr, M.E.; Abboud, K.A.; McElwee-White, L., *Inorg. Chem.*, **2000**, *39*, 3942-3944.

3. "Electrochemical Oxidation of Methanol with Ru/Pd, Ru/Pt and Ru/Au Heterobimetallic Complexes," Matare, G.J.; Tess, M.E.; Abboud, K.A.; Yang, Y.; McElwee-White, L., *Organometallics*, in press (web posted 1/15/02).

D. LIST OF PRESENTATIONS

Invited Presentations at Conferences:

1. "Bimetallic Complexes as Methanol Oxidation Catalysts," Fourth DOE/BES Research Conference on Homogeneous Catalysis and Organometallic Chemistry, June 1998, Baltimore, Maryland.

2. "Heterobimetallic catalysts for the electrooxidation of methanol," McElwee-White, L.; Tess, M.E.; Torraca, K.E. Symposium on Molecular Crystallography in the Service of Inorganic and Organometallic Chemistry, 220th National Meeting of the American Chemical Society, August 2000, Washington, D.C.

3. "Heterobimetallic catalysts for the electrochemical oxidation of methanol," Symposium on Multidentate Ligand Design, 222nd National Meeting of the American Chemical Society, August 2001, Chicago, Illinois, Abstract INOR 17.

Contributed Presentations at Conferences:

1. "Synthesis And Oxidation Of Heterobimetallic Ru/Pt Complexes Of 1,10-Phenanthroline-5,6-dione," Lee, L.Y.; Hill, P.L.; Orth, S.D.; Younkin, T.R.; and McElwee-White, L. 7th Symposium on the Latest Trends in Organic Synthesis, October 1996, Gainesville, Florida
2. "Synthesis and Electrooxidation of Bridged Ruthenium/Platinum Complexes of 1,10-Phenanthroline-5,6-Diolate," Lee, L.Y.; Hill, P.L.; Orth, S.D.; Younkin, T.R.; McElwee-White, L. 1997 Florida Catalysis Conference, April 1997, Palm Coast, Florida.
3. "Synthesis and Electrooxidation of Bridged Ruthenium/Platinum Complexes of 1,10-Phenanthroline-5,6-Diolate," Lee, L.Y.; Hill, P.L.; Orth, S.D.; Younkin, T.R.; and McElwee-White, L. 1997 Annual Meeting of the Florida Sections of the American Chemical Society, May 1997, Orlando, Florida
4. "The Synthesis and Electrochemical Characterization of Ru/Pt Heterobimetallic Complexes," Kerr, M.E.; Lee, L.Y.; Hill, P.L.; McElwee-White, L. 1998 Florida Catalysis Conference, April 1998, Palm Coast, Florida.
5. "Synthesis and Electrooxidation Of Bridged Mo/Pt Bimetallic Complexes," Lee, L.Y.; Hill, P.L.; Kerr, M.; McElwee-White, L. 1998 Florida Catalysis Conference, April 1998, Palm Coast, Florida.
6. "Synthesis and Electrooxidation Of Bridged Mo/Pt Bimetallic Complexes," Lee, L.Y.; Hill, P.L.; Kerr, M.; McElwee-White, L. 1998 Florida Annual Meeting and Exposition, May 1998, Orlando, Florida.
7. "The Synthesis and Electrochemical Characterization of Ru/Pt Heterobimetallic Complexes," Kerr, M.E.; Lee, L.Y.; Hill, P.L.; McElwee-White, L. 1998 Florida Annual Meeting and Exposition, May 1998, Orlando, Florida.
8. "The Synthesis and Electrochemical Characterization of Ru/Pt Heterobimetallic Complexes," Kerr, M.E.; Lee, L.Y.; Hill, P.L.; McElwee-White, L. 216th National Meeting of the American Chemical Society, August 1998, Boston, Massachusetts. Abstract INOR 513.
9. "Investigations into the Electrocatalytic Oxidation of Methanol Using Heterobimetallic Systems," Torraca, K.E.; Hill, P.L.; Lee, L.Y.; Kerr, M.; McElwee-White, L. 1999 Florida Catalysis Conference. April 1999, Palm Coast, Florida.
10. "Investigations into the Electrocatalytic Oxidation of Methanol Using Heterobimetallic Systems," Tess, M.E.; Torraca, K.E.; Hill, P.L.; McElwee-White, L. 2000 Florida Catalysis Conference, April 2000, Palm Coast, Florida.
11. "Heterobimetallic catalysts for the electrooxidation of methanol." McElwee-White, L.;

Tess, M.E.; Torraca, K.E. 220th National Meeting of the American Chemical Society, August 2000, Washington, D.C. Abstract INOR 325.

12. "Heterobimetallic catalysts for the electrooxidation of methanol," Matare, G.; Tess, M.E.; Torraca, K.E.; McElwee-White, L. 221st National Meeting of the American Chemical Society, April 2001, San Diego, California. Abstract INOR 103.

13. "Heterobimetallic catalysts for the electrooxidation of methanol," Matare, G.; Tess, M.E.; Torraca, K.E.; Yang, Y.; McElwee-White, L. 2001 Florida Catalysis Conference, April 2001, Palm Coast, Florida.

14. "Electrochemical Oxidation of Methanol Catalyzed by Heterobimetallic Complexes," Matare, G.J.; Tess, M.E.; Abboud, K.A.; Yang, Y.; McElwee-White, L., 2001 Gordon Research Conference on Organometallic Chemistry, July 2001, Newport, Rhode Island.

E. PARTICIPATING SCIENTIFIC PERSONNEL

Graduate Students:

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F. UNEXPENDED FUNDS

none