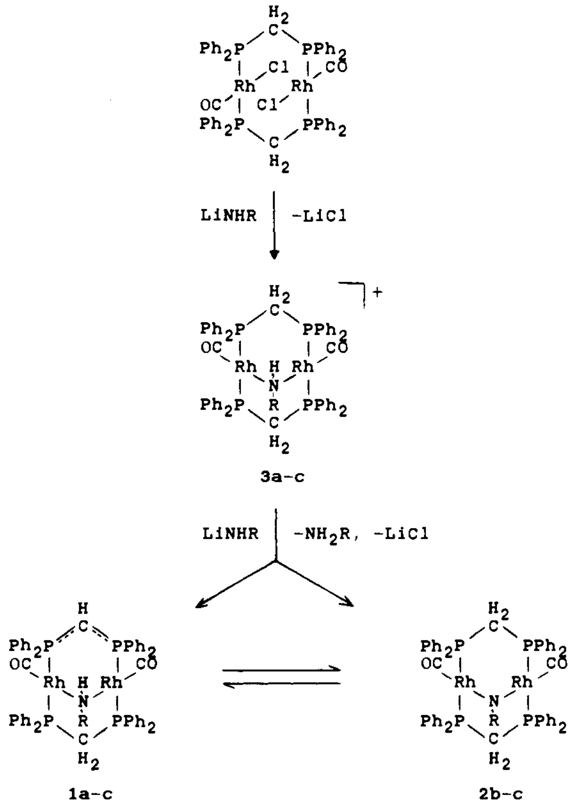
Scheme I



(a, R = Me; b, R = Ph; c, R = p-MePh)

spectrum only being obtained at -80 °C (R = *p*-MePh, $\Delta G^{\ddagger} \sim$ 40 kJ/mol).[12] A structure similar to **1a** is assigned to **1b**,**c** based on the similarity of the spectroscopic data. The spectroscopic data for **2b**,**c** are very similar to the data for $Rh_2(\mu\text{-}S)(CO)_2(\mu\text{-dppm})_2$[2] and $Rh_2(\mu\text{-}O)(CO)_2(\mu\text{-dppm})_2\cdot LiBF_4$.[1] We therefore formulate these products as the imido complexes $Rh_2(\mu\text{-NR})(CO)_2(\mu\text{-dppm})_2$, **2b** (R = Ph) and **2c** (R = *p*-MePh). Thus, **1** and **2** are tautomers in a tautomeric equilibrium (Scheme I).[13] Although **1a** is apparently not in equilibrium with its tautomer, at least on the NMR time scale (NMR spectra are invariant from −60 to 100 °C), the structure of **1a** does show how well the hydrogen (HN) is positioned for the shift needed to interconvert the tautomers (Figure 1). Indeed, HN is within hydrogen bonding distance of the methanide carbon, C3.

A likely reaction pathway for the formation of **1** and **2** is shown in Scheme I. Protonation of **1a** or the equilibrium mixtures **1b**/**2b** or **1c**/**2c** gives the proposed intermediate, **3a**, **3b**, or **3c**[14] (eq 2). The protonation is reversed upon addition of LiNHR.

$$\mathbf{1a}\text{ or }\mathbf{1b}/\mathbf{2b}\text{ or }\mathbf{1c}/\mathbf{2c} \underset{\text{LiNHR}}{\overset{H^+}{\rightleftharpoons}} [Rh_2(\mu\text{-NHR})(CO)_2(\mu\text{-dppm})_2]^+ \quad (2)$$

3a, R = Me
3b, R = Ph
3c, R = *p*-MePh

In contrast to **3a–c** the isoelectronic complexes $[M_2(\mu\text{-OH})(CO)_2(\mu\text{-dppm})_2]^+$ (M = Rh[15] and Ir[16]) are deprotonated solely at the bridging OH ligand and not at a dppm ligand.[1] While this may be due solely to the difference in acidity of the OH and NHR protons, the incorporation of Li^+ into the OH deprotonation product, $M_2(\mu\text{-}O)(CO)_2(\mu\text{-dppm})_2\cdot LiBF_4$ (most likely by coordination to the μ-oxo ligand), complicates comparisons. The presence of the imido complex when R = Ph (**2b**) or *p*-MePh (**2c**) but not when R = Me reflects the greater acidity of the amido group in **3b** and **3c** on replacing the methyl group in **3a** with electron-withdrawing phenyl groups. This effect is further illustrated by the ratio of the tautomers (IR, 22 °C) which increases on going from R = Ph (**1b**:**2b** ~ 1:3) to less electron withdrawing R = *p*-MePh (**1c**:**2c** ~ 1:1).

Preliminary work on the reaction chemistry of **1** and **2** shows facile insertion of CO into the Rh–N bond. Details of this work will be reported in a forthcoming publication.

Acknowledgment. We acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation, and the UMC Research Council for support of this work and Johnson Matthey for a loan of $RhCl_3$. The National Science Foundation provided a portion of the funds for the purchase of the x-ray (CHE-7820347) and NMR (PCM-8115599) equipment. We thank G. Wei and Dr. R. Taylor for some of the NMR experiments.

Supplementary Material Available: Tables of fractional coordinates and thermal parameters (9 pages). Ordering information is given on any current masthead page.

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[13] A similar tautomeric equilibrium has been postulated to explain the incorporation of deuterium into the dppm methylene groups of $Rh_2(\mu\text{-OHCl})(CO)_2(\mu\text{-dppm})_2$.[15]

[14] **3a** (R = Me). Anal. Calcd (found) for $C_{54}H_{48}F_3NO_5P_4Rh_2S\cdot 0.6CH_2Cl_2$ ($CF_3SO_3^-$ salt): C, 52.01 (51.76); H, 3.93 (4.07); N, 1.11 (0.84); P, 9.83 (9.82). IR (cm^{-1}) (CH_2Cl_2) 1993 sh and 1980 vs (ν_{CO}); (mineral oil) 3290 w (ν_{NH}). ^1H NMR (300 MHz, $CDCl_3$) δ 7.24–7.94 (m, 40, phenyl), 5.32 (s, CH_2Cl_2), 4.20 and 3.54 (m, 2 and 2, CH_2), 2.35 (br s, 3, NCH_3), 2.03 (br s, 1, NH). ^{31}P NMR (121 MHz, $CDCl_3/CH_2Cl_2$, external H_3PO_4 reference) δ 21.6 (unsymmetrical doublet with apparent J_{RhP} = 117 Hz). **3b** (R = Ph). IR (cm^{-1}) (CH_2Cl_2) 1995 sh and 1977 vs (ν_{CO}); (mineral oil) 3218 w (ν_{NH}). ^{31}P NMR (121 MHz, C_6D_6/CH_2Cl_2, external H_3PO_4 reference) complex pattern centered at 21 ppm. Data for **3c** (R = *p*-MePh) are essentially identical.

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In Situ Intercalative Polymerization of Pyrrole in FeOCl: A New Class of Layered, Conducting Polymer–Inorganic Hybrid Materials

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Prepared by the chemical or electrochemical oxidation of pyrrole, polypyrrole ($[(Ppy)^{+y}(X^-)_y]_n$, X = ClO_4^-, BF_4^-, NO_3^-, etc.)[1] is one of the most robust and chemically flexible members of the current generation of electrically conductive polymers.[2] In addition, substantial property modifications can be achieved via "alloying" with other polymers.[1,3] However, despite an extensive

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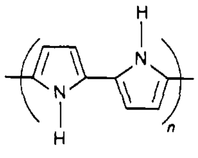
body of experimental and theoretical work, polypyrrole microstructure/morphology characteristics beyond the basic proposed repeat unit (A),[1] e.g., overall chain conformation and packing,



A

degree of cross-linking, etc., remain poorly understood and largely uncontrolled. How these factors affect collective properties is unknown.

We report here a structural form of polypyrrole in which polymerization and intercalation of pyrrole are brought about within the constrained van der Waals gap of a layered inorganic solid (FeOCl). Oxidative intercalation of organic molecules with concomitant reduction of the inorganic lattice is well established for FeOCl,[4] and in the present case affords a novel class of conductive polymer–inorganic hybrid materials.[5] The reaction[6] of FeOCl with excess neat pyrrole (60 °C) yields a material analyzing as $(Ppy)_{0.34}FeOCl$ (**1**).[7] X-ray diffraction measurements reveal high crystallinity[8] and an increase in FeOCl interlayer (*b*-axis) spacing from 7.980 (2) to 13.210 (4) Å. This 5.23-Å expansion is comparable to that observed in the formation of $(pyridine)_{0.33}FeOCl$[9] and $(pyridine)_{0.5}TaS_2$,[10] where radical cation mediated dimerization of pyridine is operative[11] and where the pyridine molecular plane is perpendicular (and the C_2-axis parallel) to the layer planes.[12] A similar structural model can be advanced

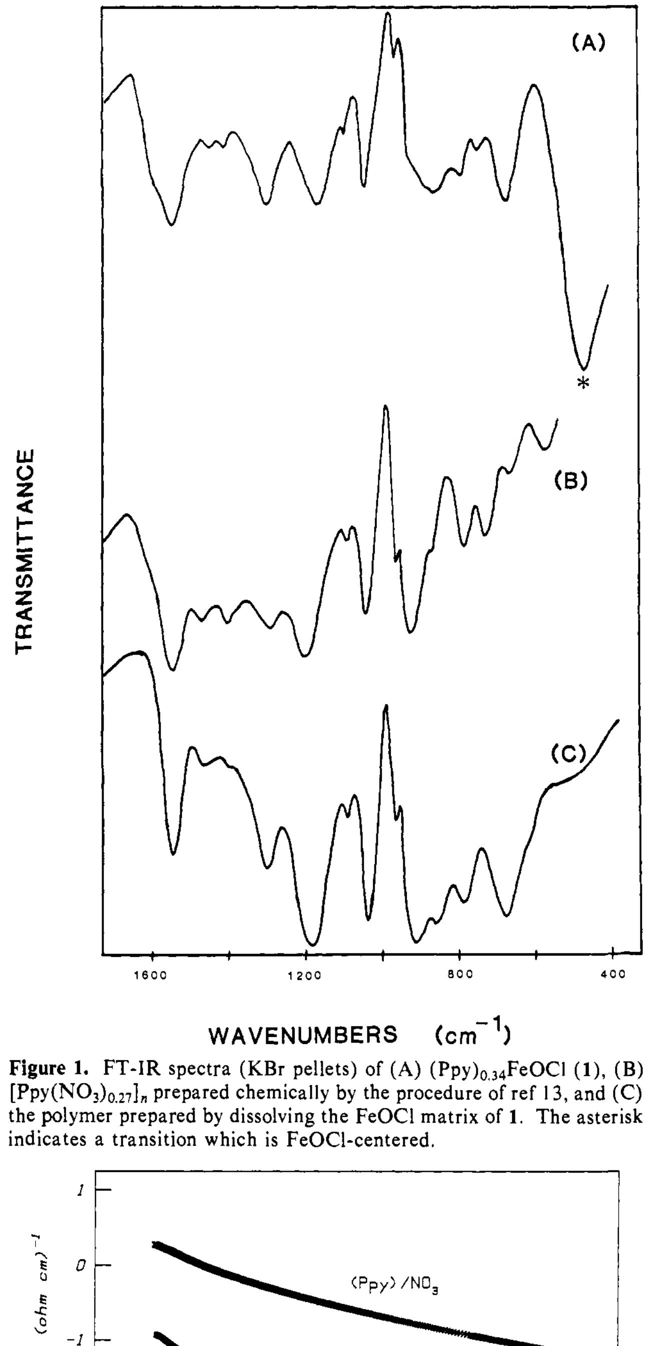


Figure 1. FT-IR spectra (KBr pellets) of (A) $(Ppy)_{0.34}FeOCl$ (**1**), (B) $[Ppy(NO_3)_{0.27}]_n$ prepared chemically by the procedure of ref 13, and (C) the polymer prepared by dissolving the FeOCl matrix of **1**. The asterisk indicates a transition which is FeOCl-centered.

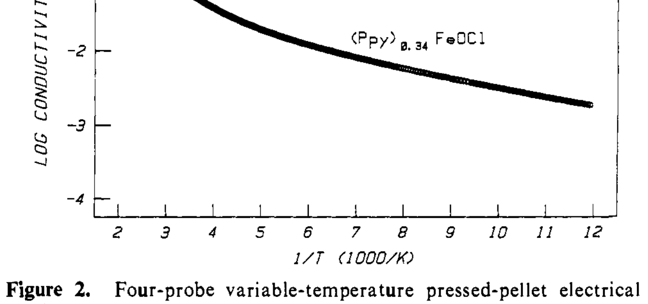


Figure 2. Four-probe variable-temperature pressed-pellet electrical conductivity data for $[Ppy(NO_3)_{0.27}]_n$ prepared chemically by the procedure of ref 13 and for $(Ppy)_{0.34}FeOCl$ (**1**).

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(5) For examples of nonconductive, photopolymerized, layered hybrid materials, see: Day, P. In ref 1a, pp 117–131.

(6) Conditions were strictly anhydrous, using doubly distilled (from freshly activated molecular sieves) pyrrole. For typical FeOCl samples, the reaction is complete in several days as judged by X-ray diffraction. Grinding or sonication of the FeOCl effects a significant rate enhancement. Samples of **1** are slightly moisture-sensitive.

(7) (a) Anal. Calcd for $(C_4H_3N)_{0.34}FeOCl$: C, 12.62; H, 0.80; N, 3.68; Fe, 43.15. Found: C, 12.43; H, 1.39; N, 3.67; Fe, 42.80 (dried in vacuo overnight). Slightly high hydrogen contents are frequently observed in polypyrroles[1,7b–d] and are thought to reflect the presence of water, some nitrogen quaternization, and/or double-bond hydrogenation. In the present case, mass balance requires hydrogen to remain either on the polymer chain or in the inorganic lattice. Since the present Mössbauer data indicate an Fe oxidation state similar to that in other FeOCl intercalates[11d,16] it seems unlikely that the bulk of the excess hydrogen is present as charge-compensating protons. (b) Diaz, A. F.; Kanazawa, K. K.; Gardini, G. P. *J. Chem. Soc., Chem. Commun.* **1979**, 635–636. (c) Ogasawara, M.; Funahashi, K.; Demura, T.; Hagiwara, T.; Iwata, K. *Synth. Met.* **1986**, *14*, 61–69. (d) Street, G. B.; Clarke, T. C.; Krounbi, M.; Kanazawa, K.; Lee, V.; Pfluger, P.; Scott, J. C.; Weiser, G. *Mol. Cryst. Liq. Cryst.* **1982**, *83*, 253–264.

(8) SEM is in accord with a single phase composed of small (~25 × 4 × 2 μm) crystallites showing chipped corners and marked striations perpendicular to (010). There is no evidence for polypyrrole formed as a separate component or coating the crystallite surfaces.

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and a reduced inorganic matrix.

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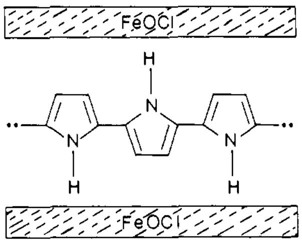
for **1** (B). Additional support for B is derived from the observation of a larger 5.84-Å interlayer expansion for the intercalative polymerization of *N*-methylpyrrole and from the observation that 2,5-dimethylpyrrole fails to intercalate in FeOCl. This latter inertness parallels the electrochemical behavior of 2,5-dimethylpyrrole.[1]



B

Further evidence that a relatively high molecular weight, conductive polypyrrole has formed in the FeOCl van der Waals gap is derived from several lines of chemical and spectroscopic/charge transport evidence. (i) Pyrolysis mass spectra (up to 350 °C) of chemically prepared[13] $[\text{Ppy}(\text{NO}_3)_{0.27}]_n$ and **1** show no evidence of pyrrole or pyrrole oligomers.[14a] This is in contrast to results[14b] for $(\text{pyridine})_{0.33}\text{FeOCl}$[11a] and $(\text{pyridine})_{0.50}\text{TaS}_2$[11a–c] where pyridine and pyridine oligomers are readily detected. (ii) Thermal gravimetric analysis (TGA) traces of $[\text{Ppy}(\text{NO}_3)_{0.27}]_n$[13] and **1** (He, up to 550 °C) are similar and evidence very high thermal stability (in contrast to the aforementioned pyridine intercalates). (iii) FT-IR spectra of polypyrroles[1] and **1** (Figure 1A,B) are very similar, differing principally in modes (500–700 cm^{-1}) known to be sensitive to polymerization conditions and counterion.[1,7c,15] The corresponding spectra of pyrrole, bipyrrole, and terpyrrole are radically different.[1b] (iv) The ^{57}Fe Mössbauer spectrum of **1** (IS = 0.41 mm/s, QS = 0.86 mm/s at 25 °C) is similar to other FeOCl redox intercalation compounds, indicating partial reduction of the FeOCl layers (cf., IS = 0.42 mm/s, QS = 0.73 mm/s for $(\text{pyridine})_{0.33}\text{FeOCl}$).[11d,16] (v) In contrast to other FeOCl intercalation compounds, **1** exhibits relatively high electrical conductivity. Furthermore, the temperature dependence of charge transport in polycrystalline samples (Figure 2) closely parallels that of $[\text{Ppy}(\text{NO}_3)_{0.27}]_n$.[1] The lower conductivity of the intercalate appears to reflect both volume and interparticle contact effects[17] in these necessarily isotropic measurements on a highly anisotropic material. The thermoelectric power of **1** is similar to that of polypyrroles[1] with predominant hole transport near room temperature, $S(T) > 0$ reaching a maximum near 260 °C and falling at lower temperatures. Above 340 K, **1** exhibits negative $S(T)$ which may indicate increasingly important valence-to-conduction band carrier excitation within the FeOCl layers. In contrast, $(\text{pyridine})_{0.33}\text{FeOCl}$ is a less conductive n-type material[14,18] at room temperature. Finally, the inorganic matrix of **1** can be removed with phenanthroline/NH$_2$OH·HCl to yield a black polymer exhibiting an IR spectrum similar to that of chemically or electrochemically prepared polypyrrole (Figure 1C). Further characterization of this polymer is in progress.

These results demonstrate that intercalative polymerization can yield unusual and informative new forms of conductive polymers. In the present case, polypyrrole can now be studied within the stringently ordered constraints of a well-defined van der Waals gap. In addition, a novel polymer–inorganic laminate has been produced. Elaboration and characterization of such materials is continuing.

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Registry No. Ppy, 30604-81-0; FeOCl, 13870-10-5.

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Selective Steroid Chlorinations Directed by Attached Pyridine Ester Templates

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We have described the process of remote chlorination of steroids and other substrates by the radical relay process.[1,2] *m*-Iodobenzoic acid or related substances were esterified to the steroids to act as templates. Under free radical chain conditions a chlorine atom becomes attached to the iodine of the template by transfer from a radical such as PhICl$^\bullet$ or ClSO$_2^\bullet$ and is then relayed to a geometrically accessible hydrogen of the substrate. We have also used the sulfur of diaryl sulfide templates[3] or of thiophene ester templates[4] to perform the radical relay process. These methods have been taken up in other laboratories as well.[5]

The use of an iodine or a sulfur to accept and deliver atomic chlorine is related to known free radical complex chemistry, in particular to the work of Russell[6] and of others[7] on the complexing of chlorine atoms by aromatic solvents. Although many such complexing effects have been examined, no studies have been done of chlorine atom binding to *pyridine* derivatives.[8] We now wish to report that the pyridine rings of nicotinic or isonicotinic acid steroid esters can geometrically direct the free radical chlorinations of the substrates. For practical applications such pyridine templates seem preferable to the iodine or sulfur template systems described previously.

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