

distinct hydrocarbon and carbonyl peaks; however, a corresponding oxygen peak is not evident. The extra carbon peak is small and could result from differential charging.

Microscopic examination using direct atomic number (BSE) sensitive SEM of the as-prepared sample of **2** and STEM of thin sections of **2** with EDX microchemical analysis, including C and O, revealed that the magnetic material is not homogeneous. The material was, however, composed of isolated and widely separated regions of pure carbon distributed in a matrix containing an intimate mixture of separate cadmium and iron (Figure 2). Thus, we believe that the reported ferromagnetic species arises from iron oxide species. The carbon phase was typically a few micrometers in size. The cadmium- and iron-containing species were dispersed on a very fine scale in varying proportions in differing areas, atomic ratio centered on 1:2:5 for Cd:Fe:O, which is lower than observed from the bulk elemental analysis. This matrix was essentially free of carbon; which was at a low level and all located in discrete carbon particles. **3** exhibits similar micrographs except, of course, that the cadmium is not present.

Registry No. Cd(O₂CMe)₂, 543-90-8; *p*-phenylenediamine, 106-50-3; 1,1'-diacetylferrocene, 1273-94-5.

Reversible Carbon Monoxide Addition to Sol-Gel Derived Composite Films Containing a Cationic Rhodium(I) Complex: Toward the Development of a New Class of Molecule-Based CO Sensors

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We are currently interested in the development of chemical sensors that are based on the incorporation of reactive molecular species into polymeric thin films by low-temperature sol-gel methods. Previous work in our laboratories and in others has demonstrated the general usefulness of sol-gel derived glasses for the encapsulation of guest molecules such as inorganic clusters, porphyrins, and lanthanide cryptate complexes.^{1,2} Herein we report

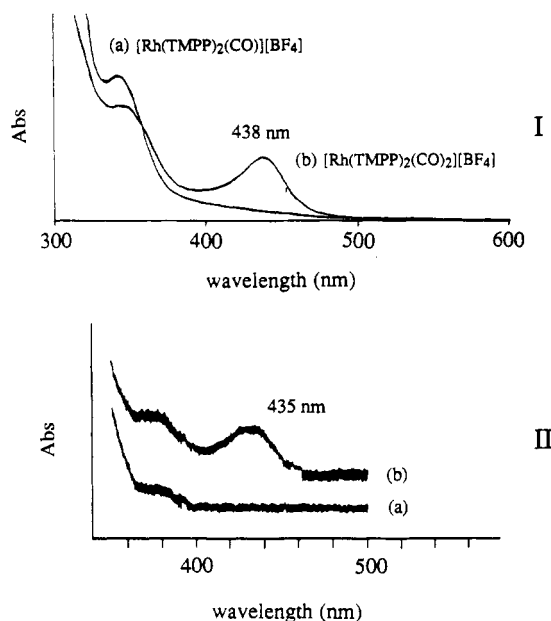
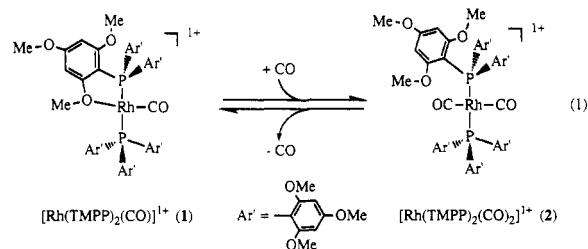


Figure 1. Electronic absorption spectra of (a) [Rh(TMPP)₂(CO)][BF₄] and (b) [Rh(TMPP)₂(CO)₂][BF₄] in (I) CH₂Cl₂ and (II) a zirconia composite film.

the synthesis and CO binding properties of zirconia and titania glasses impregnated with a rhodium ether-phosphine compound, the results of which are promising for future adaptations of such molecular species as chemical sensors.

Recently, we reported the reversible solution chemistry of the novel mononuclear Rh(II) complex [Rh(η³-TMPP)₂][BF₄]₂ (TMPP = tris(2,4,6-trimethoxyphenyl)-phosphine) with carbon monoxide.³ The reaction was found to proceed by a redox pathway that involves the formation of the Rh(I) carbonyl intermediates [Rh(TMPP)₂(CO)][BF₄] (**1**) and [Rh(TMPP)₂(CO)₂][BF₄] (**2**); these complexes have been fully characterized by X-ray crystallography, cyclic voltammetry, and infrared and NMR spectroscopies.³ In solution, complex **1** rapidly and reversibly binds carbon monoxide under ambient conditions to form the dicarbonyl species **2** (eq 1). In the



absence of a CO atmosphere, **2** loses CO to re-form **1**. The facile nature of the carbon monoxide addition to [Rh(TMPP)₂(CO)][BF₄] (**1**) is exemplified by the observation that finely divided powder and Nujol mull samples of **1** are also capable of reversibly uptaking CO. Not surprisingly, these reaction rates are sluggish due to poor diffusion of CO into the solid; this situation prompted us to investigate the incorporation of **1** into a porous material that would trap the molecular cationic species yet facilitate diffusion of CO into the matrix. The use of sol-gel techniques provides for the immobilization of a sensing molecule, in this case [Rh(TMPP)₂(CO)][BF₄] (**1**), in an en-

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vironment that can be probed by both spectroscopic and electrochemical techniques, while the porous nature of the films permits facile diffusion of an exogenous substrate, such as CO, that can then bind to the sensing molecule.

Sol-gel derived titania and zirconia composite films containing $[\text{Rh}(\text{TMPP})_2(\text{CO})][\text{BF}_4]$ (1) were prepared by addition of a methylene chloride solution of 1 to titania and zirconia film solutions.⁴ Thin films were fabricated by either spin casting for 5 min or by application to the substrate with a cotton swab followed by drying in a stream of cool air. Infrared spectroscopic studies on the films were performed by casting the composite zirconia or titania films onto a germanium crystal and placing the crystal in an liquid ATR cell holder. Initially, a single carbonyl stretch was seen at 1975 cm^{-1} , which corresponds to the cation species $[\text{Rh}(\text{TMPP})_2(\text{CO})]^+$ (1) ($\nu(\text{CO})_{\text{CH}_2\text{Cl}_2} = 1970\text{ cm}^{-1}$) immobilized in the film. Upon exposure of the film to a CO atmosphere, the band at 1975 cm^{-1} disappears and a second, more intense, band appears at 2013 cm^{-1} , signaling the binding of CO to 1 to yield the dicarbonyl species $[\text{Rh}(\text{TMPP})_2(\text{CO})_2][\text{BF}_4]$ (2; $\nu(\text{CO})_{\text{CH}_2\text{Cl}_2} = 2011\text{ cm}^{-1}$ Figure 1). The absence of the 1975 cm^{-1} band indicates that the conversion of 1 to 2 within the film is quantitative. With regard to sensitivity, the presence of CO was observable in gas mixtures of CO and Ar containing less than 2% CO, which was the lowest measurable concentration based on our present method for determining flow rates. In the lower concentration range, the conversion of 1 to 2 is less than quantitative as evidenced by the continued presence of the CO band for 1 at 1975 cm^{-1} . Removal of CO from the system was effected by purging the IR cell with argon for 1 min, whereupon the band at 2013 cm^{-1} diminished with concomitant reappearance of the 1975 cm^{-1} band; this observation is consistent with complete conversion of $[\text{Rh}(\text{TMPP})_2(\text{CO})_2][\text{BF}_4]$ (2) back to the parent molecular species $[\text{Rh}(\text{TMPP})_2(\text{CO})][\text{BF}_4]$ (1). Alternatively, the loss of CO from the material may be achieved by simply exposing the film to the atmosphere, although the process is significantly slower under these conditions. As judged by the invariance of the IR spectra, zirconia and titania composite films of $[\text{Rh}(\text{TMPP})_2(\text{CO})][\text{BF}_4]$ (1) are selective for CO in the presence of other gases such as O_2 , CO_2 , N_2 , and H_2 .

In addition to infrared spectroscopy, the reversible addition of CO to $[\text{Rh}(\text{TMPP})_2(\text{CO})][\text{BF}_4]$ (1) within the composite films was monitored by electronic spectroscopy. A zirconia composite film containing 1 was spin cast on a quartz slide and placed in a 1-cm quartz cuvette capped with a rubber septum. The cell was purged for 15 min with CO, giving rise to an electronic spectral feature at 435 nm which is comparable to that seen in solution for $[\text{Rh}(\text{TMPP})_2(\text{CO})_2][\text{BF}_4]$ (2; $\lambda_{\text{max,CH}_2\text{Cl}_2} = 438\text{ nm}$; Figure 2). Subsequent removal of CO from the cell by purging with Ar resulted in the disappearance of the transition at 435 nm , leading to the conclusion that 2 had been reconverted to the monocarbonyl derivative 1.

Initial electrochemical studies of the sol-gel derived composite films containing $[\text{Rh}(\text{TMPP})_2(\text{CO})][\text{BF}_4]$ (1) were carried out by casting a zirconia film onto a platinum disk electrode.⁵ A cyclic voltammogram of the composite

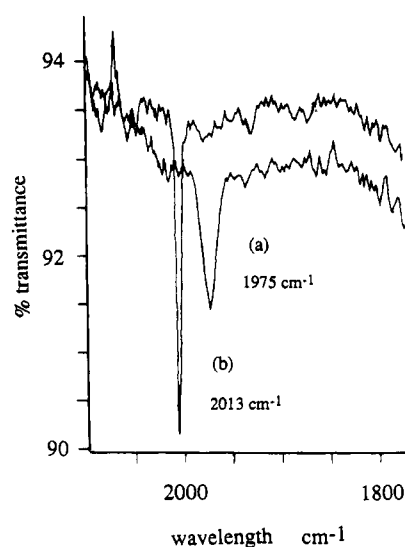


Figure 2. Infrared spectra of a zirconia composite film of $[\text{Rh}(\text{TMPP})_2(\text{CO})][\text{BF}_4]$ (1) (a) in the absence of CO and (b) exposed to CO.

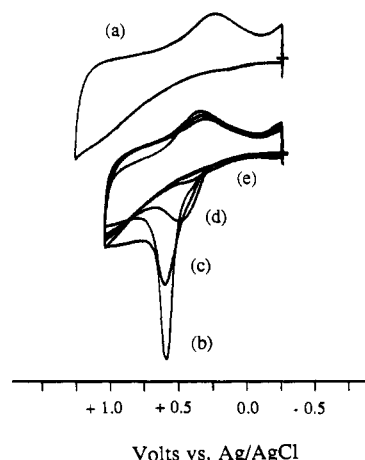


Figure 3. Cyclic voltammograms of a zirconia composite film containing $[\text{Rh}(\text{TMPP})_2(\text{CO})][\text{BF}_4]$ (1) and LiCF_3SO_3 cast onto a platinum disk electrode:⁶ (a) under a N_2 atmosphere; (b) after purging the cell for 30 s with CO. (c-e) after flushing the CO saturated cell with N_2 for 2, 5, and 10 min, respectively.

film in 0.1 M $\text{LiCF}_3\text{SO}_3/\text{H}_2\text{O}$ exhibited an essentially featureless voltammogram (Figure 3).⁶ Upon purging the electrochemical cell with CO for a brief period of time (<30 s), an irreversible oxidation wave appears at $+0.74\text{ V}$ with a chemical return wave located at $+0.31\text{ V}$ vs Ag/AgCl. After purging with N_2 for several minutes, the oxidation wave gradually disappears and the original cyclic voltammogram is obtained. Purging the solution with N_2 removes CO from the system and results in re-formation of 1, in agreement with the reversible addition of CO that was observed spectroscopically. Although the electrochemical behavior of the carbonyl complexes 1 and 2 incorporated in these composite films differs from the solution behavior, it is apparent that CO is binding to the rhodium center; more importantly, the process is reversible. Such behavior is in contrast to the irreversible CO chemistry reported for conducting polymer films containing ferrocenyl-ferrazetene.⁷ To make electrochemical detection a more

(4) An amount of lauric acid (0.161 g, 0.80 mmol) was added to 1 mL of 70% $\text{Zr}(\text{OPr})_4$ in propanol (2.23 mmol) in a glass vial. The mixture was placed in a sonicator (Bransonic 220) until the lauric acid had completely dissolved. To this solution, was added an amount of valeric acid (1.7 mL, 15.6 mmol) and 0.2 mL of water. A solution of 1 (5.9 mg, 4.6×10^{-3} mmol) in 50 μL of CH_2Cl_2 was added to 1 mL of the zirconia film solution. The resulting yellow solution was filtered through a 0.22-mm Millex-GS millipore filter. Titania films were prepared in a similar manner using 0.25 g of lauric acid (1.25 mmol), 1 mL of neat $\text{Ti}(\text{OPr})_4$ (3.36 mmol), 2.5 mL of valeric acid (23 mmol), and 0.3 mL of water.

(5) To make the films electrochemically active, 2.0 mg of LiCF_3SO_3 (0.013 mmol) was added to 0.1 mL of the film solution as a supporting electrolyte.

(6) Cyclic voltammetry measurements were performed in 0.1 M $\text{LiCF}_3\text{SO}_3/\text{H}_2\text{O}$ at a scan rate of 200 mV/s using a platinum disk working electrode and a Ag/AgCl reference electrode.

viable means of sensing CO in the present case, the use of a more conducting matrix is in order. To this end, we are currently investigating the incorporation of $[\text{Rh}(\text{TMPP})_2(\text{CO})][\text{BF}_4]$ (1) into solid ionic conducting polymer films such as MEEP (poly[bis(2-(2-methoxy)ethoxy)phosphazene]).⁸

These studies demonstrate that the molecular cationic complex $[\text{Rh}(\text{TMPP})_2(\text{CO})]^+$ (1) reversibly binds CO within a glassy polymer matrix to form the dicarbonyl species $[\text{Rh}(\text{TMPP})_2(\text{CO})_2]^+$ (2). The facile nature of the chemistry is a direct consequence of an exceedingly labile metal-methyl, phenyl ether bond, which facilitates substitution reactions even in the solid state. The addition of CO conveniently gives rise to dramatic changes in the spectroscopic and redox properties of the rhodium cation, commensurate with coordination of a strong π -acceptor to the metal center. On the basis of these preliminary results with titania and zirconia films incorporating $[\text{Rh}(\text{TMPP})_2(\text{CO})][\text{BF}_4]$ (1), the development of other CO sensing films using molecular composites of ether-phosphine complexes appears attractive.

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A Sol-Gel-like Route to Crystalline Cadmium Phosphide Nanoclusters

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Herein we describe a metalloorganic route to semiconductor nanoclusters³ that is analogous to the sol-gel process. Our method was designed to parallel the variant of sol-gel processing that affords monodispersed oxide par-

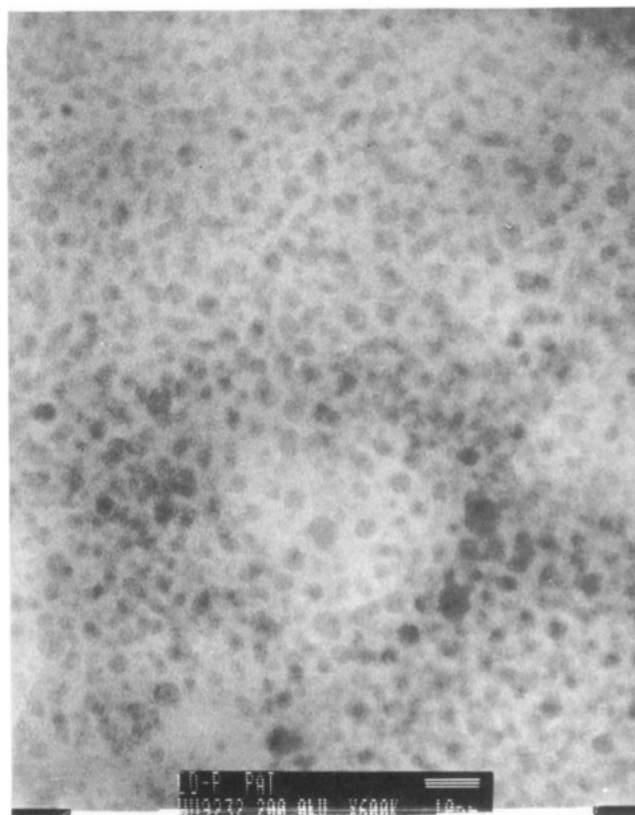
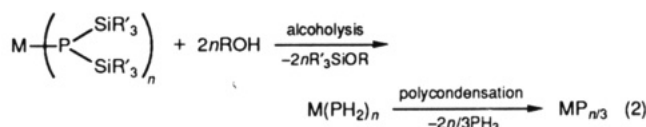
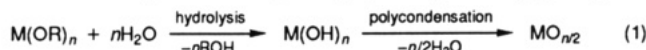


Figure 1. TEM image of Cd_3P_2 nanoclusters obtained from eq 3 and deposited on an amorphous carbon substrate. The striped bar is 100 Å in length.

titles by the controlled hydrolysis and polycondensation of alkoxide precursors (see eq 1).⁴ By analogy, we pro-



posed the growth of phosphide nanoclusters by alcoholysis and polycondensation of disilylphosphido precursors (see eq 2).⁵ The first success of our strategy is the synthesis of soluble, crystalline, cadmium phosphide nanoclusters (nano- Cd_3P_2).

The nano- Cd_3P_2 was prepared from the new disilylphosphido precursor $\text{Cd}[\text{P}(\text{SiPh}_3)_2]_2$.⁶ Initial studies re-

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