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Chemical Vapor Deposition

Full Paper

Preparation of Pt–Ru Alloyed Thin Films Using a Single-Source CVD Precursor**

By *Shu-Fen Huang*, *Yun Chi*,* *Chao-Shiuan Liu*,* *Arthur J. Carty*,* *Kristina Mast*, *Christina Bock*, *Barry MacDougall*, *Shie-Ming Peng*, and *Gene-Hsiang Lee*

Treatment of (dimethylaminomethyl)ruthenocene with *cis*-$Pt(DMSO)_2Cl_2$ led to the formation of a ruthenocenyl platinum complex $[CpRu(\eta^5\text{-}C_5H_3CH_2NMe_2)Pt(DMSO)Cl]$ (**1**); subsequent treatment of **1** with [Na(hfac)] afforded an air-stable Pt–Ru complex $[CpRu(\eta^5\text{-}C_5H_3CH_2NMe_2)Pt(hfac)]$ (**2**). Its volatility and other physical data relevant to CVD experiments were assessed by thermogravimetric analysis (TGA). The Pt–Ru thin films were then deposited at two deposition temperatures, 300 °C and 400 °C, using O_2 as the reactive carrier gas. The as-deposited thin films were characterized using energy dispersive X-ray (EDX), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD). Results indicated the formation of a homogeneous Pt–Ru solid solution at the lower deposition temperature. However, upon raising the temperature to 400 °C, phase separation between Pt and Ru occurred, which then induced the growth of RuO_2 grains at the substrate surface and caused depletion of the alloy in ruthenium. The electrocatalytic activities of the films, in respect of methanol oxidation, were investigated, in half-cell experiments, by cyclic voltammetry.

Keywords: Fuel cell, Methanol oxidation, Platinum, Ruthenium

1. Introduction

Binary Pt–Ru alloys with an approximate atomic ratio of 1:1 are among the most active catalysts for direct methanol fuel cells (DMFCs).[1] Various synthetic methods are available for the required Pt–Ru catalysts, including; co-impregnation,[2] co-precipitation,[3] and electrochemical deposition,[4] or direct reduction of a mixture of Ru and Pt metal salts.[5] Nevertheless, devising new synthetic procedures for these Pt–Ru catalysts that will result in increased performance remains a formidable challenge.

The synthesis of the bimetallic $Pt_{0.5}Ru_{0.5}(NOct)_4Cl$ colloid serves as one example that illustrates this endeavor. Its electrocatalytic properties have been measured to assess its potential for the preparation of electro-oxidation catalysts.[6] More recently, Shapley and co-workers have reported an effective conversion from metal carbonyl clusters $PtRu_5C(CO)_{16}$ and $Pt_2Ru_4(CO)_{18}$ to $PtRu_5$, and $PtRu_2$/carbon nanocomposites.[7] Pan et al. used the dual precursors, $Pt(dba)_2$ (dba = dibenzylidene acetone) and Ru(COD)(COT), in the presence of poly(vinyl pyrrolidone) (PVP) to obtain Pt–Ru catalysts with a variety of stoichiometric ratios.[8] Lukehart and co-workers used microwave irradiation to covert the single-source $(\eta\text{-}C_2H_4)(Cl)Pt(\mu\text{-}Cl)_2Ru(Cl)(DMOD)$, DMOD = η^3:η^3-2,7-dimethyloctadienediyl to the Pt-Ru/Vulcan carbon nanocomposites.[9] It appears that the choice of precursors and the reaction conditions can have a strong influence on both the composition and size of the alloy particles, important factors in determining their electrocatalytic activity.

In this paper, we report the preparation of the desired Pt–Ru catalysts using CVD. We believe that CVD is of potential importance since it offers mild processing conditions, good compatibility with the needs of scale-up, and the ability to accurately control the microstructure.[10] The source reagent selected was a newly designed complex $[CpRu(\eta^5\text{-}C_5H_3CH_2NMe_2)Pt(hfac)]$, which has the required Pt/Ru stoichiometry of 1:1, sufficient volatility, and good stability at low temperatures. We therefore, expect this compound to have considerable potential for the fabrication of methanol fuel cell electrodes.

2. Results and Discussion

For the synthesis of the required Pt–Ru single-source CVD precursor, a ruthenocenyl amine compound $CpRu(\eta^5$-

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$C_5H_4CH_2NMe_2$) was first obtained via a direct treatment of ruthenocene with *N,N,N′,N′*-tetramethyldiaminomethane.[11] The resulting ruthenocenyl amine complex readily reacts with *cis*-Pt(DMSO)$_2$Cl$_2$ in the presence of a weak base, such as sodium acetate, to afford a cycloplatinate product [CpRu(η^5-$C_5H_3CH_2NMe_2$)Pt(DMSO)Cl] (**1**). To remove the chloride and DMSO solvate, complex **1** was then treated with sodium hexafluoroacetylacetonate Na(hfac) to give the expected, relatively more volatile compound, [CpRu(η^5-$C_5H_3CH_2NMe_2$)Pt(hfac)] (**2**) in good yield. The design principle and synthetic strategy, schematically depicted in Scheme 1, are similar to that utilized for the preparation of a related ferrocenyl complex [CpFe(η^5-$C_5H_3CH_2NMe_2$)Pt(DMSO)Cl][12] and the corresponding Ru–Pd complex [CpRu(η^5-$C_5H_3CH_2NMe_2$)Pd (acac)].[13]

The Pt–Ru complex **2** is a dark red, air-stable solid with a melting point of 185 °C. Its ^{1}H NMR spectrum was recorded revealing one sharp signal at δ 4.53 and three signals at δ 4.54 (doublet, $J_{HH} = 2.0$ Hz), 4.47 (triplet, $J_{HH} = 2.0$ Hz), and 4.42 (doublet, $J_{HH} = 2.0$ Hz) with an intensity ratio of 5:1:1:1, which are assigned to the unsubstituted Cp and the substituted Cp ring protons. Interestingly, the methyl signals of the NMe$_2$ group at δ 3.18 and δ2.95 showed a pair of ^{195}Pt satellite signals with coupling constant $J_{PtH} \sim 39$ Hz, which provided the required evidence for direct attachment to the Pt metal center.

A single-crystal XRD study was carried out to confirm the molecular structure. As indicated in Figure 1, the platinum atom resides in a square-planar environment and is coordinated to both oxygen atoms of the hfac ligand, the amine nitrogen atom, and the C(1) atom of the ruthenocenyl group. As a result, a five-membered metallacycle is formed from the platinum atom, the amine nitrogen atom, and three carbon atoms C(1), C(5), and C(6) of the ruthenocenyl fragment, confirming the occurrence of metal-catalyzed C–H activation, leading to the formation of a more stable Pt–C(sp^2) σ-bond during the treatment of CpRu(η^5-$C_5H_4CH_2NMe_2$) with *cis*-Pt(DMSO)$_2$Cl$_2$. The Pt-ligand coordination distances are unexceptional, though the Pt–O bond (2.113(5) Å) *trans* to carbon is slightly longer than that *trans* to nitrogen (2.009(4) Å), consistent with a stronger *trans* influence imposed by the Pt–C(1) bonding vs. that of the N(1)→Pt dative interaction. Moreover, the Ru–C(1) distance (2.220(6) Å) is slightly longer than the other Ru–C(Cp ring) distances (2.152–2.187(7) Å), showing a secondary effect of bond weakening, probably caused by Pt coordination.

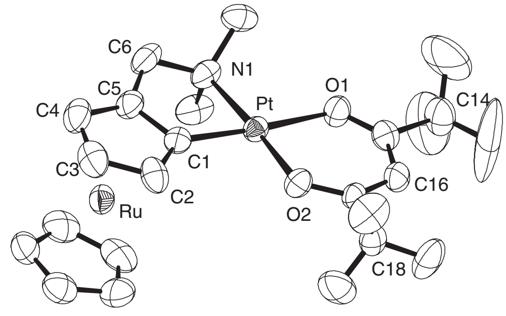


Fig. 1. ORTEP drawing of complex **2** with thermal ellipsoids shown at 30 % probability level; selected bond distances [Å]: Pt–O(1) = 2.113(5), Pt–O(2) = 2.009(4), Pt–N(1) = 2.061(5), Pt–C(1) = 1.956(6), Ru–C(1) = 2.220(6), Ru–C(2) = 2.176(7), Ru–C(3) = 2.152(7), Ru–C(4) = 2.158(7), and Ru–C(5) = 2.187(7).

The TGA data for **2** were used to assess its volatility and other physical data relevant to CVD experiments. As indicated in Figure 2, complex **2** starts to evaporate over the temperature range 160–200 °C under a reduced pressure of 1.5 torr, and affords very small amounts (4 %) of solid residual upon increasing the temperature to 500 °C. This behavior is in good agreement with previous observations when the sublimation was typically carried out at 120 °C under a pressure of 400 mtorr. For the TGA experiment carried out under a N$_2$ atmosphere, a much slower loss of mass occurred at a higher temperature range, 180–220 °C. The greater residual mass (62 %) indicated the occurrence of severe sample decomposition, a result of less sample evaporation at the higher pressure. For the experiment conducted in dry air, the initial pattern of mass loss recorded at a temperature below 220 °C is somewhat similar to that conducted under N$_2$, except that a continuous loss of mass, arising from the combustion of sample, was observed at the higher temperature, and no further change of mass was

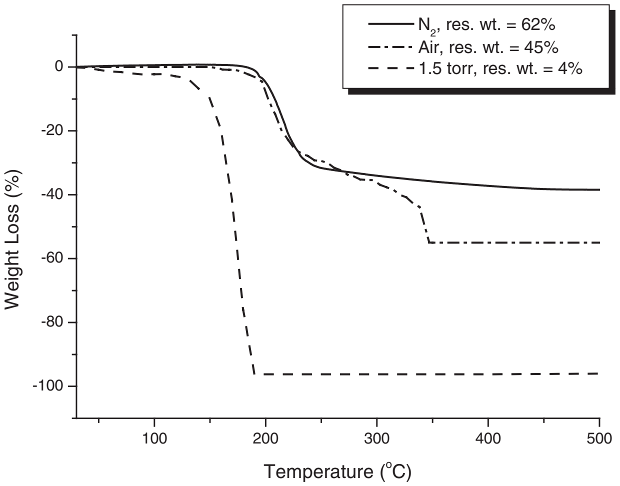
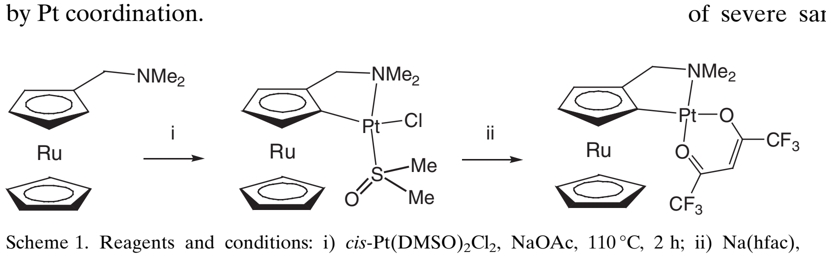


Fig. 2. TGA data of complex **2**. Experiments were carried out under atmospheric pressure of N$_2$, in compressed air (100 sccm) or at a pressure of 1.5 torr; heating rate was 10 °C min^{-1} for all experiments.



Scheme 1. Reagents and conditions: i) *cis*-Pt(DMSO)$_2$Cl$_2$, NaOAc, 110 °C, 2 h; ii) Na(hfac), 110 °C, 3 h.

observed above 340 °C. The residual mass (45 %) observed in this experiment is essentially identical to the total Pt-Ru metal content (43 %) present in **2**, indicating complete sample combustion giving the expected Pt–Ru alloy, but with a trace amount of metal oxide such as RuO_2, inevitable in the presence of excess oxygen.

Deposition of Pt–Ru thin film alloy was conducted using complex **2** as a source reagent. For the experiments carried out under a slow flow of O_2 carrier gas, well-adherent Pt–Ru thin films were obtained for all substrate surfaces including carbon paper, Pyrex glass, and Si wafer, at deposition temperatures of 300–400 °C. The observed Pt–Ru compositional ratio was approximately 1:1, estimated according to the EDX analyses of the respective Pt M_α and Ru L_α signals. A representative EDX spectrum is depicted in Figure 3. However, upon switching to the reductive carrier gas H_2, no formation of thin film was observed at temperatures below 450 °C. By increasing the temperature to 500 °C, a poor quality, metal-containing thin film with a Pt–Ru ratio of 4:1 was obtained. This result indicates that the O_2 carrier gas is superior to H_2 for depositing Pt–Ru alloy with a stoichiometry of 1:1 at lower temperatures, which is consistent with the CVD conditions reported for the deposition of pure Pt and Ru elements.[14]

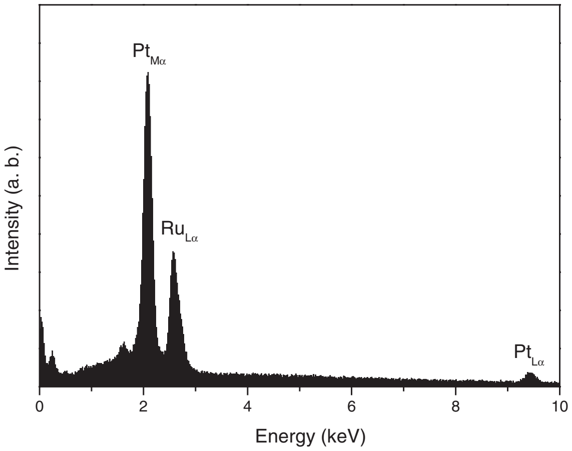


Fig. 3. EDX spectrum of the Pt–Ru film deposited on carbon paper at $T_R/T_S = 120\,°C/300\,°C$.

The as-deposited thin films exhibited a dark gray metallic cast. The SEM images of two thin films (a and b) are depicted in Figure 4. These were deposited on carbon paper at a reservoir temperature, T_R, and substrate temperature, T_S, of 120 °C/300 °C and 140 °C/300 °C, respectively. It appears that the higher partial pressure of the source reagent, which is qualitatively determined by T_R, produces a relatively rough morphology composed of larger metal particulates.

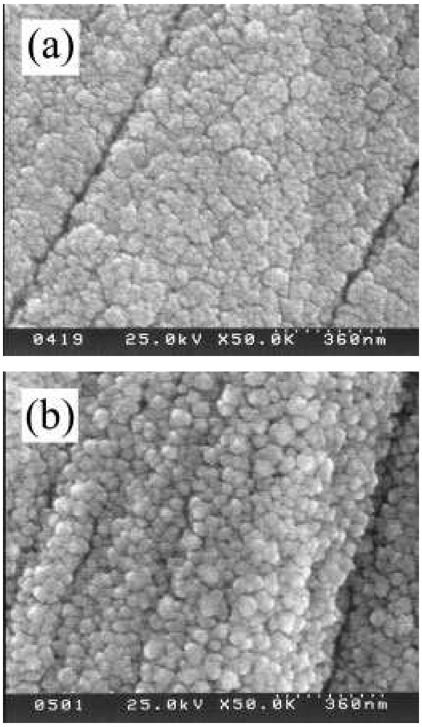


Fig. 4. SEM images of the Pt–Ru films deposited on carbon paper: a) $T_R/T_S = 120\,°C/300\,°C$; b) $T_R/T_S = 140\,°C/300\,°C$.

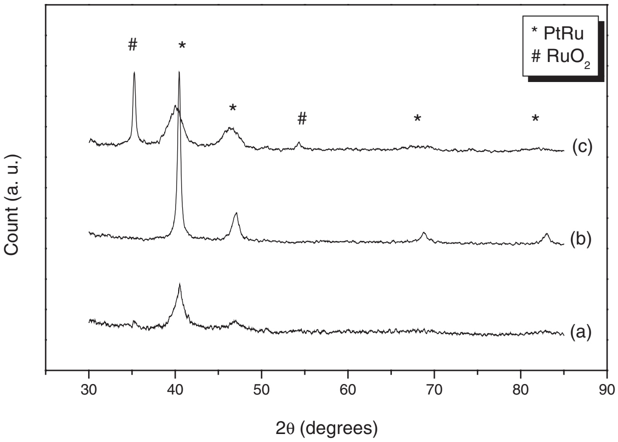


Fig. 5. XRD pattern of the Pt–Ru thin films deposited on Pyrex: a) $T_R/T_S = 120\,°C/300\,°C$; b) $T_R/T_S = 140\,°C/300\,°C$; c) $T_R/T_S = 140\,°C/400\,°C$.

XRD spectra of the Pt–Ru films deposited on SiO_2 at 300 °C and 400 °C are shown in Figure 5. The XRD spectrum of the first sample, grown at T_R/T_S of 120 °C/300 °C, reveals diffraction patterns consistent with a fcc unit cell having a lattice constant ~3.869 Å. This is slightly smaller than that reported for pure Pt metal (3.9231 Å), and is in good agreement with the report showing reduction of this lattice parameter to 3.884 Å for a PtRu catalyst of 1:1 stoichiometry deposited on a carbon support.[15] This decrease of the unit cell constant is obviously caused by the replacement of platinum atoms on the face-centered cubic (fcc) structure by the smaller, ruthenium atoms. Thus, our observation has provided unambiguous evidence for the formation of a Pt–Ru homogeneous solution, rather than a physical mixture involving two discrete metal particles.[16] The diffraction signals became much sharper upon increasing T_R from 120 °C to 140 °C, indicating the formation of larger crystallites under these experimental conditions. XPS analysis of these thin film samples revealed a spin-orbit split doublet of $Ru_{3d_{5/2}}$ and $Ru_{3d_{3/2}}$ at 280.2 eV and 284.2 eV, respectively. These data are in good agreement with the literature value of the metallic Ru standard that would appear in the range 279.9–280.3 eV ($Ru_{3d_{5/2}}$) and 284.0–284.5 eV ($Ru_{3d_{3/2}}$),[17] but the full width at half maximum (FWHM) of the $Ru_{3d_{5/2}}$ component was found to be ~1.4 eV. This value is too large, so that it is difficult to establish the exact amount of the oxidized species (RuO_2) in the sample for which the expected binding energies of the RuO_2 $Ru_{3d_{5/2}}$ and $Ru_{3d_{3/2}}$ doublet are only slightly higher (280.7–281.0 eV and 284.9–285.2 eV). However, the presence of RuO_2 was then indicated from the O(1s) XPS analysis, which exhibited one peak at 532.1 eV and another at 529.8 eV. The latter is characteristic of the lattice oxide and its relative intensity increases upon raising T_R.[18]

Moreover, upon further increasing T_S from 300 °C to 400 °C, the diffraction signals assigned to the Pt–Ru fcc structure became much broader and shifted slightly to the smaller $2<\theta$ value, showing the generation of a Pt-rich metal alloy phase. A sharp signal was also observed at 2θ approximately 35°, a good match with the (101) signal of the RuO_2 rutile phase. Therefore, these two observations indicate that increasing the deposition temperature to 400 °C induces phase separation between Pt and Ru which is then oxidized, or that the oxidation of surface Ru atoms causes the growth of RuO_2 grains at the surface of the material and depletion of ruthenium in the alloy. For comparison, the Ru CVD conducted under ambient O_2 pressure at the higher temperature has similarly produced the more stable RuO_2, rather than the metallic Ru phase.[19] In addition, the XPS spectrum showed that the bonding energy of the $Ru_{3d_{5/2}}$ component was found at 280.3 eV, and the corresponding FWHM was further increased to 1.66 eV, showing an obvious increase in the extent of surface oxidation.

The cyclic voltammograms (CVs) for the Pt–Ru thin films deposited on carbon paper are shown in Figure 6. It should be noted that, at this time, no satisfactory method is available for the electro-active Pt surface area estimation, so that the current density of our thin film is normalized for the real Pt surface area calculated from CO stripping experiments. In the present work, the electrochemical CH_3OH oxidation data are interpreted assuming that CO only adsorbs onto Pt, despite the fact that this assumption introduces an error. As we can see, the Pt–Ru thin film deposited at $T_S = 300$ °C shows similar methanol oxidation currents, shifted to less positive potentials by more than 200 mV for the onset potential, compared to the Pt electrode, and this characteristic agrees with that of the Pt–Ru alloy reported in the literature.[20] However, the Pt–Ru thin film deposited at a higher T_S of 400 °C exhibits a deteriorated current density vs. voltage behavior, becoming much closer to that observed for pure Pt metal. We attributed this to the formation of the RuO_2 phase (as observed by XRD analysis) which has been suggested to inhibit both the adsorption and the catalytic oxidation of the methanol molecule in solution.[21] It is also possible that heating to 400 °C introduces phase separation between RuO_2 and Pt, resulting in a poor distribution of Pt and RuO_2 sites. This, in turn, would be seen in a reduced CH_3OH oxidation activity.

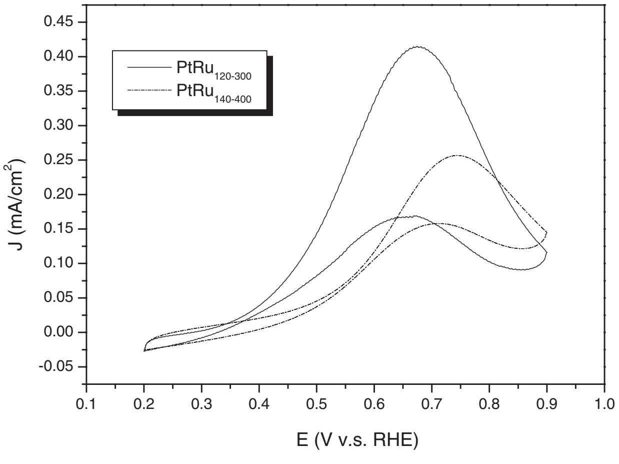


Fig. 6. Cyclic voltammograms at 10 mV s^{-1} for Pt–Ru thin films on carbon paper in 0.5 M H_2SO_4 and 0.5 M CH_3OH at 60 °C based on the fifth sweep.

3. Conclusion

The Pt–Ru compound **2** has been demonstrated to be suitable for preparing, by CVD, thin films consisting of highly dispersed Pt–Ru binary alloy. At the substrate temperature $T_S = 400$ °C, we obtained a mixture of RuO_2 and Pt-rich metal alloy showing only marginal enhancement of activity compared with that of typical Pt metal. However, by lowering the temperature T_S to 300 °C, the as-deposited Pt–Ru alloy thin film showed both reduced particle sizes and good activity in respect of the electro-oxidation of methanol. These results suggest that CVD, as well as our carefully executed precursor design, can be considered as promising techniques for the preparation of the Pt–Ru catalysts for fuel cells.

4. Experimental

*Synthesis of Complex **1***: A solution of sodium acetate (1.8 mmol) in 2 mL of methanol was added to a solution of *cis*-$Pt(DMSO)_2Cl_2$ (762 mg, 1.8 mmol) and $CpRu(\eta^5\text{-}C_5H_4CH_2NMe_2)$ (520 mg, 1.8 mmol) dissolved in 50 mL of toluene. The mixture was heated at reflux for 2 h under N_2. The solution was then filtered through a short silica gel column using a 1:1 mixture of CH_2Cl_2 and ether as the eluent, giving a light yellow, needle-like material $[CpRu(\eta^5\text{-}C_5H_3CH_2NMe_2)Pt(DMSO)Cl]$ (**1**, 994 mg, 1.66 mmol) in 93 % yield.

*Synthesis of Complex **2***: A mixture of complex **1** (180 mg, 0.3 mmol) and Na(hfac) (139 mg, 0.6 mmol) in 50 mL toluene was heated at reflux for 3 h. After the reaction was stopped, solvent was evaporated in vacuo and the residue was separated using silica gel column chromatography. By eluting with pure CH_2Cl_2, a red component was obtained, and this was further purified by vacuum sublimation (120 °C/400 mtorr), followed by recrystallization from a mixture of CH_2Cl_2 and hexane at room temperature, giving 134 mg of $[CpRu(\eta^5\text{-}C_5H_3CH_2NMe_2)Pt(hfac)]$ (**2**, 0.04 mmol) as a dark red, crystalline solid. Trace amounts of unreacted starting material **1** (45 mg) were recovered by flushing the silica gel column with diethylether. The yield of **2** was calculated to be 86 %, based on the consumption of starting material **1**. Single crystals suitable for XRD study were obtained from a mixed solution of CH_2Cl_2 and hexane at room temperature.

Spectral Data of **2**: MS (EI, ^{102}Ru): *m*/*z* 689 M^+. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 6.04 (s, 1H, CH), 4.54 (d, 1H, $J_{HH} = 2.0$ Hz, C_5H_3), 4.52 (s, 5H, C_5H_5), 4.47 (t, 1H, $J_{HH} = 2.0$ Hz, C_5H_3), 4.42 (d, 1H, $J_{HH} = 2.0$ Hz, C_5H_3), 3.60 (d, 1H, $J_{HH} = 14.0$ Hz, CH_2), 3.18 (s, 3H, $J_{PtH} = 39.0$ Hz, NCH_3), 3.17 (d, 1H, $J_{HH} = 14.0$ Hz, CH_2), 2.95 (s, 3H, $J_{PtH} = 39.0$ Hz, NCH_3). Anal. Calcd. for $C_{18}H_{20}F_3NO_2PtRu$: C, 31.36; H, 2.49; N, 2.03. Found: C, 31.56; H, 3.02; N, 2.46. Selected X-ray data: $C_{18}H_{20}F_3NO_2PtRu$, M = 689.49, Monoclinic, space group $C2/c$, $a = 22.590(2)$ Å, $b = 8.307(2)$ Å, $c = 21.001(2)$ Å; $\beta = 97.832(8)°$, $V = 3904.3(9)$ Å^3, $Z = 8$, $\sigma_{calcd} = 2.346$ mg m^{-3}, $F(000) = 2592$, λ(Mo Kα) = 0.7107 Å, $T = 293$ K, $\mu = 8.002$ mm^{-1}, $R_1 = 0.0295$, $wR_2 = 0.0764$ for $[I > 2\sigma(I)]$.

CVD Procedures: The binary Pt–Ru thin films were prepared using a custom-made cold-wall CVD apparatus described elsewhere [22]. The precursor reservoir was typically loaded with 20 mg of **2**, the flow rate of carrier gas was 5 sccm, and the deposition time set to 30–90 min. The deposition of Pt–Ru thin films was carried out on three substrate surfaces, carbon paper (TGPH060, Toray, Japan), Pyrex glass (SiO_2), and Si wafers. Four CVD runs were carried out at the sample reservoir and substrate temperatures: T_R/T_S = 120 °C/300 °C, 140 °C/300 °C, and 140 °C/400 °C under O_2 and 140 °C/500 °C under H_2.

Electrochemical Studies: A conventional three-electrode, two-compartment, glass cell was employed for the electrochemical studies. High surface area platinum gauze served as a counter electrode, and a mercury sulfate electrode (MSE), Hg/Hg_2SO_4/sat. K_2SO_4, –0.640 V vs. reversible hydrogen electrode (RHE) was used as a reference to avoid Cl^- contamination. The as-deposited Pt–Ru thin film on carbon paper was used as a working electrode. These thin films were glued to a metal wire using silver paste, and epoxy resin was applied to the electrical contact for protection. The films were then wrapped with Teflon tape in order to adjust the exposed surface area to 0.1 cm^2. To minimize the background current of the electrolyte solution, it was first purged with argon for at least 30 min, and then placed under an argon atmosphere during measurements. The real Pt surface area of the as-deposited thin films was determined using anodic CO stripping voltammetry.

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