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Inorganica Chimica Acta 361 (2008) 3237–3246

Inorganica Chimica Acta

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Electrochemical oxidation of methanol using alcohol-soluble Ru/Pt and Ru/Pd catalysts

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Received 26 September 2007; accepted 28 October 2007
Available online 6 November 2007

Dedicated to Robert J. Angelici

Abstract

The heterobimetallic Ru/Pt and Ru/Pd complexes [η^5-$C_5H_4CH_2CH_2N(CH_3)_2 \cdot HI$]Ru($PPh_3$)(μ-I)(μ-dppm)$PtCl_2$ (**7**), [η^5-$C_5H_4CH_2CH_2N(CH_3)_2 \cdot HI$]Ru($PPh_3$)(μ-I)(μ-dppm)$PtI_2$ (**8**), [η^5-$C_5H_4CH_2CH_2N(CH_3)_2 \cdot HI$]Ru($PPh_3$)(μ-I)(μ-dppm)$PdCl_2$ (**9**), and [η^5-$C_5H_4CH_2CH_2N(CH_3)_2 \cdot HI$]Ru($PPh_3$)(μ-I)(μ-dppm)$PdI_2$ (**10**) were prepared by the reaction of [η^5-$C_5H_4CH_2CH_2N(CH_3)_2 \cdot HI$]Ru($PPh_3$)I($\kappa^1$-dppm) (**6**) with Pt(COD)Cl_2, Pt(COD)I_2, and Pd(COD)Cl_2, respectively. Electronic interaction between the two metals is significant for the iodide-bridged compounds **7**–**10**, as evidenced by the shifts of their redox potentials in comparison to the mononuclear complexes. The electrochemical oxidation of methanol was carried out with heterobimetallic complexes **7**–**10** and leads to the formation of dimethoxymethane (DMM) and methyl formate (MF) as the major oxidation products. The chloride complexes **7** and **9** are the most active catalysts, as evidenced by their TON and current efficiencies. Addition of water at the beginning of the electrolysis results in increased formation of the more oxidized product MF along with higher current efficiencies and TON.

Keywords: Heterobimetallic complexes; Methanol oxidation; Electrocatalysis

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1. Introduction

Interest in potential catalytic applications has led to extensive research on heterobimetallic complexes, due to the possibility of exploiting the different reactivity of the two metals in chemical transformations [1–7]. The close proximity of two adjacent metal centers offers the possibility of cooperative reactivity and/or different mechanistic roles of the metal centers [2,8–14]. It has been shown that the cooperative effect in heterobimetallic complexes can enhance catalytic activities or can result in unique properties not observed in monometallic models [12,15–19].

The interest in the possibility of such a cooperative effect between two different metal centers in homogeneous electrochemical oxidation of alcohols led to preparation of the heterobimetallic complexes Cp(PPh_3)Ru(μ-Cl)(μ-dppm)$PtCl_2$ (**1**) [20] Cp(PPh_3)Ru(μ-Cl)(μ-dppm)$PdCl_2$ (**2**) [21] and Cp(PPh_3)RuCl(μ-dppm)AuCl (**3**) [21], followed by investigation of their electrochemical properties. Electrooxidation of methanol with complexes **1**–**3** provided evidence that interaction of the two metal centers was beneficial as these catalysts showed significant increases in the current efficiencies compared to those of the mononuclear model compounds CpRu(κ^2-dppm)Cl [22] or CpRu($PPh_3)_2$Cl [23].

Previous studies on electrooxidation of methanol by **1**–**3** and related compounds [22] were carried out in non-polar aprotic media (1,2-dichloroethane) due to the insolubility of the complexes in polar solvents. In order to facilitate the electrochemistry by moving to protic media, we have now prepared derivatives of **1**–**3** in which the cyclopentadienyl ligand is functionalized with a quaternized amino group to improve solubility in polar solvents. This

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doi:10.1016/j.ica.2007.10.046

approach has been used in the past to adapt organometallic catalysts for use in water [24–28]. Although the compounds presented in this work are only minimally soluble in water, they are soluble in methanol, allowing the electrooxidation of methanol to be carried out in the absence of additional solvent. We now report the synthesis of new heterobimetallic Ru/Pt and Ru/Pd complexes and their catalytic behavior in the electrochemical oxidation of neat methanol.

2. Experimental

2.1. General considerations

All reactions and manipulations were performed under an argon atmosphere using standard Schlenk techniques. Pentane and ethyl ether were dried by distillation from Na/Ph_2CO. Acetonitrile and 1,2-dichloroethane were dried by distillation from CaH_2. Methanol was dried by distillation from magnesium. Benzene and dichloromethane were dried using an MBraun solvent purification system. All solvents were saturated with argon prior to use. All deuterated solvents (Cambridge Isotope Laboratories) for NMR measurements were degassed via freeze–pump–thaw cycles and stored over molecular sieves (4 Å). ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded at room temperature on a Varian Mercury 300 spectrometer operating at 300 and 121 MHz, respectively, with chemical shifts (δ, ppm) reported relative to residual solvent peaks (^1H NMR) or 85% H_3PO_4 (^{31}P NMR). IR spectra were obtained as neat films on NaCl using a Varian 2000 FT-IR spectrophotometer. $[(\eta^5\text{-}C_5H_4CH_2CH_2N(CH_3)_2 \cdot HCl]Ru(PPh_3)_2Cl$ (**4**) was prepared according to published procedures [29]. 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 using an EG&G PAR model 263A potentiostat/galvanostat. Cyclic voltammograms (CV) were recorded in 3.5 mL of DCE/0.1 M tetrabutylammonium trifluoromethanesulfonate (TBAT) or MeOH/0.1 M tetrabutylammonium tetrafluoroborate ($TBABF_4$) at ambient temperature under nitrogen. All potentials are reported versus NHE and referenced to Ag/Ag^+. The reference electrode consisted of a silver wire immersed in an acetonitrile solution containing freshly prepared 0.01 M $AgNO_3$ and 0.1 M TBAT or $TBABF_4$. The Ag^+ solution and silver wire were contained in a 75 mm glass tube fitted at the bottom with a Vycor tip. Cyclic voltammetry was performed in a three-compartment H-cell separated by a medium-porosity sintered glass frit in 2.5–3.5 mL of DCE/0.1 M TBAT or MeOH/0.1 M $TBABF_4$ at room temperature under nitrogen. A highly polished glassy carbon electrode (diameter 3 mm) was the working electrode and a platinum flag was used as the counter electrode. All electrochemical measurements were performed inside the glove box. The constant potential electrolysis was performed in similar equipment except that the glassy carbon working electrode was replaced by a vitreous carbon electrode. The E_o values for the ferrocenium/ferrocene couple in DCE/0.1 M TBAT and MeOH/0.1 M $TBABF_4$ were +0.67 and +0.61 V.

Electrolysis products were analyzed by gas chromatography on a Shimadzu GC-17A chromatograph using 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 products produced during the electrolysis of methanol were quantitatively determined with the use of a known amount of *n*-heptane as an internal standard. Product identification was confirmed by comparison of the retention times of the oxidation product with authentic samples.

2.2. Synthesis of the complexes

2.2.1. $[\eta^5\text{-}C_5H_4CH_2CH_2N(CH_3)_2 \cdot HI]Ru(PPh_3)_2I$ (*5*)

A solution of **4** (1.52 g, 1.91 mmol) in methylene chloride (100 mL) was washed with 150 mL solution of degassed 1 M HCl. The organic layer was dried under $MgSO_4$ and the solvent was evaporated. The resulting orange solid, after drying, was reacted with sodium iodide (2.85 g, 19.1 mmol) in degassed dichloromethane at room temperature. After 48 h, the resulting mixture was washed with H_2O (3 × 50 mL). After drying the organic layer, evaporation of the solvent and recrystallization from CH_2Cl_2/hexanes, compound **5** was obtained as a red brown solid (1.68 g, 85.5% yield). IR (neat film): ν(N–H) 2669 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.77–2.90 (m, 2H, $CH_2CH_2N(CH_3)_2 \cdot H^+$), 2.85 (s, 6H, $N(CH_3)_2 \cdot H^+$), 3.20–3.30 (m, 2H, $CH_2CH_2N(CH_3)_2 \cdot H^+$), 3.53 (br s, 2H, C_5H_4), 3.82 (br s, 2H, C_5H_4), 7.10–7.40 (m, 30H, $P(C_6H_5)_3$), 12.38 (br s 1H, N–*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 37.85. HRMS (ESI): calcd for $C_{45}H_{45}INP_2Ru$ *m*/*z* 890.1115 $(M{-}I)^+$, found 890.1125.

2.2.2. $[\eta^5 - C_5H_4CH_2CH_2N(CH_3)_2 \cdot HI]$ $Ru(PPh_3)$ $(\kappa^1 - dppm)I$ (*6*)

A 500 mL Schlenk flask was charged with **5** (1.68 g, 1.65 mmol), bis(diphenylphosphino)methane (dppm) (1.25 g, 3.25 mmol) and 250 mL of THF. The orange mixture was stirred for 7 days at ambient temperature and the solvent was evaporated on a vacuum line. The resulting crude mixture contained κ^1-dppm compound **6**, excess dppm and PPh_3. After evaporation of the solvent on a rotary evaporator, purification was achieved by recrystallization from dichloromethane/hexane to afford 1.71 g of a red-orange solid (92% yield). IR (neat film): ν(N–H) 2666 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.79 (s, 6H, $N(CH_3)_2 \cdot H^+$), 2.87–3.30 (m, 4H, $CH_2CH_2N(CH_3)_2 \cdot H^+$), 3.34 (br s, 1H, $Ph_2PCHHPPh_2$), 3.47 (br s, 1H, $Ph_2PCHHPPh_2$), 4.22 (br s, 2H, C_5H_4), 4.52 (br s, 2H, C_5H_4), 6.89–7.79 (m, 35H, $(C_6H_5)_2PCH_2P(C_6H_5)_2 + P(C_6H_5)_3$), 10.67 (br s, 1H, N–*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 43.85 (dd, Ru–$PPh_2CH_2PPh_2$, $J_{PP} = 3$, 41 Hz), 33.89 (dd, Ru–PPh_3, $J_{PP} = 21$, 41 Hz), −26.64 (dd, Ru–$PPh_2CH_2PPh_2$, $J_{PP} =$