Selective electrochemical oxidation of methanol to dimethoxymethane using Ru/Sn catalysts

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Abstract

The Ru/Sn heterobimetallic complexes $CpRu(PPh_3)_2(SnCl_3)$ (**1**), $(Ind)Ru(PPh_3)_2(SnCl_3)$ (**2**) and $CpRu(TPPMS)_2(SnCl_3)$ (**3**) were studied as homogeneous catalysts for the electrooxidation of methanol to dimethoxymethane (DMM) and methyl formate (MF). Complexes **1**, **2** and **3** exhibited significantly higher turnover numbers and current efficiencies than the corresponding mononuclear complexes $CpRu(PPh_3)_2Cl$ (**4**) and $CpRu(TPPMS)_2Cl$ (**5**). The highest current efficiency (92.4%) and selectivity (100%) for DMM formation were obtained from the electrooxidation of methanol with complex **3**.
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1. Introduction

The selective oxidation of methanol has been of interest as a route to several important organic chemicals such as formaldehyde [1], dimethoxymethane (DMM) [2–5] and methyl formate (MF) [6]. Direct conversion of methanol to DMM by heterogeneous catalysis [2–5] has been recently investigated as a possible replacement for the two-step process involving oxidation of methanol to formaldehyde followed by the condensation of the methanol/formaldehyde mixtures to yield DMM. Rhenium oxides [2,3] and heteropolyacids with Keggin structures [4,5] have been reported to catalyze the selective oxidation of methanol vapor to DMM, typically at temperatures above 400 K. Among these catalysts, $SbRe_2O_6$ [2,3] has the highest selectivity for DMM, converting 6.5% of the methanol feed at 573 K with a selectivity as high as 92.5%.

Electrooxidation of methanol typically yields a complex mixture of products (Scheme 1), with the major product and selectivity dependent upon the reaction conditions [7–10]. Product distributions have been determined in conjunction with studies on direct methanol fuel cells [7,9–16], using Pt black [7,11,12], Pt/Ru [11,12] and Pt/Nafion (Pt-SPE) [9,10,13] anodes. The general trend is that the absence of water and lower methanol concentrations favor formaldehyde formation, with yields of DMM rising as the concentration of methanol increases. The presence of water favors formation of MF and/or complete oxidation to CO_2.

We previously reported Ru/Pt, Ru/Pd and Ru/Au heterobimetallic catalysts for the electrooxidation of methanol [17–19]. The non-Ru metal center was shown to improve the catalytic properties of these complexes as compared to the mononuclear model compound $CpRu(\eta^2$-dppm)Cl. Related beneficial effects of a Lewis acidic tin center in a thermal reaction had previously been reported for $CpRu(PPh_3)_2(SnCl_3)$ (**1**), which selectively oxidizes methanol to methyl acetate at elevated temperatures [20,21]. In order to explore the possible role of the second metal center as a Lewis acidic site, the Ru/Sn complexes $CpRu(PPh_3)_2(SnCl_3)$ (**1**), $(Ind)Ru(PPh_3)_2(SnCl_3)$ (**2**) and $CpRu(TPPMS)_2(SnCl_3)$ (**3**) were investigated as catalysts for the electrooxidation of methanol [21]. We now report the selective electrooxidation of methanol to DMM using Ru/Sn complexes **1**–**3** as catalysts.

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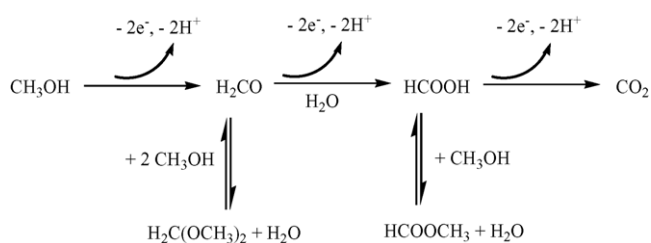
Scheme 1. Electrooxidation of methanol.

2. Experimental

2.1. General considerations

Standard Schlenk/vacuum techniques were used throughout. All NMR solvents were degassed via three freeze–pump–thaw cycles and stored over 4 Å molecular sieves. ^{1}H and ^{31}P NMR spectra are referenced to the residual proton in the deuterated solvent and to 85% H_3PO_4, respectively. High-resolution mass spectrometry was performed by the University of Florida analytical service. CpRu(PPh$_3$)$_2$Cl [22], (Ind)Ru(PPh$_3$)$_2$(SnCl$_3$) [23] and CpRu(PPh$_3$)$_2$(SnCl$_3$) [21] were prepared as previously described. TPPMS was prepared using a slight modification of the published procedure [24]. Tetra-*n*-butylammonium triflate (TBAT) and RuCl$_3$·xH$_2$O were purchased from Sigma-Aldrich. (Ind)Ru(PPh$_3$)$_2$Cl was purchased from Strem Chemicals. All other starting materials were purchased in reagent grade purity and used without further purification.

Electrochemical experiments were performed at ambient temperature in a glove box under a nitrogen atmosphere using an EG&G PAR model 263A potentiostat/galvanostat. Cyclic voltammetry (CV) was performed with a normal three-electrode configuration consisting of a glassy carbon working electrode (3 mm diameter), a Pt flag counterelectrode and a Ag/Ag$^+$ reference electrode. For experiments performed in 1,2-dichloroethane (DCE) or methanol, the reference electrode consisted of an acetonitrile or methanol solution, respectively, containing freshly prepared 0.01 M AgNO$_3$ and 0.1 M TBAT along with a silver wire. The Ag$^+$ solution and silver wire were contained in a 75 mm glass tube fitted at the bottom with a Vycor tip. Constant potential electrolysis was carried out with similar equipment except for the working electrode being replaced with a vitreous carbon electrode. All potentials are reported versus NHE and are not corrected for the junction potential of the Ag/Ag$^+$ reference electrode. The E^0 values for the ferrocenium/ferrocene couple in 0.7 M TBAT/DCE and 0.1 M TBAT/MeOH were +0.50 and +0.795 V, respectively.

Electrolysis products were analyzed by gas chromatography on a Shimadzu GC-17A chromatograph containing a 15 m × 0.32 mm column of AT-WAX (Alltech, 0.5 μm film) on fused silica. The column was attached to the injection port with a neutral 5 m × 0.32 mm AT-WAX deactivated guard column. The electrolysis products were quantitatively determined with the use of *n*-heptane as an internal standard. Products were identified by comparison to authentic samples.

2.2. Synthesis of the Ru–TPPMS complexes

2.2.1. CpRu(TPPMS)$_2$Cl (**5**)

In a 250 mL flask, CpRu(PPh$_3$)$_2$Cl (1.0 g, 1.4 mmol) and TPPMS (0.89 g, 2.3 mmol) in 100 mL of toluene were refluxed under N$_2$ for 2 days. The resulting orange solid was then collected on a medium frit, washed with approximately 200 mL of diethyl ether and dried under vacuum at 80 °C. Yield: 0.97 g, 90%. ^{1}H NMR (DMSO-d$_6$): δ 7.72–7.52 (m, 4H), 7.25–7.08 (m, 24H), 4.07 (s, 5H, Cp) ppm. ^{31}P NMR (DMSO-d$_6$): δ 40.1 (s, PPh$_3$) ppm. HRMS (FAB): calc. for C$_{41}$H$_{37}$O$_8$Na$_2$ClP$_2$RuS$_2$ m/z 932.0325 [MH$^+$ − Cl]; found 932.0313. Anal. Calc. for C$_{41}$H$_{37}$O$_8$Na$_2$ClP$_2$RuS$_2$: C, 50.96; H, 3.86. Found: C, 50.71; H, 3.68.

2.2.2. CpRu(TPPMS)$_2$(SnCl$_3$) (**3**)

CpRu(TPPMS)$_2$Cl (0.71 g, 0.76 mmol) and SnCl$_2$ (0.17 g, 0.89 mmol) in 25 mL ethanol were stirred under N$_2$ at room temperature overnight. The solution was then evaporated to dryness and the resulting yellow solid recrystallized from ethanol/diethyl ether. Yield: 0.73 g, 85%. ^{1}H NMR (CD$_3$OD): δ 7.86–7.70 (m, 4H), 7.35–7.08 (m, 24H), 4.65 (s, 5H, Cp) ppm. ^{31}P NMR (CD$_3$OD): δ 46.0 (s, PPh$_3$) ppm. Anal. Calc. for C$_{41}$H$_{37}$O$_8$Na$_2$Cl$_3$P$_2$RuS$_2$Sn: C, 42.60; H, 3.23. Found: C, 42.87; H, 3.07.

3. Results and discussion

3.1. Synthesis of CpRu(TPPMS)$_2$Cl (**5**) and CpRu(TPPMS)$_2$(SnCl$_3$) (**3**)

In our hands, the literature procedure for the synthesis of **5** [25] yielded complex reaction mixtures in which unreacted triphenylphosphine monosulfonate (TPPMS) and TPPMS oxide were the only identifiable compounds. Samples of **5** were instead prepared by an alternate route involving displacement of PPh$_3$ from complex **4** with TPPMS. Heterogeneous reaction between **4** and TPPMS in refluxing toluene yielded **5** as an orange, moderately air stable solid. The ^{31}P NMR spectrum of **5** is very similar to that of **4**, consisting of a singlet at 40 ppm.

The Ru/Sn complex **3** was prepared in an analogous manner to **1** [21] by reacting **5** with a slight excess of SnCl$_2$ in refluxing ethanol. The resulting yellow solid is moderately stable in air and in solutions of methanol and acetonitrile, but decomposes rapidly when dissolved in water. As expected from the ^{31}P{^{1}H} NMR spectrum of CpRu(PPh$_3$)$_2$(SnCl$_3$) [21], the ^{31}P NMR spectrum of **3** consists of one singlet at 46 ppm.

Table 1
Formal potentials for complexes **1**–**5**[a]

Complex	E_{pa} (V)	$E_{1/2}$[b] (V)	ΔE_p (mV)	i_{pa}/i_{pc}
CpRu(PPh$_3$)$_2$(SnCl$_3$) (**1**)	1.48	1.44	85	0.92
(Ind)Ru(PPh$_3$)$_2$(SnCl$_3$) (**2**)	1.39	1.34	106	0.95
CpRu(TPPMS)$_2$(SnCl$_3$) (**3**)	1.58			
CpRu(TPPMS)$_2$(SnCl$_3$) (**3**)[c]	1.29			
CpRu(PPh$_3$)$_2$Cl (**4**)	0.87	0.82	90	1.03
CpRu(TPPMS)$_2$Cl (**5**)	0.93	0.89	104	1.06
CpRu(TPPMS)$_2$Cl (**5**)[c]	0.79	0.73	90	0.94
CpRu(PPh$_3$)$_2$Cl[d]	0.93	0.87	120	1.00
(Ind)Ru(PPh$_3$)$_2$Cl[e]		0.69	66	

[a] All potentials obtained in 0.7 M TBAT/DCE unless otherwise specified.
[b] $E_{1/2}$ reported for reversible waves.
[c] Potential obtained in 0.1 M TBAT/MeOH.
[d] Ref. [26], potential originally reported vs. SCE.
[e] Ref. [27], potential originally reported vs. SCE.

3.2. Cyclic voltammetry of **1**–**5**

The cyclic voltammograms of complexes **1**–**5** each display a single oxidation wave in the potential range of 0.50–1.60 V. This oxidation process has previously been assigned for CpRu(PPh$_3$)$_2$Cl [26] and (Ind)Ru(PPh$_3$)$_2$Cl [27] (Table 1) as the reversible one electron oxidation of the Ru metal center. Based on this precedent, the oxidation waves observed for **1**–**5** have been assigned to the Ru(II/III) couple. When analyzed in DCE, the one electron oxidation of complex **4** (Fig. 1) at 0.82 V and complex **5** at 0.89 V are chemically reversible with $i_{pa}/i_{pc} \approx 1$ (Table 1). When small amounts of methanol are added to the DCE solutions, no significant change is observed in the cyclic voltammograms of **4** and **5** at potentials less than 1.60 V.

The CV of **1** in DCE exhibits a reversible Ru(II/III) couple at 1.44 V (Fig. 2). The Ru(II/III) couple is shifted by approximately 600 mV positive with respect to the corresponding Ru(II/III) wave of CpRu(PPh$_3$)$_2$Cl (**4**). This positive shift is consistent with the electron-withdrawing SnCl$_3$$^-$ ligand rendering the Ru center of **1** electron-poor relative to that of complex **4**. Sn(II) is not redox active within the solvent window (-0.50 to 2.5 V versus NHE) for these experiments. In the presence of methanol, there is a significant increase in the current that coincides with the oxidation of the Ru metal center (Fig. 2). This effect is indicative of an electrocatalytic oxidation process.

The CV of **2** is very similar to that of complex **1**, exhibiting a reversible Ru(II/III) couple in DCE (Table 1). The Ru(II/III) couple, however, at 1.34 V is 100 mV negative with respect to the analogous Ru(II/III) couple of complex **1**. This shifting of the II/III couple [27] is due to additional electron density associated with the indenyl ligand. The current rise from electrooxidation of methanol by **2** also coincides with its Ru(II/III) redox wave, as evidenced by a significant increase in the current at 1.34 V in the presence of methanol.

The CV of **3** exhibits a single irreversible wave in DCE at 1.58 V (Table 1). This irreversible redox wave has been assigned to the oxidation of the metal center from Ru(II) to Ru(III). Cyclic voltammetry of **3** in DCE exhibits a significant increase in the catalytic current at the Ru(II/III) wave when methanol is introduced. A similar catalytic effect was observed for **1** and **2**.

3.3. Bulk electrolysis of methanol

Complexes **1**–**5** all exhibited some catalytic activity for the electrooxidation of methanol in the potential range of 1.55–1.70 V in DCE or 1.25–1.40 V in neat methanol (Table 2). The bimetallic complexes **1**–**3** are more active, exhibiting greater TON and current efficiencies than the corresponding RuCl complexes **4** and **5**. Control experiments
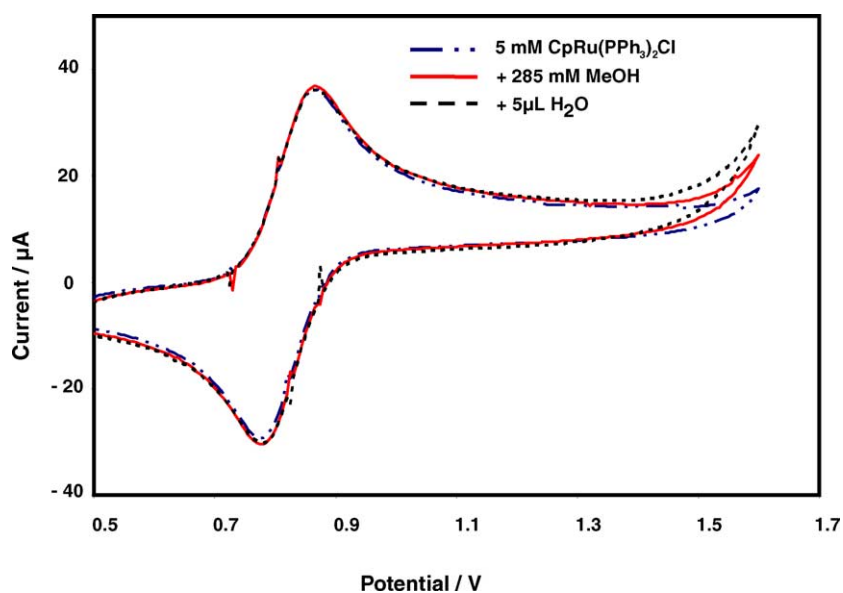

Fig. 1. Cyclic voltammograms of **4** under nitrogen in 3.5 mL of DCE/0.7 M TBAT; glassy carbon working electrode; Ag/Ag+ reference electrode; 50 mV/s; solutions as specified in figure.
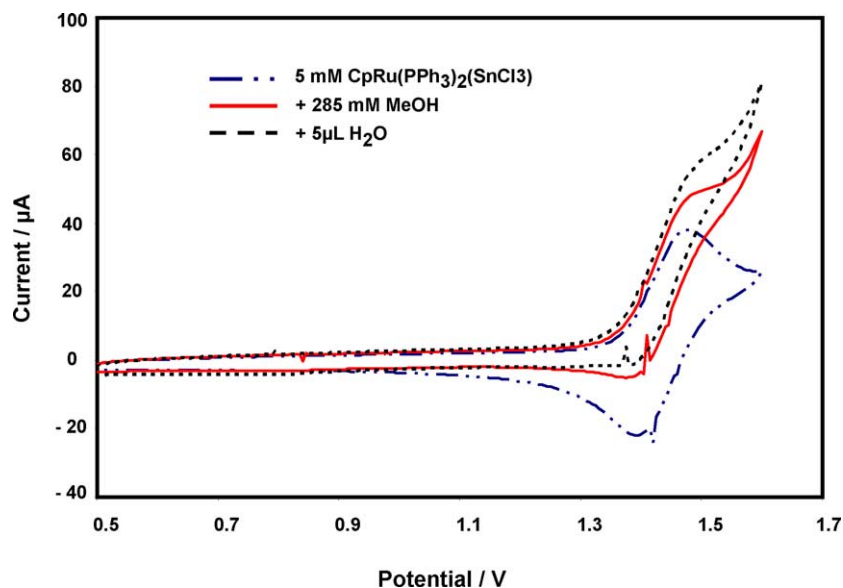
Fig. 2. Cyclic voltammograms of **1** under nitrogen in 3.5 mL of DCE/0.7 M TBAT; glassy carbon working electrode; Ag/Ag+ reference electrode; 50 mV/s; solutions as specified in figure.

in the absence of catalyst did not result in the formation of detectable quantities of oxidation products when either DCE (1.70 V) or methanol (1.40 V) was used as the solvent. The oxidation of methanol to DMM and MF is therefore facilitated by the oxidized Ru species. The formation of DMM and MF under these conditions contrasts with the thermal reaction of methanol with $CpRu(PPh_3)_2(SnCl_3)$ [20,21], where methyl acetate was the only product isolated.

As previously discussed, the cyclic voltammograms of complexes **1**–**3** exhibit a significant current increase at the Ru(II/III) couple in the presence of methanol. In contrast, the simple Ru species **4** and **5** exhibit no significant change at the Ru(II/III) wave when methanol is introduced. Bulk electrolyses of the sulfonated species complexes **3** and **5** were performed in methanol as the solvent. As expected, when the electrolysis is performed in methanol instead of DCE, there is a significant increase in the current efficiency and TON (Table 2). This increase is attributed to the improved electron

transfer kinetics and to the higher concentration of methanol substrate when it is also the solvent.

To probe the effect of the oxidation potential on the electrooxidation process, the catalytic activities of all the complexes were investigated at two potentials. The electrooxidation of methanol in DCE containing **1**, **2** or **4** was performed at 1.55 and 1.70 V. Bulk electrolysis of TPPMS complexes **3** and **5** in methanol was performed at 1.25 and 1.40 V. Varying the oxidation potential has a significant effect on the TON and on the selectivity of the methanol electrooxidation reaction. As expected, the amounts of products formed and the TON are dependent upon the oxidation potential (Table 2). Methyl formate formation is favored by higher potentials, rising from 5 to 33% of the product mixture from catalyst **1** as the potential is increased from 1.55 to 1.70 V.

The CVs of the heterobimetallic complexes **1**–**3** all display a slight increase in the catalytic current when small amounts of water are added to the reaction mixtures (Fig. 2). It should

Table 2
Bulk electrolysis data for complexes **1**–**5**[a] after 5 h of electrolysis

Complex	Oxidation potential (V)	TON[b]	Current efficiency[c] (%)	Methanol consumed (10^{-4} mol)	DMM (%)	MF (%)
$CpRu(PPh_3)_2Cl$ (**4**)	1.55	1.0	5.6	0.98	76.8	23.2
$CpRu(PPh_3)_2Cl$ (**4**)	1.70	2.6	7.3	2.47	75.2	24.8
$CpRu(PPh_3)_2(SnCl_3)$ (**1**)	1.55	3.0	18.2	3.12	95.0	5.0
$CpRu(PPh_3)_2(SnCl_3)$ (**1**)	1.70	3.4	13.1	4.14	67.4	32.6
$(Ind)Ru(PPh_3)_2(SnCl_3)$ (**2**)	1.55	2.8	16.3	2.84	92.6	7.4
$(Ind)Ru(PPh_3)_2(SnCl_3)$ (**2**)	1.70	4.7	17.9	4.55	73.6	26.4
$CpRu(TPPMS)_2Cl$ (**5**)[d]	1.25	13.4	63.2	14.09	100	0
$CpRu(TPPMS)_2Cl$ (**5**)[d]	1.40	15.1	76.9	15.73	98.5	1.5
$CpRu(TPPMS)_2(SnCl_3)$ (**3**)[d]	1.25	33.4	89.4	35.08	100	0
$CpRu(TPPMS)_2(SnCl_3)$ (**3**)[d]	1.40	40.0	90.1	40.69	90.5	9.5

[a] All electrolyses performed in 0.7 M TBAT/DCE with 1.0 mmol methanol unless otherwise specified.
[b] Moles of product formed per mole of catalyst.
[c] Moles of product formed per mole of charge passed.
[d] Electrolyses performed in 0.1 M TBAT/MeOH.

Table 3
Bulk electrolysis of wet methanol[a]

Complex	Oxidation potential (V)	TON[b]	Current efficiency[c] (%)	Methanol consumed (10^{-4} mol)	DMM (%)	MF (%)
$CpRu(PPh_3)_2(SnCl_3)$ (**1**)	1.55	2.5	17.2	2.35	73.7	26.3
$(Ind)Ru(PPh_3)_2(SnCl_3)$ (**2**)	1.55	2.9	20.7	2.67	65.7	34.3
$CpRu(TPPMS)_2(SnCl_3)$ (**3**)[d]	1.25	15.3	74.2	14.89	78.6	21.4

[a] All electrolyses performed in 0.7 M TBAT/DCE with 1.0 mmol methanol and 5.0 μL H_2O unless otherwise specified.

[b] Moles of product formed per mole of catalyst.

[c] Moles of product formed per mole of charge passed.

[d] Electrolyses performed in 0.1 M TBAT/MeOH with 5.0 μL H_2O.

be noted that all of the samples contain some water due to the condensation of methanol with formaldehyde to generate DMM (Scheme 1). The effect of additional water on the electrocatalytic reaction was probed by introducing 5 μL of water before starting the electrolysis. The presence of water favors the formation of MF (Table 3) as previously described for heterogeneous [3] and similar ruthenium [17,18] catalysts.

3.4. Bulk electrolysis of dimethoxymethane

The electrooxidation of DMM was studied in order to test the competency of DMM as an intermediate on the pathway to methyl formate. Control experiments have established that the electrooxidation of DMM in DCE does not proceed in the absence of catalyst at a potential of 1.70 V. The CV of **1** exhibits no catalytic current in the presence of DMM. Complex **1**, however, converts only 4.5 and 6.6% of the DMM to MF when the oxidation potential is 1.55 and 1.70 V, respectively. This effectively rules out the direct conversion of DMM to MF as a major pathway for the electrooxidation of methanol to MF.

4. Conclusions

The electrochemical oxidation of complexes **1**–**5** catalyzes the conversion of methanol to DMM and MF. The introduction of water favors the formation of methyl formate. Under the reaction conditions, DMM is converted to MF too slowly to be an intermediate on the main pathway to MF. Although all of the complexes are more selective for DMM formation at lower potentials, this effect is more pronounced for the Ru/Sn complexes **1**–**3**. The electrochemical oxidation of methanol is more efficient and selective for the TPPMS complexes **3** and **5**, which allow the oxidation to be performed in methanol as the solvent.

Acknowledgment

References

[1] I.E. Wachs, L.E. Briand, WO Patent 2,002,022,539 (2002).
[2] Y. Yuan, H. Liu, H. Imoto, T. Shido, Y. Iwasawa, J. Catal. 195 (2000) 51–61.
[3] Y. Yuan, K. Tsai, H. Liu, Y. Iwasawa, Top. Catal. 22 (2003) 9–15.
[4] H. Liu, N. Bayat, E. Iglesia, Angew. Chem. Int. Ed. 42 (2003) 5072–5075.
[5] H.C. Liu, E. Iglesia, J. Phys. Chem. B 107 (2003) 10840–10847.
[6] M. Yoneoka, T. Ikarashi, K. Watabe, K. Nakumura, EP Patent 625,502 (1994).
[7] K. Otsuka, T. Ina, I. Yamanaka, Appl. Catal. A: Gen. 247 (2003) 219–229.
[8] P.S. Fedkiw Jr., R. Liu, J.A. Trainham III, US Patent 5,223,102 (1993).
[9] I. Yamanaka, K. Otsuka, Chem. Lett. (1988) 753–756.
[10] K. Otsuka, I. Yamanaka, Appl. Catal. 26 (1986) 401–404.
[11] W.F. Lin, J.T. Wang, R.F. Savinell, J. Electrochem. Soc. 144 (1997) 1917–1922.
[12] S. Wasmus, J.T. Wang, R.F. Savinell, J. Electrochem. Soc. 142 (1995) 3825–3833.
[13] R. Liu, P.S. Fedkiw, J. Electrochem. Soc. 139 (1992) 3514–3523.
[14] T. Iwasita, Electrochim. Acta 47 (2002) 3663–3674.
[15] S. Wasmus, A. Kuver, J. Electroanal. Chem. 461 (1999) 14–31.
[16] C.L. Childers, H.L. Huang, C. Korzeniewski, Langmuir 15 (1999) 786–789.
[17] M.E. Tess, P.L. Hill, K.E. Torraca, M.E. Kerr, K.A. Abboud, L. McElwee-White, Inorg. Chem. 39 (2000) 3942–3944.
[18] G. Matare, M.E. Tess, K.A. Abboud, Y. Yang, L. McElwee-White, Organometallics 21 (2002) 711–716.
[19] Y. Yang, K.A. Abboud, L. McElwee-White, Dalton Trans. (2003) 4288–4296.
[20] H. Einaga, T. Yamakawa, S. Shinoda, J. Coord. Chem. 32 (1994) 117–119.
[21] P.A. Robles-Dutenhefner, E.M. Moura, G.J. Gama, H.G.L. Siebald, E.V. Gusevskaya, J. Mol. Catal. A: Chem. 164 (2000) 39–47.
[22] M.I. Bruce, R.C. Wallis, Aust. J. Chem. 32 (1979) 1471–1485.
[23] L.A. Oro, M.A. Ciriano, M. Campo, C. Foces-Foces, F.H. Cano, J. Organomet. Chem. 289 (1985) 117–131.
[24] P.J. Roman Jr., D.P. Paterniti, R.F. See, M.R. Churchill, J.D. Atwood, Organometallics 16 (1997) 1484–1490.
[25] T. Suárez, B. Fontal, M. Reyes, F. Bellandi, R. Contreras, G. León, P. Cancines, React. Kinet. Catal. Lett. 76 (2002) 161–169.
[26] S.K. Mandal, A.R. Chakravarty, Indian J. Chem. A 29A (1990) 18–21.
[27] M.P. Gamasa, J. Gimeno, C. Gonzalez-Bernardo, B.M. Martin-Vaca, D. Monti, M. Bassetti, Organometallics 15 (1996) 302–308.