centrosymmetric $P2_1/c$.[13] The difference of the structure ($P2_1/c$ and $P2_1/n$) between *p*NA·HCl samples is probably due to the polymorphism and does not change the following discussion. The neighboring *p*NA·H^+ molecules in *p*NA·HCl crystal are packed alternately in an antiparallel alignment along *c* axis. Therefore, the *p*NA·HCl crystal is SHG inactive. In the *Pn* crystal structure of *p*NA·HNO_3, the dipoles of *p*NA·H^+ molecules are packed alternately in an antiparallel alignment along the *b* axis, and this compound is therefore SHG inactive, although *Pn* is a member of the polar space groups. The structure of the SHG-active *p*NA·HBr and AN·HCl were members of the polar space groups.

The structures of *p*NA·HBr is illustrated in Figure 1. *p*NA·HBr crystallizes in the orthorhombic space group *Fdd2* consisting of *p*NA·H^+ and Br^- ions. There were 16 molecules per unit cell. *p*NA·H^+ molecules are not packed alternately in antiparallel alignment along the *a* axis; the angle between the dipoles of *p*NA·H^+ molecules along *a* axis was 151°. This is the reason the *p*NA·HBr crystal is SHG active.

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Registry No. *p*Na, 100-01-6; HBr, 10035-10-6; *p*Na·HBr, 29084-75-1.

Supplementary Material Available: Crystallographic data for *p*NA·HBr (Table A), X-ray data collection and structure refinement of *p*NA·HBr (Table B), crystallographic data for *p*NA·HCl (Table C), X-ray data collection and structure refinement of *p*NA·HCl (Table D), infrared spectra of *p*NA, *p*NA·HCl, *p*NA·HBr, *p*NA·HNO_3, and $(pNA)_2{\cdot}H_2SO_4$ (Figure A), dependencies of SHG intensities of *p*NA·HBr on laser power (Figure B), structure of *p*NA·HCl (Figure C), and possible structure of *p*NA·HNO_3 (Figure D) (10 pages). Ordering information is given on any current masthead page.

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Composition and Morphology of the Magnetic Reaction Product of 1,1'-Diacetylferrocene and *p*-Phenylenediamine. Caveat Emptor

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The search for ferromagnetic behavior in polymeric materials is a focus of contemporary research.[1,2] Reports of ferromagnetic polymeric materials, however, have been plagued by ill-defined compositions, low yields, lack of characterization, and poor reproducibility.[3] Recently Zhao et al.[4] reported an ambient temperature, stable organometallic ferromagnet formed from the reaction of the reaction product of 1,1'-diacetylferrocene and *p*-phenylenediamine with cadmium acetate. Herein, we describe composition, morphology, and magnetic properties of this magnetic material.

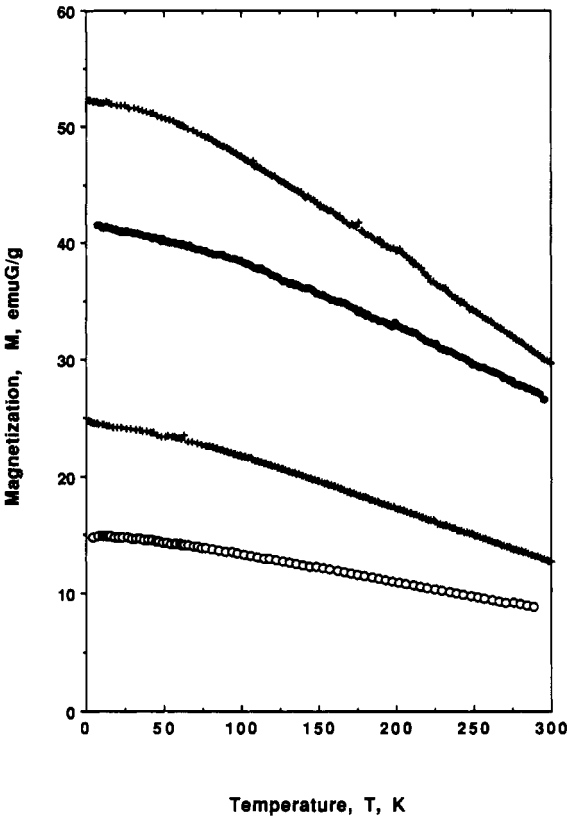

Figure 1. Magnetization as a function of temperature, $M(T)$, at 19 500 G for **2** (+) and **3** (○) plotted along with the 50 000-G data reported in ref 4 (●).

Zhao et al. report the formation of $Cd_2Fe_2C_{36}H_{38}N_4O_4$ (**1**)[5] which results from the addition of $Cd(O_2CMe)_2{\cdot}H_2O$ to an *n*-amyl alcohol solution of 1:1 1,1'-diacetylferrocene and *p*-phenylenediamine which has been heated to reflux for 6 h. The resulting black precipitate was reported to be a ferromagnet at room temperature. We have repeated this synthesis with the following modifications: a commercially available sample (Aldrich) of 1,1'-diacetylferrocene was recrystallized from hexane prior to use, and commercial $Cd(O_2CMe)_2{\cdot}2H_2O$ (Aldrich) was used instead of the monohydrate. *n*-Amyl alcohol (EN) was dried and

† Contribution 6116.

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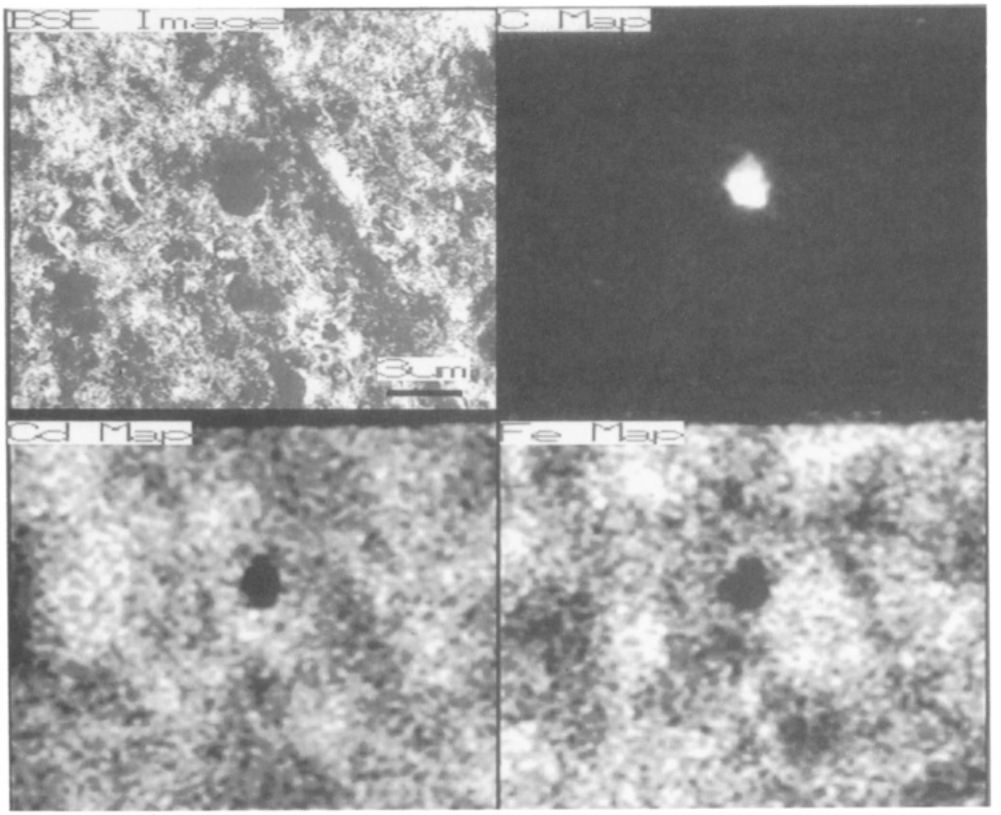

Figure 2. BSE image of a typical section of **2** showing the C, Cd, and Fe maps.

then distilled over K_2CO_3[6] under nitrogen prior to use. The entire reaction was carried out under nitrogen. The reaction was repeated twice on the 5 mmol scale,[5] and 340 and 276 mg of the black product (**2**) were isolated. Each batch was sufficiently magnetic to be attracted to a stirring-bar magnet at room temperature. The reaction was repeated without addition of the $Cd(O_2CMe)_2 \cdot 2H_2O$, and a darker black precipitate (**3**) was isolated (54 mg), which was also sufficiently magnetic to be attracted to a stirring-bar magnet at room temperature.

The magnetization as a function of temperature at different applied fields for **2** and **3** were qualitatively similar to each other and with the data reported for **1** (Figure 1). A room-temperature hysteresis loop with a coercivity of 19 Oe was observed for **2**. Thus, we confirm the high-field-dependent room-temperature magnetic behavior for **1** as well as in a material in which cadmium acetate was not used.

The elemental composition for **1** was not reported although two compositional formulas are identified.[5] In separate preparations of **2** we find (Onieda Research Services) %C = 1.50 and 1.93, %H = 0.75 and 0.99, %N = 0.00 and 0.05, %Fe = 48.00 and 60.10, and %Cd = 24.25 and 14.20. Thus, **2** is metal rich and ligand poor. Assuming only oxygen remains, i.e., 25.2 and 22.8%) then the Cd:Fe:O ratios are 1:4:7.2 and 1:8.5:11.2. For **3** we find %C = 41.68, %H = 3.28, %N = 2.76, %Fe = 27.26; assuming %O is 25.02, then the empirical formula is $C_{17.7}H_{16.7}NFe_{2.5}O_{7.9}$.

The IR (Nujol and Fluorolube) spectrum for **2** has only four major absorptions at 3608, 3400, 1550, and 1420 cm^{-1}. The highest energy absorption is extraordinarily sharp and is initially assigned to crystalline water. A dryed authentic sample of $Ca(OH)_2 \cdot xH_2O$ (Aldrich) possesses absorptions (Nujol and Fluorolube) at 3599 vs, 3520 m, and 3486 s cm^{-1}. The remaining absorptions are broad with the former characteristic of water/hydroxyl and perhaps carboxylate. The IR spectrum of **3** is different with water/hydroxyl absorptions at 3220, 3360, and 3460 cm^{-1}, and aliphatic CH absorptions at 2875, 2930, and 2960 cm^{-1}, and a carbonyl absorption at 1700 cm^{-1}. Unassigned absorption bands occur at 1655, 1622, 1608, 1512, 1460, 1430, 1380, and 1355 cm^{-1}.

Powder X-ray diffraction of **2** reveals broad reflections with *d* spacings (relative intensity) at 4.663, 4.672 (28, 27), 3.021, 3.029 (78, 100), 2.544, 2.553 (100, 80), 2.412, 2.376 (22, 14), 2.087, 2.126 (5, 3), 1.859, 1.866 (37, 28), 1.746, 1.749 (31, 39), 1.637, 1.640 (26, 24), 1.512, 1.515 (19, 7), 1.441, 1.441 (15, 14), 1.399, 1.401 (12, 6), 1.273, 1.276 (8, 6), 1.171, 1.171 (5, 3), 1.143, 1.144 (5, 3), and 1.112, 1.114 Å (5, 6). These are in good agreement for $Cd(OH)_2$ [4.701 (90), 3.027 (85), 2.546 (100), 2.356 (14), 1.859 (60), 1.747 (40), 1.638 (35), 1.570 (5), 1.514 (11), 1.441 (20), 1.404 (10), 1.394 (16), 1.274 (13), 1.168 (6), 1.144 (8), and 1.112 Å (15)] and thus, consistent with the infrared spectral results, support that $Cd(OH)_2$ is the dominant crystalline phase present in **2**. In contrast **3** exhibits a few very broad reflections with *d* spacings (relative intensity) at 4.00 (25), 3.58 (48), 2.49 (64), and 1.48 Å (100).

ESCA (VG ESCA Lab MKII) analysis shows that the topmost surface of **2** is composed of organic carbon (24 atomic %; C_{1s} at 284.6 eV), oxygen (47%; O_{1s} at 530.9 eV), oxidized cadmium (23%; Cd_{3d5} at 404.6 eV), and oxidized iron (6%; Fe_{2p^3} at 709.5 eV). (All binding energies are referenced to the hydrocarbon at 284.6 eV.) There are two species in the oxygen region; the larger at 530.9 eV is assigned to iron oxide while the shoulder at 529.2 eV has a binding energy close to CdO. Thus, cadmium is present as either the oxide or the hydroxide. The iron peak is characteristic of Fe(II) oxide.[7] The carbon spectra has

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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. $Cd(O_2CMe)_2$, 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 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.

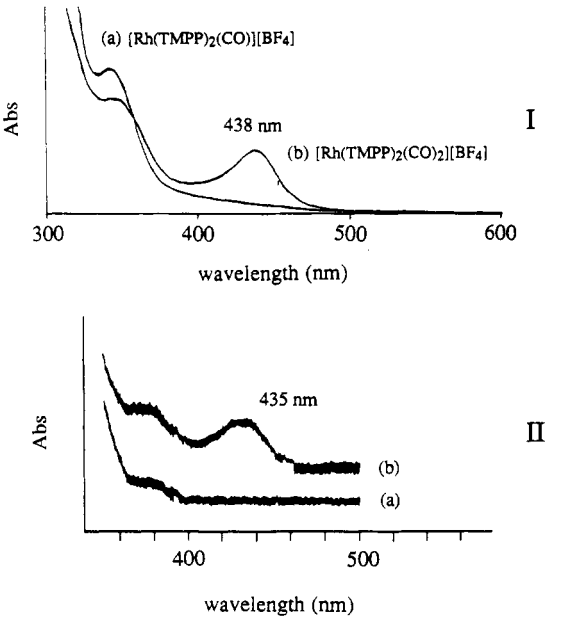
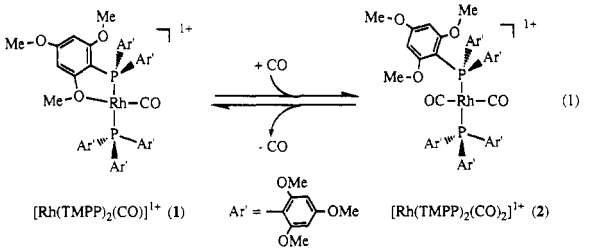


Figure 1. Electronic absorption spectra of (a) $[Rh(TMPP)_2(CO)][BF_4]$ and (b) $[Rh(TMPP)_2(CO)_2][BF_4]$ in (I) CH_2Cl_2 and (II) a zirconia composite film.

Recently, we reported the reversible solution chemistry of the novel mononuclear Rh(II) complex $[Rh(\eta^3\text{-}TMPP)_2][BF_4]_2$ (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 $[Rh(TMPP)_2(CO)][BF_4]$ (**1**) and $[Rh(TMPP)_2(CO)_2][BF_4]$ (**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 $[Rh(TMPP)_2(CO)][BF_4]$ (**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 $[Rh(TMPP)_2(CO)][BF_4]$ (**1**), in an en-



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† Departments of Chemical and Agricultural Engineering.
‡ Department of Chemistry.
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