

# Coordination Chemistry in Thin Polymeric Films of poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>], poly-vbpy. Binding and Reduction of [Rh(COD)Cl] and PdCl<sub>2</sub>

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Thin polymeric films of poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>], poly-vbpy (vbpy is 4-methyl-4'-vinyl-2,2'-bipyridine) undergo reactions with transition-metal compounds via the cyano groups or the uncoordinated vinyl-2,2'-bipyridine. The reaction between the dicyano/vbpy film and [Rh(COD)Cl]<sub>2</sub> led to the incorporation of one or two [Rh(COD)Cl] units into the film. Short reaction periods, <0.5 h, led to the incorporation of one [Rh(COD)Cl] unit by binding to the uncoordinated vbpy group to give poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>], poly-[Rh(vbpy)(COD)]Cl, a second group is incorporated at >0.5 h by binding to one of the cyano groups to give poly-{Fe(vbpy)<sub>2</sub>(CN)[CNRh(COD)Cl]}, poly-[Rh(vbpy)(COD)Cl]Cl. Binding sites and compositions within the films were established by FTIR, UV-visible, and XPS measurements. The dicyano/vbpy films also react with PdCl<sub>2</sub>(PhCN)<sub>2</sub> (PhCN = benzonitrile) incorporating two [PdCl<sub>2</sub>] units to give poly-{Fe(vbpy)<sub>2</sub>(CN)[CNPdCl<sub>2</sub>(NCCH<sub>3</sub>)]}, poly-Pd(vbpy)Cl<sub>2</sub>. PdCl<sub>2</sub> incorporation is more rapid than [Rh(COD)Cl]. Electrochemical reduction of films containing Rh<sup>I</sup> or Pd<sup>II</sup> resulted in the production of Rh<sup>0</sup> or Pd<sup>0</sup> particles in/on the films. Reduction of a poly-{Fe(vbpy)<sub>2</sub>(CN)[CNPdCl<sub>2</sub>(NCCH<sub>3</sub>)]}, poly-Pd(vbpy)Cl<sub>2</sub> film with PdCl<sub>2</sub>(PhCN)<sub>2</sub> in the external solution led to the dispersion of Pd<sup>0</sup> particles on the film surface as shown by SEM measurements. Films with surface-dispersed palladium or rhodium are active electrocatalysts for the reduction of carbon dioxide.

## Introduction

The applications of coordination chemistry to the design and synthesis of supramolecular structures and extended solids has attracted much attention in recent years, in part, because of potential applications of these materials in such areas as catalysis and sensors.<sup>1–13</sup> In two reports we described the binding and reduction of

silver ions in polymeric films of poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>], poly-vpy.<sup>14,15</sup> In these studies, we demonstrated that electrochemical reduction of the cyano-bound silver ions in poly-[Fe(vbpy)<sub>2</sub>(CN)Ag(CN)], poly-vbpy led to formation of dispersed silver particles throughout the films. The resulting particles had an agglomeration number of 4–6 and a radius <5 nm. Further reduction resulted in formation of colloidal silver particles localized near the electrode/film interface. Further reduction with AgNO<sub>3</sub> in the external solution, resulted in formation of <0.5 to 2–3 μm sized particles on the film surface as shown by SEM measurements.

Coordinatively active thin films provide a generalized environment for the preparation of supramolecular assemblies. In this report, we describe the binding and reduction of [Rh(COD)Cl]<sub>2</sub> and PdCl<sub>2</sub>(PhCN)<sub>2</sub> in thin polymeric films of poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>], poly-vbpy, characterization of the coordination chemistry by XPS, FTIR, UV-vis, and electrochemical measurements, and the behavior of the reduced films as catalysts for CO<sub>2</sub> reduction.

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(1) Wu, Y.; Pfenning, B. W.; Bocarsly, A. B. *Inorg. Chem.* **1995**, *34*, 4262.

(2) Pfenning, B. W.; Bocarsly, A. B. *J. Phys. Chem.* **1992**, *96*, 226.  
(3) Pfenning, B. W.; Bocarsly, A. B. *Coord. Chem. Rev.* **1991**, *111*, 91.

(4) Pfenning, B. W.; Bocarsly, A. B.; Prud'homme, R. K. *J. Am. Chem. Soc.* **1993**, *115*, 2661.

(5) Pfenning, B. W.; Bocarsly, A. B. *Inorg. Chem.* **1991**, *30*, 660.  
(6) Bell, C. M.; Keller, S. W.; Lynch, V. M.; Mallouk, T. E. *Mater. Chem. Phys.* **1993**, *35*, 225.

(7) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546.  
(8) Abrahams, B. F.; Hoskins, B. F.; Liu, J.; Robson, R. *J. Am. Chem. Soc.* **1991**, *113*, 3045.

(9) Eller, S.; Fisher, R. D. *Inorg. Chem.* **1990**, *29*, 1289.  
(10) Adam, M.; Brimah, A. K.; Li, X. F.; Fisher, R. D. *Inorg. Chem.* **1990**, *29*, 1595.

(11) Bignozzi, C. A.; Argazzi, R.; Schoonover, J. R.; Gordon, K. C.; Dyer, R. B.; Scandola, F. *Inorg. Chem.* **1992**, *31*, 5260.

(12) Kalyanasundaram, K.; Gratzel, M.; Nazeeruddin, M. K. *Inorg. Chem.* **1992**, *31*, 5243.

(13) Scandola, F.; Indelli, M. T.; Chiorboli, C.; Bignozzi, C. A. *Top. Curr. Chem.* **1990**, *158*, 73.

(14) MacKay, S. G.; Bakir, M.; Musselman, I. H.; Meyer, T. J.; Linton, R. W. *Anal. Chem.* **1991**, *63*, 60.

(15) Bakir, M.; MacKay, S. G.; Linton, R. W.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 3945.

## Experimental Section

**Materials.** The compound 4-vinyl-4'-methyl-2,2'-bipyridine (vbpy) and the salt  $[\text{Fe}(\text{vbpy})_3](\text{PF}_6)_2$  were prepared as described in the literature.<sup>16</sup> Tetra-*n*-butylammonium hexafluorophosphate,  $[\text{N}(\text{n-Bu})_4](\text{PF}_6)$ , was purchased from Aldrich Chemical Co. Inc., recrystallized twice from ethanol/water, and dried under vacuum for 24 h. Tetraethylammonium cyanide,  $[\text{N}(\text{Et})_4]\text{CN}$ , was purchased from Fluka Chemical Co. and used as received. Solvents were of the highest purity grade quality and were deoxygenated prior to use by a  $\text{N}_2$  purge. The compounds  $[\text{Rh}(\text{COD})\text{Cl}]_2$  and  $\text{PdCl}_2(\text{PhCN})_2$  were purchased from Strem Chemical Co. and used as received.

**Instrumentation.** Electrochemical experiments were performed in  $\text{CH}_3\text{CN}$  solutions that were 0.1 M in  $[\text{N}(\text{n-Bu})_4](\text{PF}_6)$ . The  $E_{\text{p,a}}$ ,  $E_{\text{p,c}}$ , and  $E_{1/2} = (E_{\text{p,a}} + E_{\text{p,c}})/2$  values were referenced to the saturated sodium chloride calomel electrode, SSCE, at room temperature and are uncorrected for junction potentials. Voltammetric experiments were performed with the use of a Princeton Applied Research (PAR) Galvanostat Model 173 and with either a PAR Model 175 Universal Programmer or a home-built supercycle.<sup>17</sup> Data were recorded on either SOLTEC or Hewlett-Packard HP-7015B X-Y recorders. Electrochemical cells were of conventional design based on scintillation vials or H-cells. Pt-button, glassy carbon buttons, planar Pt, indium-tin oxide (ITO), or Au sputtered on Cr/Si/SiO plates were used as working electrodes. Controlled-potential electrolysis experiments were performed by using a home-built three-compartment cell which used modified vitreous carbon working electrodes.<sup>18</sup> The reference electrode was the same in the cyclic voltammetric experiment and the auxiliary electrode was a vitreous carbon electrode.  $\text{CO}_2$  reduction products were analyzed on a Hewlett-Packard 5890A gas chromatograph equipped with FID and TCD detectors. A molecular sieve column was employed for analysis of gaseous products, and a Porapak Q column was used for solution products. Specular reflectance IR spectra of films formed on either planar Pt or Au electrodes were recorded with the use of a Nicolet 20DX FT-IR spectrometer in conjunction with a variable-angle specular reflectance attachment (Barnes Analytical). Electronic absorption spectra of films formed on tin-doped indium oxide (ITO) optically transparent electrodes were recorded by using an HP-8452A spectrophotometer. X-ray photoelectron spectra (XPS) of the films cast on Pt electrodes were obtained by using a Perkin-Elmer Physical Electronics Model 5400 XPS spectrometer equipped with a differentially pumped Ar ion gun. The X-ray source in these studies was Mg K $\alpha$  radiation (1253.6 eV), with an analysis area of 1.1 mm<sup>2</sup>, hemispherical analyzer pass energy of 35.75 eV, and anode power of 400 W (15 kV). Electron micrographs were taken for films cast on Pt electrodes by using an ISI DS-130 scanning electron microscope (SEM) with an accelerating voltage of 6 keV and secondary electron detection.

**Preparation and Modification of the Films.** (a) *Film Chemistry of poly-[Fe(vbpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> and poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>]-poly-vbpy.* Electrodes coated with films of poly-[Fe(vbpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> and poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>]-poly-vbpy were prepared by reductive electropolymerization as described earlier.<sup>14,15</sup> Potentials of the electrodes were cycled negatively into the vbpy reduction region in  $\text{CH}_3\text{CN}$  with 0.1 M  $[\text{N}(\text{n-Bu})_4](\text{PF}_6)$  as the supporting electrolyte.

(b) *Reaction of poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>]-poly-vbpy with [Rh(COD)Cl]<sub>2</sub>.* Formation of poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>]-poly-[Rh(vbpy)(COD)]Cl. A film of poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>]-poly-vbpy was soaked in  $\text{CH}_3\text{CN}$  solutions 0.1 M in  $[\text{Rh}(\text{COD})\text{Cl}]_2$  for 15 min. The resulting film was removed from solution, washed with  $\text{CH}_3\text{CN}$ , and dried.

(c) *Formation of poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>]-poly-vbpy with [Rh(vbpy)(COD)]Cl.* The title film was prepared by a procedure identical with that described in (b) except the soaking period was 12 h.

(d) *Reaction of poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>]-poly-vbpy with PdCl<sub>2</sub>(PhCN)<sub>2</sub>.* Thin films of poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>]-poly-vbpy which contained  $\text{PdCl}_2$  were prepared by soaking films of poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>]-poly-vbpy in  $\text{CH}_3\text{CN}$  solutions that were 0.1 M in  $\text{PdCl}_2(\text{PhCN})_2$  for 10 min. The resulting red films were removed from solution, washed with  $\text{CH}_3\text{CN}$ , and dried. Shorter soaking times (2 min) resulted in partial reaction as evidenced by electrochemical measurements.

(e) *Removal of bound Rh(COD)Cl from films of poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>]-poly-vbpy.* Films of poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>]-poly-vbpy were soaked in  $\text{CH}_3\text{CN}$  solutions that were 0.1 M in  $[\text{N}(\text{Et})_4]\text{CN}$  for 12 h. The resulting green films were removed from solution, washed with  $\text{CH}_3\text{CN}$ , dried, and identified as poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>]-poly-vbpy from their electrochemical and spectroscopic properties.

(f) *Removal of Bound PdCl<sub>2</sub> from Films of poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>]-poly-vbpy.* Thin films of poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>]-poly-vbpy were soaked in  $\text{CH}_3\text{CN}$  solutions that were 0.1 M in  $[\text{N}(\text{Et})_4]\text{CN}$  for 12 h. The resulting green films were removed from solution, washed with  $\text{CH}_3\text{CN}$ , dried, and identified as poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>]-poly-vbpy from their spectroscopic properties.

(g) *Reduction of Bound Rh(COD)Cl or PdCl<sub>2</sub> in poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>]-poly-vbpy.* Dicyano films containing  $\text{Rh}(\text{COD})\text{Cl}$  or  $\text{PdCl}_2$  were reduced electrochemically in 0.1 M  $[\text{N}(\text{n-Bu})_4](\text{PF}_6)/\text{CH}_3\text{CN}$  solution to form  $\text{Rh}^0$  by repetitive scans between -0.7 and -1.7 V. The resulting films were removed from solution, washed with  $\text{CH}_3\text{CN}$ , and dried before XPS analysis.

(h) *Electrodeposition of Rh<sup>0</sup> or Pd<sup>0</sup> Particles in Films.* Films containing  $[\text{Rh}(\text{COD})\text{Cl}]$  or  $\text{PdCl}_2$  units were reduced electrochemically by repetitive scans between -0.7 and -1.7 V in 0.1 M  $[\text{N}(\text{n-Bu})_4](\text{PF}_6)/\text{CH}_3\text{CN}$  solutions that were 0.01 M in  $[\text{Rh}(\text{COD})\text{Cl}]_2$  or  $\text{PdCl}_2(\text{PhCN})_2$ . The resulting films were removed from solution, washed with  $\text{CH}_3\text{CN}$ , and dried.

(i) *Electrocatalytic Reduction of CO<sub>2</sub> by Rh<sup>0</sup> or Pd<sup>0</sup> Dispersed in Films of poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>]-poly-vbpy.* Films reduced to form  $\text{Pd}^0$  or  $\text{Rh}^0$  were immersed in 0.1 M  $[\text{N}(\text{n-Bu})_4](\text{PF}_6)/\text{CH}_3\text{CN}$  saturated with  $\text{CO}_2$  gas, and cyclic voltammograms were measured. For product analysis, controlled-potential electrolyses were conducted in 0.1 M  $[\text{N}(\text{n-Bu})_4](\text{PF}_6)/\text{CH}_3\text{CN}$  solutions saturated with  $\text{CO}_2$  at -1.8 V on films containing dispersed  $\text{Rh}^0$  or  $\text{Pd}^0$  prepared as described above on vitreous carbon electrodes. The products were analyzed by procedures similar to those reported earlier.<sup>18</sup> No attempt was made to carry out the electrolyses quantitatively.

## Results

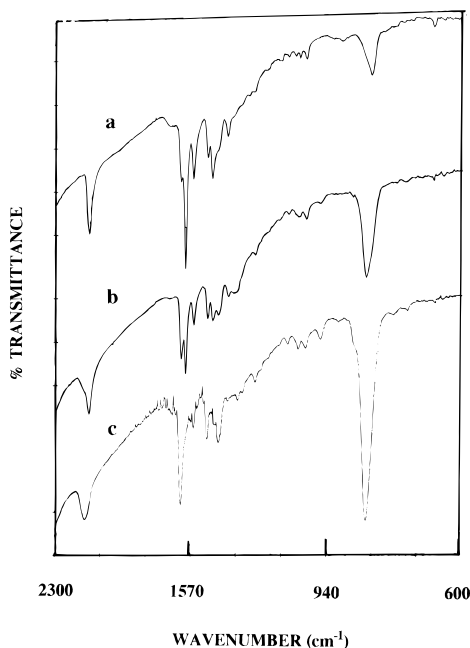
**Incorporation of [Rh(COD)Cl] into Films of poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>]-poly-vbpy.** When films of poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>]-poly-vbpy were exposed to  $\text{CH}_3\text{CN}$  solutions 0.1 M in  $[\text{Rh}(\text{COD})\text{Cl}]_2$  poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>]-poly-[Rh(vbpy)(COD)]Cl was formed after short reaction times (<0.5 h) and poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>]-poly-[Rh(vbpy)(COD)]Cl at longer reaction times (>0.5 h). A visible change in color from green to red was observed after only 15 min.

Evidence for the incorporation of  $[\text{Rh}(\text{COD})\text{Cl}]$  units into the films, film composition, and the nature of the film binding were inferred from the results of a number of experiments. In Figure 1 are shown reflectance FT-IR spectra of three films, poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>]-poly-vbpy; poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>]-poly-[Rh(vbpy)(COD)]Cl; and poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>]-poly-[Rh(vbpy)(COD)]Cl on Pt substrates. In comparing the spectra of poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>]-poly-vbpy, and poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>]-poly-[Rh(vbpy)(COD)]Cl, the  $\nu(\text{CN})$  stretch at 2080 cm<sup>-1</sup> was unchanged upon addition of  $[\text{Rh}(\text{COD})\text{Cl}]$ .

(16) (a) Abruna, H. D.; Denisevich, P.; Umana, M.; Meyer, T. J.; Murry, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 1. (b) Denisevich, P.; Abruna, H. D.; Leidner, R. C.; Meyer, T. J.; Murray, R. W. *J. Am. Chem. Soc.* **1982**, *21*, 2153.

(17) Woodward, W. S.; Rocklin, R. D.; Murray, R. W. *Chem. Biomed. Environ. Instrum.* **1979**, *9*, 95.

(18) Bolinger, C. M.; Story, N.; Sullivan, B. P.; and Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 4582.



**Figure 1.** Specular reflectance FT-IR spectra of thin films of (a) poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>],poly-vbpy, (b) poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>],poly-[Rh(vbpy)(COD)]Cl, and (c) poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>(CNRh(COD)Cl)]poly-[Rh(vbpy)(COD)]Cl on planar Pt electrodes.

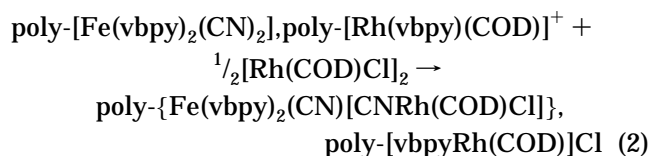
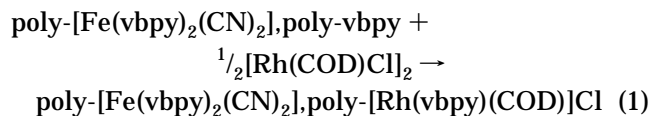
Cl]. The features of note that do change are the appearance of new bands due to  $\nu(\text{CH}=\text{CH})$  out-of-plane bending and  $\nu(\text{C}=\text{C})$  stretching modes of COD at 830 and 1616  $\text{cm}^{-1}$ , respectively. Ring stretching modes of vbpy and COD appear between 1300 and 1500  $\text{cm}^{-1}$ . The IR results suggest the presence of uncoordinated Fe-CN with incorporation of [Rh(COD)Cl] by binding to the uncoordinated vbpy group. For films exposed to [Rh(COD)Cl]<sub>2</sub> for extended periods,  $\nu(\text{CN})$  shifts to 2100  $\text{cm}^{-1}$  from 2080  $\text{cm}^{-1}$  in poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>],poly-vbpy and poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>],poly-[Rh(vbpy)(COD)]Cl. The  $\nu(\text{CH}=\text{CH})$  out-of-plane bending and  $\nu(\text{C}=\text{C})$  stretching modes in the disubstituted film were observed at 845 and 1616  $\text{cm}^{-1}$ , respectively. The intensity of the  $\nu(\text{CH}=\text{CH})$  out-of-plane bending mode of COD (as measured from peak areas) in poly-[Fe(vbpy)<sub>2</sub>(CN)-[CNRh(COD)Cl]],poly-[Rh(vbpy)(COD)]Cl is approximately twice that in poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>],poly-[Rh(vbpy)(COD)]Cl.

In the electronic absorption spectrum of poly-[Fe(vbpy)<sub>2</sub>(CN)[CNRh(COD)Cl]],poly-[Rh(COD)Cl]Cl formed on optically transparent ITO electrodes, the lowest energy absorption band appears at 560 nm in CH<sub>3</sub>CN compared to 612 nm for the dicyano film. The shift to higher energy is consistent with the spectral changes that occur on binding of Ag<sup>+</sup> in other dicyano films<sup>15</sup> and in related cyano-bridged complexes in solution.<sup>15,19</sup> The visible absorption bands originate in  $d\pi(\text{Fe}) \rightarrow \pi^*$ -(bpy) metal-to-ligand charge-transfer (MLCT) transitions. With binding to Rh(COD)Cl, the cyano group becomes a better  $\pi$  acceptor, stabilizing the  $d_\pi$  orbitals by backbonding. This increases the  $d\pi \rightarrow \pi^*$  energy gap and the absorption energy.

The elemental composition of the films was investigated by XPS. The XPS spectrum of a dicyano film exposed to CH<sub>3</sub>CN solutions containing [Rh(COD)Cl]<sub>2</sub>

for 12 h includes bands for Cl 2p (198 eV), C 1s(285.3 eV), Rh 3d (308.7 and 313.5 eV), N 1s (400 eV), and Fe 2p (709 and 722 eV). Quantitative analysis of the XPS bands gave a Rh:Fe ratio of 2.98:1.39 and Rh:Cl of 2.71:1.39. These results are consistent with the incorporation of two [Rh(COD)Cl] units into the film and the formulation, poly-[Fe(vbpy)<sub>2</sub>(CN)[CNRh(COD)Cl]],poly-[Rh(vbpy)(COD)]Cl.

On the basis of the spectroscopic and XPS results, one [Rh(COD)Cl] unit binds to vbpy at shorter reaction times, eq 1, and a second at a cyano group at longer reaction times, eq 2.



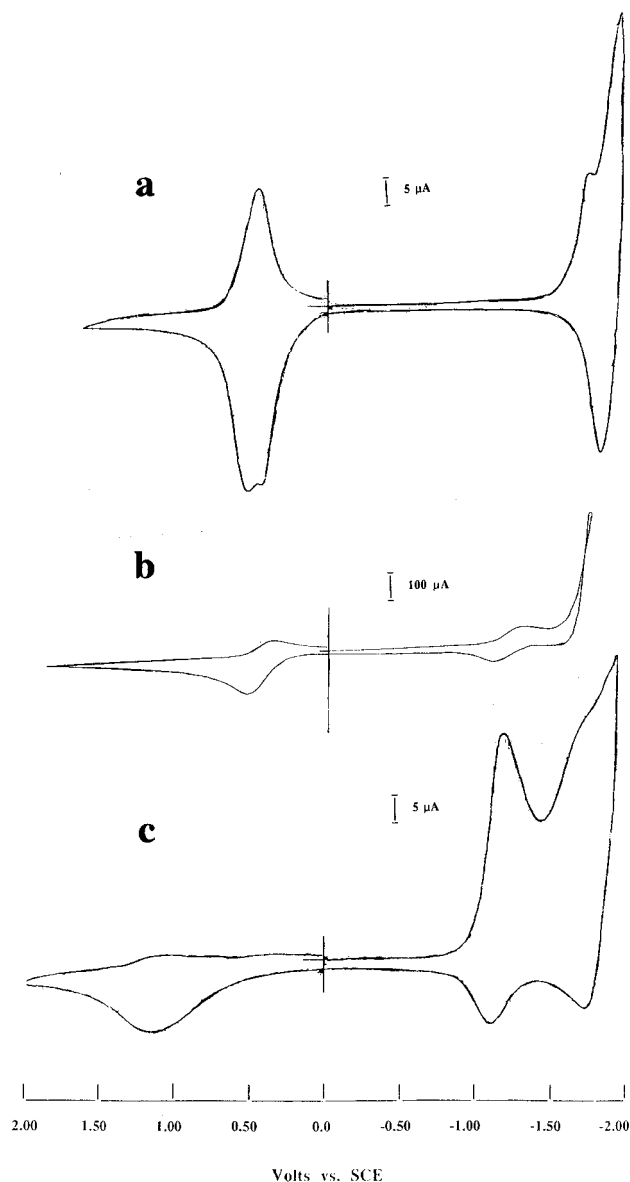
The bound Rh(COD)Cl units are labile. They could be removed from the films by soaking in 0.1 M [NEt<sub>4</sub>]CN/CH<sub>3</sub>CN for 15 min, resulting in the recovery of the dicyano films as shown by spectroscopic and electrochemical measurements.

**Electrochemistry.** In the cyclic voltammogram of poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>],poly-vbpy in Figure 2a, an Fe<sup>III/II</sup> wave appears at +0.44 V with prewaves appearing on the vbpy reduction and Fe<sup>III/II</sup> waves. For poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>],poly-[Rh(vbpy)(COD)]Cl (Figure 2b) an Fe<sup>III/II</sup> wave appears at  $E_{1/2} = +0.44$  V which is only partly chemically reversible ( $E_{p,a} = +0.52$  V, and  $E_{p,c} = +0.37$  V with  $i_{p,a} > i_{p,c}$ ) and a reversible Rh<sup>I/0</sup> wave appears at  $E_{1/2} = -1.2$  V. For poly-[Rh<sup>I</sup>(vbpy)(COD)]<sup>+</sup> a reversible Rh<sup>I/0</sup> wave appears at  $E_{1/2} = -1.14$  V in 0.2 M [N(*n*-Bu)<sub>4</sub>]Br/CH<sub>3</sub>CN.<sup>20</sup> For [Rh<sup>I</sup>(Me<sub>2</sub>bpy)(COD)]<sup>+</sup> (Me<sub>2</sub>bpy = 4,4'-(CH<sub>3</sub>)<sub>2</sub>-2,2'-bipyridine) and [Rh<sup>I</sup>(bpy)(COD)]<sup>+</sup> reversible reduction waves appear at  $-1.24^{20}$  and  $-1.26$  V,<sup>19</sup> respectively. In Figure 2c is shown a cyclic voltammogram of poly-[Fe(vbpy)<sub>2</sub>(CN)[CNRh(COD)Cl]],poly-[vbpyRh(COD)]Cl in which waves appear at  $E_{1/2} = -1.12$  V ( $E_{p,c} = -1.16$  V,  $E_{p,a} = -1.08$  V;  $i_{p,c} > i_{p,a}$ ),  $E_{1/2} = -1.68$  V ( $E_{p,c} = -1.7$  V,  $E_{p,a} = -1.68$  V), and an oxidation at  $E_{1/2} = 1.05$  which is partially reversible chemically ( $E_{p,a} = +1.10$  V,  $E_{p,c} = +1.0$  V;  $i_{p,a} > i_{p,c}$ ). In the cyclic voltammogram of the dicyano film in Figure 2a, a reversible reduction occurs at  $-1.87$  V. The increase in  $E_{1/2}$  for the Fe<sup>III/II</sup> wave is consistent with Rh<sup>I</sup> binding at cyanide. A similar effect has been observed upon binding of Ag<sup>+</sup>.<sup>12</sup> For poly-[Fe(vbpy)<sub>3</sub>]<sup>2+</sup> the Fe<sup>III/II</sup> wave is at  $E_{1/2} = +1.00$  V, and bpy reductions are observed at  $E_{1/2} = -1.33$ ,  $-1.53$ , and  $-1.76$  V. Sharp prewaves appear at  $E_{p,c} = -1.62$ ,  $E_{p,a} = +0.31$  V for poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>],poly-vbpy and at  $E_{p,c} = +1.12$  V,  $E_{p,a} = 0.88$  V for poly-[Fe(vbpy)<sub>3</sub>]<sup>2+</sup>. These appear

(20) Meyer, T. J.; Sullivan, B. P.; Caspar, J. V. *Inorg.Chem.* **1987**, 26, 4145.

(21) (a) Peterson, S. H.; Demas, J. N. *J. Am. Chem. Soc.* **1976**, 98, 7880. (b) Peterson, S. H.; Demas, J. N. *J. Am. Chem. Soc.* **1979**, 101, 6576. (c) Kinnaird, M. G.; Whitten, D. G. *Chem. Phys. Lett.* **1982**, 88, 275. (d) Bignozzi, C. A.; Scandola, F. *Inorg. Chem.* **1984**, 23, 1540.

(19) Fordyce, W. A.; Pool, K. H.; and Crosby, G. A. *Inorg. Chem.* **1982**, 21, 1027.



**Figure 2.** Cyclic voltammograms of thin films on Pt electrodes ( $0.125 \text{ cm}^2$ ) in  $\text{CH}_3\text{CN}$   $0.1 \text{ M}$  in  $[\text{N}(n\text{-Bu})_4]\text{PF}_6$ , at a scan rate of  $10 \text{ mV/s}$  vs SSCE (scans were initiated just  $+0 \text{ V}$  and scanned negatively): (a) poly-[ $\text{Fe}(\text{vbpy})_2(\text{CN})_2$ ].poly-vbpy, (b) poly-[ $\text{Fe}(\text{vbpy})_2(\text{CN})_2$ ].poly-[ $\text{Rh}(\text{vbpy})(\text{COD})$ ] $^+$ , and (c) poly-[ $\text{Fe}(\text{vbpy})_2(\text{CN})[\text{CNRh}(\text{COD})\text{Cl}]$ ].poly-[ $\text{Rh}(\text{vbpy})(\text{COD})$ ] $^+$ .

in related films and have been attributed to structural changes or trap sites.<sup>16</sup>

**Electrodeposition of  $\text{Rh}^0$ .**  $\text{Rh}^0$  particles were deposited on films of poly-[ $\text{Fe}(\text{vbpy})_2(\text{CN})_2$ ].poly-vbpy or poly-[ $\text{Fe}(\text{vbpy})_3$ ] $^{2+}$  by repetitive voltammetric scans ( $10$ ) between  $-0.7$  and  $-1.70 \text{ V}$  with  $[\text{Rh}(\text{COD})\text{Cl}]_2$  ( $0.01 \text{ M}$ ) in the external solution. In cyclic voltammograms following this procedure a prewave appeared at  $E_{p,a} = -1.52 \text{ V}$ , a reversible reduction wave at  $E_{1/2} = -1.84 \text{ V}$ , and an irreversible oxidation wave at  $E_{p,a} = +1.06 \text{ V}$ . In cyclic voltammograms of poly-[ $\text{Fe}(\text{vbpy})_3$ ] $^{2+}$  containing dispersed  $\text{Rh}^0$ , reversible reductions appeared at  $E_{1/2} = -1.17$  and  $-1.37 \text{ V}$  and an irreversible oxidation at  $E_{p,a} = +1.15 \text{ V}$ . The irreversible oxidations in both films are presumably due to oxidation of  $\text{Rh}^0$  to  $\text{Rh}^{\text{I}}$ . Cyclic voltammogram of  $0.1 \text{ M}$   $[\text{N}(n\text{-Bu})_4]\text{PF}_6/\text{CH}_3\text{CN}$  solutions containing  $0.01 \text{ M}$   $[\text{Rh}(\text{COD})\text{Cl}]_2$  have an irreversible oxidation wave at  $E_{p,a} = +0.94 \text{ V}$  following a potential scan to  $-1.7 \text{ V}$  and reversal. On an initial oxidative

scan a wave was observed at  $E_{p,a} = +0.88 \text{ V}$  presumably due to oxidation of  $\text{Rh}^{\text{I}}$ .

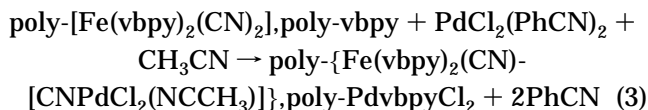
**Electrocatalytic Reduction of  $\text{CO}_2$  by  $\text{Rh}^0$ .** Films containing dispersed  $\text{Rh}^0$  particles display no significant reactivity toward  $\text{CO}_2$  dissolved in  $0.1 \text{ M}$   $[\text{N}(n\text{-Bu})_4]\text{PF}_6/\text{CH}_3\text{CN}$  in cyclic voltammograms. In the presence of small amounts of water a catalytic current was observed with a wave at  $E_{p,c} = -0.9 \text{ V}$  which displayed a hysteresis effect upon scan reversal. These properties are similar to those observed for  $\text{Rh}^0$  particles dispersed in films of poly-[ $\text{Rh}(\text{vbpy})\text{Cl}]^+$ .<sup>22</sup>

**Reaction of  $\text{PdCl}_2(\text{PhCN})_2$  with films of poly-[ $\text{Fe}(\text{vbpy})_2(\text{CN})_2$ ].poly-vbpy.** When a green film of poly-[ $\text{Fe}(\text{vbpy})_2(\text{CN})_2$ ].poly-vbpy was soaked in  $\text{CH}_3\text{CN}$  solution  $0.1 \text{ M}$  in  $\text{PdCl}_2(\text{PhCN})_2$  a reaction proceeds as evidenced by the red color that develops. Spectroscopic and electrochemical measurements show that this reaction requires at least  $10 \text{ min}$  for completion. The red film is poly-[ $\text{Fe}(\text{vbpy})_2[\text{CNPd}(\text{CH}_3\text{CN})\text{Cl}_2](\text{CN})$ ].poly-vbpy $\text{PdCl}_2$  as shown by spectroscopic and electrochemical measurements.

In the IR spectrum of a dicyano film exposed to  $0.1 \text{ M}$   $\text{PdCl}_2(\text{PhCN})_2$  in  $\text{CH}_3\text{CN}$  a  $\nu(\text{CN})$  stretch appears at  $2114 \text{ cm}^{-1}$  and a shoulder at  $2094 \text{ cm}^{-1}$ . The shift to higher energy compared to the dicyano film ( $2080 \text{ cm}^{-1}$ ) is found in cyano-bridged complexes.<sup>23</sup> In the  $\nu(\text{bpy})$  ring stretching modes from  $1300$  to  $1650 \text{ cm}^{-1}$  only minor changes were noted. A band at  $1593 \text{ cm}^{-1}$  disappears and a band of lower intensity appears at  $1609 \text{ cm}^{-1}$ .

The electronic absorption spectrum of poly-[ $\text{Fe}(\text{vbpy})_2[\text{CNPd}(\text{CH}_3\text{CN})\text{Cl}_2](\text{CN})$ ].poly-vbpy $\text{PdCl}_2$  has its lowest absorption band at  $512 \text{ nm}$ . The shift to higher energy is comparable to that observed upon binding  $[\text{Rh}(\text{COD})\text{Cl}]$  or  $\text{Ag}^+$  to the dicyano film.

The elemental composition of the Pd-containing film was determined from XPS measurements. The XPS spectrum of a dicyano film soaked in  $0.1 \text{ M}$   $\text{PdCl}_2(\text{PhCN})_2$  in  $\text{CH}_3\text{CN}$  for  $15 \text{ min}$  includes peaks due to Cl  $2p$  ( $190 \text{ eV}$ ), C  $1s$  ( $285.2 \text{ eV}$ ), Pd  $3d$  ( $338.6$  and  $343.9 \text{ eV}$ ), N  $1s$  ( $399.6 \text{ eV}$ ), O  $1s$  ( $532.2 \text{ eV}$ ), and Fe  $2p$  ( $708$  and  $721.5 \text{ eV}$ ).<sup>24</sup> The binding energy for Pd  $3d$  is similar to those reported for films containing  $\text{PdCl}_2$ .<sup>25</sup> From quantitative peak analysis the ratio of elemental concentrations of Pd  $3d$  to Fe  $2p$  was  $1.86:1.0$ .<sup>24</sup> In comparing the binding energy of the palladium-bound film to the starting dicyano film, the N  $1s$  (vbpy) peak is shifted  $+0.5 \text{ eV}$  to higher energy, and the N  $1s$  (CN)  $+1.0 \text{ eV}$  higher. These results point to the presence of two  $\text{PdCl}_2$  units, one bound to the free vbpy and the other to one cyano group eq 3. This result is similar to the result



found for incorporation of  $[\text{Rh}(\text{COD})\text{Cl}]$  units at long soaking times and suggests the reaction in eq 3. The

(22) O'Toole, T. R.; Meyer, T. J.; Sullivan, B. P. *Chem. Mater.* **1989**, *1*, 574.

(23) (a) Shriver, D. F.; Posner, J. *J. Am. Chem. Soc.* **1966**, *88*, 1672. (b) Kinnaid, M. G.; Whitten, D. G. *Chem. Phys. Lett.* **1982**, *88*, 275.

(c) Bignozzi, C. A.; Scandola, F. *Inorg. Chem.* **1984**, *23*, 1540.

(24) Kumar, G.; Blackburn, J. R.; Albridge, R. G.; Moddeman, W. E.; Jones, M. M. *Inorg. Chem.* **1972**, *11*, 296.

(25) Kim, K. S.; Grossmann, A. F.; Winograd, N. *Anal. Chem.* **1974**, *46*, 197.

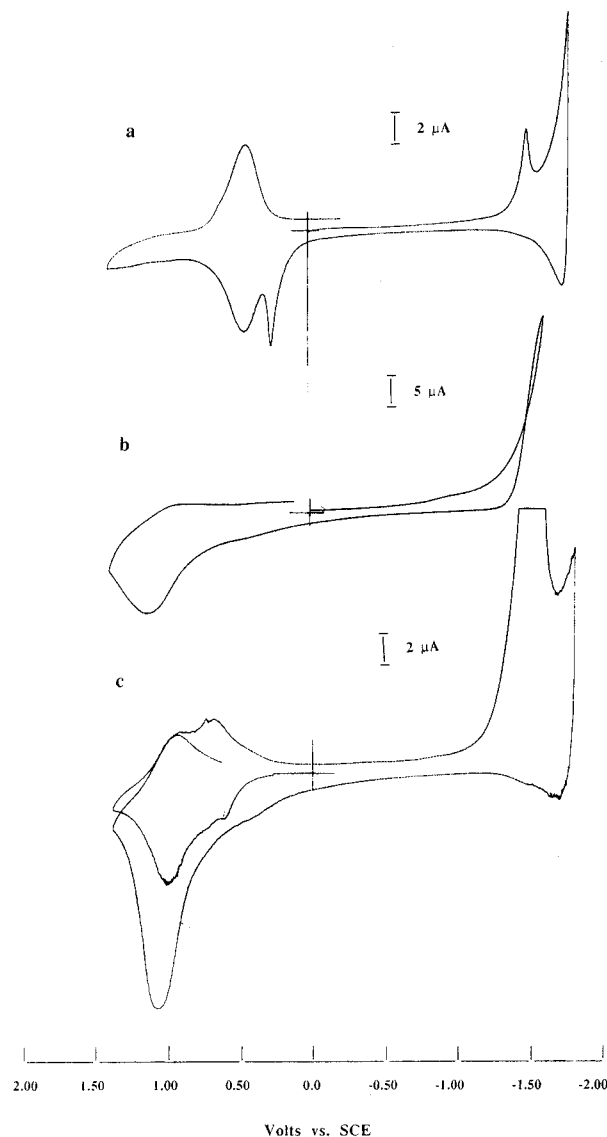
presence of  $\text{CH}_3\text{CN}$  in the fourth coordination site at  $\text{Pd}(\text{II})$  is only a suggestion based on the prediction of four-coordination for  $\text{Pd}(\text{II})$  and the fact that  $\text{CH}_3\text{CN}$  was the solvent.

The bound  $\text{PdCl}_2$  units are labile and could be removed by soaking in 0.01 M  $[\text{N}(\text{n-Bu})_4]\text{CN}/\text{CH}_3\text{CN}$  to form poly- $[\text{Fe}(\text{vbpy})_2(\text{CN})_2]$ , poly-vbpy as shown by electrochemical and spectroscopic measurements.

Sputter depth profile experiments were conducted to study the effect of dynamic sputtering on the distribution of  $\text{PdCl}_2$  in poly- $\{\text{Fe}(\text{vbpy})_2(\text{CN})[\text{CNPdCl}_2(\text{CH}_3\text{CN})]\}$ , poly- $\text{Pd}(\text{vbpy})\text{Cl}_2$ .  $\text{Ar}^+$  ions were used to expose the surface for analysis at a removal rate of 150 Å of material sputter removed per minute. A typical film thickness of 1000 Å required 5–7 min to reach the film/electrode interface. A plot of intensity versus sputter time for Pd/C and Pt in this film reveals a relatively homogeneous distribution of  $\text{PdCl}_2$  throughout the film without significant concentration at the electrode–film or film–solution interfaces. Curve-fitting reveals the presence of two Pd peaks, at 337.8 and 336.0 eV, the latter consistent with reduced Pd. The appearance of reduced Pd appears to be a sputter-induced effect.

**Electrochemistry of poly- $\{\text{Fe}(\text{vbpy})_2(\text{CN})[\text{CNPdCl}_2(\text{CH}_3\text{CN})]\}$ , poly- $\text{Pd}(\text{vbpy})\text{Cl}_2$ .** Cyclic voltammograms of poly- $\{\text{Fe}(\text{vbpy})_2(\text{CN})[\text{CNPdCl}_2(\text{NCCH}_3)]\}$ , poly-vbpy $\text{PdCl}_2$  in  $\text{CH}_3\text{CN}$  are shown in Figure 3b,c and of poly- $[\text{Fe}(\text{vbpy})_2(\text{CN})_2]$ , poly-vbpy in Figure 3a for comparison. The prewaves were mentioned above. Upon reductive scanning (Figure 3b), there is evidence for  $\text{Pd}^{\text{II}}$  reduction by the appearance of an ill-defined, slowly rising reductive current before the first bpy-based reduction of the dicyano film at  $-1.50$  V. The existence of a coupled, chemically irreversible reaction is suggested by the hysteresis when the scan is reversed. In this voltammogram the  $\text{Fe}^{\text{III/II}}$  couple was observed as a quasireversible wave at  $E_{1/2} + 1.05$  V ( $E_{p,a} = 1.10$  and  $E_{p,c} = 1.0$  V;  $i_{p,a} > i_{p,c}$ ). This is the potential for the  $\text{Fe}^{\text{III/II}}$  couple of poly- $[\text{Fe}(\text{vbpy})_3](\text{PF}_6)_2$ . Evidence for an additional oxidation ( $\text{Pd}^0$  to  $\text{Pd}^{\text{II}}$ ) was found on continuing the scan past the  $\text{Fe}^{\text{III/II}}$  couple where there is a current enhancement. On an initial oxidative scan on poly- $[\text{Fe}(\text{vbpy})_2(\text{CN})[\text{CNPdCl}_2]]$ , poly-vbpy $\text{PdCl}_2$  (Figure 3c), two closely spaced, reversible oxidative couples appear at  $E_{1/2} = +0.68$  and  $+0.94$  V ( $E_{p,a} = +0.70$  and  $0.98$  and  $E_{p,c} = +0.66$  and  $0.90$  V) with an oxidative prewave at  $E_{p,a} = +0.6$  V. In a subsequent reductive scan a reductive wave of higher peak current appeared at  $E_{p,c} = -1.5$  V. The oxidation wave at  $E_{1/2} = +0.68$  V in poly- $\{\text{Fe}(\text{vbpy})_2(\text{CN})[\text{CNPdCl}_2(\text{NCCH}_3)]\}$ , poly- $\text{Pd}(\text{vbpy})\text{Cl}_2$  is probably the  $\text{Fe}^{\text{III/II}}$  couple of the  $\text{PdCl}_2$ -bound cyano unit, and the oxidative wave at  $E_{1/2} = 1.05$  V the  $\text{Fe}^{\text{III/II}}$  wave of poly- $[\text{Fe}(\text{vbpy})_3]^{2+}$ . The formation of the tris-chelate complex must follow oxidative loss of  $\text{CN-PdCl}_2$  units from the films. Oxidation to  $\text{Fe}^{\text{III}}$  is known to labilize the  $\text{Fe-CN}$  bond resulting in formation of poly- $[\text{Fe}(\text{vbpy})_3]^{2+}$ .<sup>15</sup> The cyclic voltammogram of poly- $\{\text{Fe}(\text{vbpy})_2(\text{CN})[\text{CNPdCl}_2(\text{NCCH}_3)]\}$ , poly- $\text{Pd}(\text{vbpy})\text{Cl}_2$  after a reductive scan, (Figure 3c) suggests the reductive loss of the cyano groups and formation of poly- $[\text{Fe}(\text{vbpy})_3]^{2+}$ .

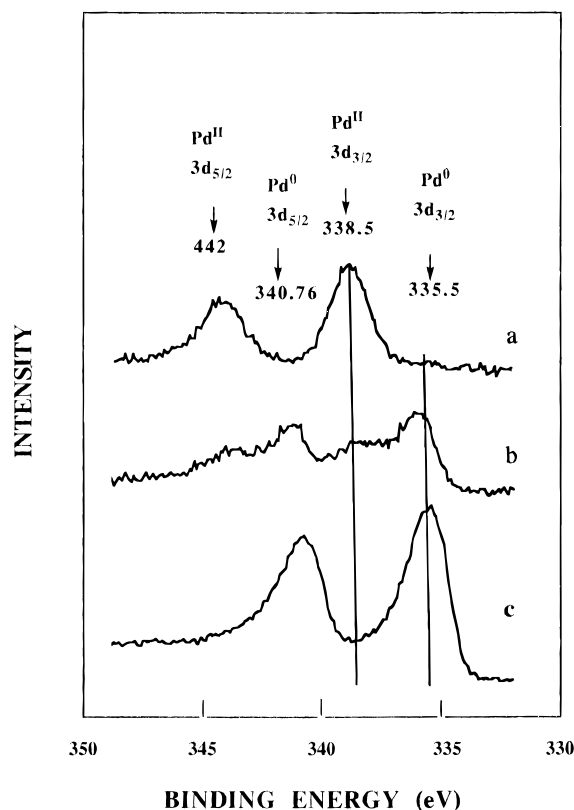
Reduction of poly- $\{\text{Fe}(\text{vbpy})_2(\text{CN})[\text{CNPdCl}_2(\text{NCCH}_3)]\}$ , poly- $\text{Pd}(\text{vbpy})\text{Cl}_2$  by reductive scans ( $> 10$  scans) between  $-0.7$  and  $-1.7$  V scans resulted in the reduction of  $\text{PdCl}_2$  to  $\text{Pd}^0$  and regeneration of poly- $[\text{Fe}(\text{vbpy})_3]^{2+}$  as shown by electrochemistry and XPS. The XPS results (Figure



**Figure 3.** Cyclic voltammograms of thin films on Pt electrodes ( $0.125 \text{ cm}^2$ ) in  $\text{CH}_3\text{CN}$  0.1 M in  $[\text{N}(\text{n-Bu})_4]\text{PF}_6$ , at a scan rate of 10 mV/s vs SSCE (a) poly- $[\text{Fe}(\text{vbpy})_2(\text{CN})_2]$ , poly-vbpy, (b) poly- $\{\text{Fe}(\text{vbpy})_2(\text{CN})[\text{CNPdCl}_2(\text{CH}_3\text{CN})]\}$  poly- $\text{Pd}(\text{vbpy})\text{Cl}_2$  with the scan initiated in the negative direction, and (c) the same as (b) with a scan initiated in the positive direction

5) show three resolvable contributions to the  $\text{Pd}3d$  signal assigned to unreduced  $\text{PdCl}_2$  (52%), palladium particles ( $\text{Pd}^0$ , 38.4%), and oxidized palladium ( $\text{PdO}$ , 9.6%).<sup>24</sup> The binding energy for  $\text{Pd}^0$  and  $\text{Pd}^{\text{II}}\text{O}$  are similar to those reported for other  $\text{Pd}^0$  and  $\text{Pd}^{\text{II}}\text{O}$  moieties incorporated in thin films.<sup>26</sup> The  $\text{Pd}^{\text{II}}\text{O}$  may have resulted from air oxidation of  $\text{Pd}^0$  during the transfer from the inert atmosphere to the XPS apparatus. There is also a partial loss of Pd, perhaps consistent with the partial loss of Pd upon oxidation. A shift of  $-0.5$  eV was observed in the reduced film compared to the  $\text{Pd}^{\text{II}}$ -bound film signaling the partial loss of  $\text{Pd}^0$  from the cyano groups upon reduction. Sputter depth profile experiments were used to study the Pd distribution versus depth in order to determine the extent of reduction. A plot of Pd as a function of sputter time is consistent with a homogeneous distribution of Pd particles throughout the film.

(26) Bird, R. J.; Swift, P. J. *Electron Spectrosc. Relat. Phenom.* **1980**, *21*, 227.



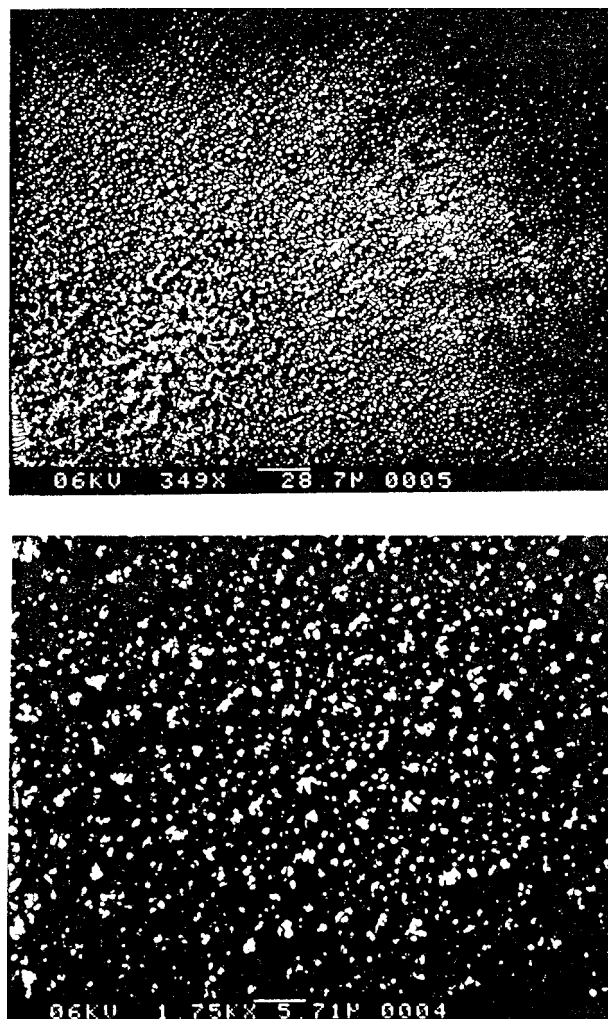
**Figure 4.** XPS Pd3d bands in (a) poly-{Fe(vbpy)<sub>2</sub>(CN)-[CNPdCl<sub>2</sub>(NCCH<sub>3</sub>)]}, poly-Pd(vbpy)Cl<sub>2</sub>, (b) poly-{Fe(vbpy)<sub>2</sub>(CN)-[CNPdCl<sub>2</sub>(NCCH<sub>3</sub>)]}, poly-Pd(vbpy)Cl<sub>2</sub> following a reductive scan between -0.7 and -1.7 V, and (c) poly-{Fe(vbpy)<sub>2</sub>(CN)-[CNPdCl<sub>2</sub>(NCCH<sub>3</sub>)]}, poly-Pd(vbpy)Cl<sub>2</sub> following reductive scans between -0.7 and -1.7 V with 0.1 M PdCl<sub>2</sub>(PhCN)<sub>2</sub> in the external solution.

**Electrodeposition of Pd<sup>0</sup> and the Electrocatalytic Reduction of CO<sub>2</sub>.** Palladium particles were deposited within and on films of poly-{Fe(vbpy)<sub>2</sub>(CN)-[CNPdCl<sub>2</sub>(NCCH<sub>3</sub>)]}, poly-Pd(vbpy)Cl<sub>2</sub> and poly-[Fe(vbpy)<sub>3</sub>]<sup>2+</sup> by repetitive scans between -0.7 and -1.7 V in the presence of 0.01 M PdCl<sub>2</sub>(PhCN)<sub>2</sub> in CH<sub>3</sub>CN. SEM micrographs at two different resolutions obtained at the end of a scan sequence (10 scans) are shown in Figure 4. These micrographs show a non-uniform distribution of Pd particles on the surface. XPS results (Figure 5) show Pd3d signals due to PdCl<sub>2</sub> (48%), Pd<sup>0</sup> (52.8%), and Pd<sup>II</sup>O (13.2%).<sup>24</sup>

The Pd<sup>0</sup> particles on and in the films are electrocatalysts for the reduction of CO<sub>2</sub>. Electrocatalytic reduction of CO<sub>2</sub> in 0.1 M [N(*n*-Bu)<sub>4</sub>]PF<sub>6</sub>/CH<sub>3</sub>CN when the potential was held at -1.8 V resulted in the formation of CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and other hydrocarbons.

**Incorporation and Reduction of PdCl<sub>2</sub>(PhCN)<sub>2</sub> into Films of poly-[Fe(vbpy)<sub>3</sub>]<sup>2+</sup>.** When a film of poly-[Fe(vbpy)<sub>3</sub>]<sup>2+</sup> is soaked in 0.1 M PdCl<sub>2</sub>(PhCN)<sub>2</sub> in CH<sub>3</sub>CN, PdCl<sub>2</sub>(PhCN)<sub>2</sub> enters the films. In cyclic voltammograms of the resulting films, the expected Fe<sup>III/II</sup> couple appears at +1.01 V, and reversible bpy reduction waves appear at *E*<sub>1/2</sub> = -1.40 and -1.55 V with a prewave at -1.3 V. For the same film before addition of PdCl<sub>2</sub>(PhCN)<sub>2</sub>, the Fe<sup>III/II</sup> couple was observed at *E*<sub>1/2</sub> = +1.02 V and bpy reduction waves appeared at *E*<sub>1/2</sub> = -1.35 and -1.54 V with a prewave at -1.22 V.

Reduction of PdCl<sub>2</sub>(PhCN)<sub>2</sub> in films of poly-[Fe(vbpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> by repetitive scans between -0.7 and -1.7 V resulted in the reduction of Pd<sup>II</sup>. A cyclic voltam-



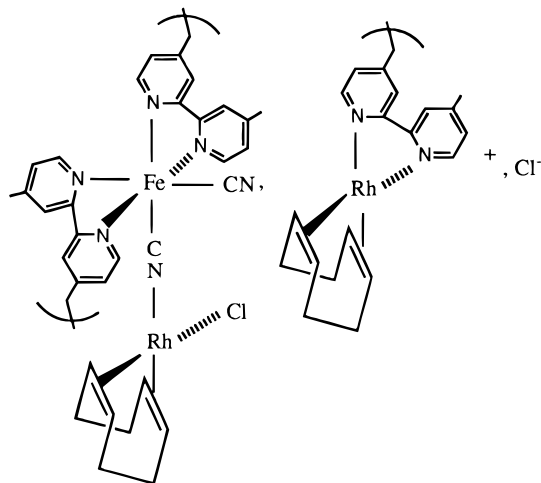
**Figure 5.** SEM micrographs of palladium particles on poly-{Fe(vbpy)<sub>2</sub>(CN)[CNPdCl<sub>2</sub>(NCCH<sub>3</sub>)]}, poly-Pd(vbpy)Cl<sub>2</sub> formed by scanning from -0.7 to -1.7 V vs SSCE in a 0.1 M [N(*n*-Bu)<sub>4</sub>]PF<sub>6</sub> solution 0.01 M in PdCl<sub>2</sub>(PhCN)<sub>2</sub> at a scan rate of 50 mV/s. The scales for (a) and (b) in μm are indicated at the bottom of the figures.

gram of the reduced film includes a chemically irreversible oxidation wave at *E*<sub>p,a</sub> = +1.1 V, an Fe<sup>III/II</sup> couple which is chemically quasi-reversible at *E*<sub>1/2</sub> = +1.04 V (*E*<sub>p,a</sub> = +1.15, *E*<sub>p,c</sub> = +0.93 V; *i*<sub>p,a</sub> > *i*<sub>p,c</sub>), a reductive wave at -1.48 V and two oxidative waves at -1.55 and -1.22 V. The oxidation wave at *E*<sub>p,a</sub> = +1.1 V is probably due to Pd<sup>0</sup> oxidation.

## Discussion

Our results reinforce those found earlier which demonstrate the ability of poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>], poly-vbpy to act as a coordinating environment for binding metal ions and complexes, in this case [Rh(COD)Cl]<sub>2</sub> and PdCl<sub>2</sub>(PhCN)<sub>2</sub>. From the available evidence the films are capable of binding either two [PdCl<sub>2</sub>] or [Rh(COD)Cl] units, but there are some differences in the coordination chemistry. For [Rh(COD)Cl]<sub>2</sub> both vbpy and -CN sites are used for binding. Kinetically, binding to the free vbpy occurs first and is completed within 5 min. Binding to the cyano group occurs more slowly (>1/2 h).

From the electrochemical and spectroscopic data a structural model for the proposed chemical binding in these films is shown below. This and the PdCl<sub>2</sub> films are interesting cases where the same metal ion is present but in different coordination environments.



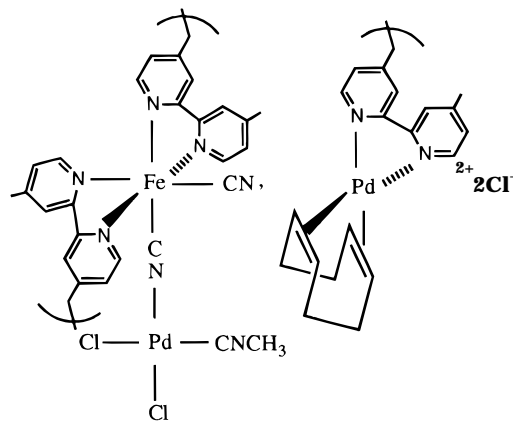
Spectroscopic evidence for the presence of the [Rh(COD)Cl] unit was obtained by FT-IR and electrochemical measurements. Bands characteristic of the COD ligand appear in the FT-IR. The presence of chloride was verified by XPS measurements. In cyclic voltammograms, a bpy-based reduction wave appears at a potential near those reported earlier for thin films of poly-[Rh(COD)(vbpy)]<sup>+</sup> and the model compounds [Rh(bpy)(COD)]<sup>+</sup> and [Rh(4,4'-met-bpy)(COD)]<sup>+</sup>.

The rhodium units in the films are slowly labilized by soaking in 0.1 M [NEt<sub>4</sub>]CN/CH<sub>3</sub>CN solution for extended periods to give poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>], poly-vbpy. The Rh(COD)Cl units are also lost upon reductive or oxidative cycling to give poly-[Fe(vbpy)<sub>3</sub>]<sup>2+</sup>.

For poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>], poly-[Rh(vbpy)(COD)Cl]-(PF<sub>6</sub>) evidence for the reduction of the vbpy bound rhodium units is shown by the appearance of a reduction wave at  $E_{1/2} = -1.18$  V. It is followed by a hysteresis at  $E_{p,c} = -1.68$  V which accompanies reduction of [Rh(COD)Cl] to Rh<sup>0</sup>. Selective binding to poly-vbpy is shown clearly in oxidative sweeps. The Fe<sup>III/II</sup> couple was observed in the same region as in the dicyano film, poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>], poly-vbpy.

Dispersed Rh particles were formed by repetitive reductive scans between  $-0.7$  and  $-1.7$  V with 0.01 M [Rh(COD)Cl]<sub>2</sub> in the external solution. The resulting films display no electrocatalytic behavior toward CO<sub>2</sub> reduction in dry acetonitrile but in the presence of small quantities of water a catalytic wave is observed similar to the results reported for rhodium particles dispersed in thin films of poly-[Rh(COD)Cl]<sup>+</sup>.<sup>22</sup>

For PdCl<sub>2</sub>(BN)<sub>2</sub> two PdCl<sub>2</sub> are incorporated as well. The evidence for Pd<sup>II</sup> binding comes from the shift of one  $\nu(\text{CN})$  band to higher energy compared to the dicyano film and from XPS measurements. The binding energy for N1s of the vbpy group shifts to higher energy and N1s for CN by 1.0 eV compared to poly-[Fe(vbpy)<sub>2</sub>(CN)<sub>2</sub>], poly-vbpy. The evidence again points to Pd<sup>II</sup> binding to one cyano group and the free vbpy as shown below.



The electrochemistry of the Pd<sup>II</sup> containing film was less well defined. There is no clear evidence on reductive scans for well-defined reduction at either Pd<sup>II</sup> or vbpy, rather a noticeable increase in current above background is seen past  $\sim -1.3$  V. Two waves appear in initial oxidative scans. A Pd<sup>II</sup> oxidation at  $E_{p,a} = +1.05$  V may overlap with the Fe<sup>III/II</sup> couple of poly-[Fe(vbpy)<sub>3</sub>]<sup>2+</sup>. Repetitive oxidative or reductive scans result in labilization of CN<sup>-</sup> and formation of poly-[Fe(vbpy)<sub>3</sub>]<sup>2+</sup>.

As in case of Ag<sup>+</sup> deposition, reductive scans with PdCl<sub>2</sub>(BN)<sub>2</sub> in the external solution results in formation of Pd<sup>0</sup> particles on the film surface. The particles are nonuniform in size and shape and fall in the size range  $<0.5$  to  $2\ \mu\text{m}$ . These films are also active toward the electrocatalytic reduction of carbon dioxide.

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