Organometallics **1989,** *8,* 2079–2080

American Chemical Society, and the University of Notre Dame is gratefully acknowledged. S.R.M. thanks the Reilly Fund for a fellowship.

Supplementary Material Available: Tables of crystal and data collection parameters, atomic positional parameters, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom positional parameters and bond lengths and angles for 3 (8 pages); a structure factor listing (12 pages). Ordering information is given on any current masthead page.

Electrical Conductivity in a Polythiophene Induced by Complexation with $[(\eta\text{-}C_5H_5)Fe(CO)_2]^+$

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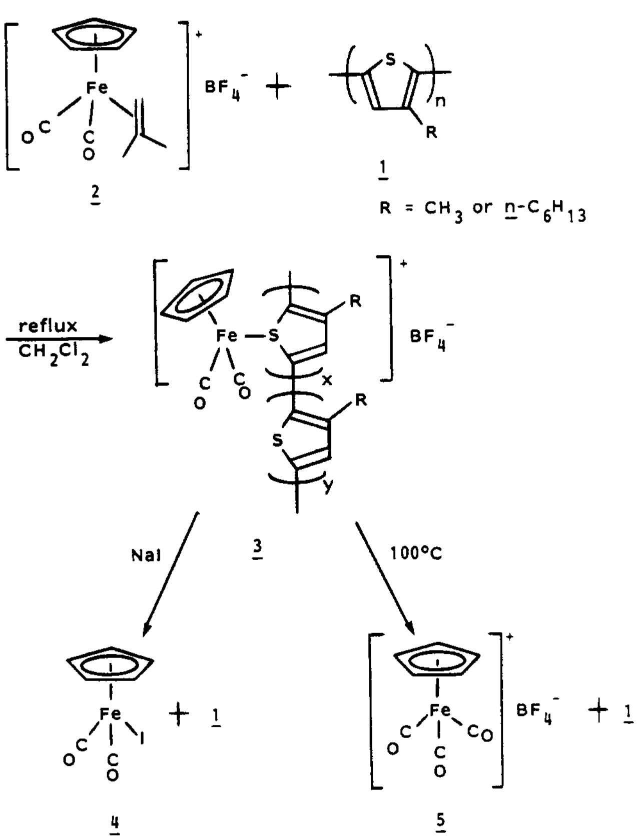
Received May 25, 1989

Summary: Treatment of an electrically nonconducting copolymer of 3-methyl- and 3-hexylthiophene (**1**) with $[CpFe(CO)_2(2\text{-methyl-1-propene})]BF_4$ gave a material (**3**) with greatly increased ($\times 10^8$) conductivity. The IR and NMR spectra of this material and of model complexes suggest that $[CpFe(CO)_2]^+$ residues which are attached to the sulfur atoms of less than 10% of the thiophene rings of the polymer backbone induce the improved conductivity.

Certain organic polymers such as polyacetylene, polypyrrole, and polythiophene become electrically conducting[1] when doped with strong oxidizing agents such as I_2 or H_2SO_4 or with strong reducing agents such as sodium or potassium metal.[2] The technological promise of such materials has encouraged the development of additional doping techniques and reagents. However, most of the systems reported are unstable in the long term due to the reactive nature of the dopants. This has led to difficulties in processing these materials and in investigating their physical properties and internal structure. Our interest in organometallic complexes embedded in polymers[3] led us to consider them as possible dopants for polythiophene. The ability of a complex to modify the electronic structure of a conjugated polymer should be a function of the metal, the organic ligands present, and the mode of bonding to the polymer (for example, σ or π). Complexes might prove to be tunable probes to study the mechanisms of conduction in such materials. We report the first example to our knowledge of the induction of improved electrical conductivity in a conjugated polymer via covalent attachment of an organometallic "dopant". Treatment of the soluble thiophene copolymer (**1**) with $[CpFe(CO)_2(Me_2CCH_2)]BF_4$ (**2**), where Cp = $\eta\text{-}C_5H_5$, gave a material whose conductivity is 8 orders of magnitude greater than that of the starting copolymer.

A 1:1 copolymer of 3-methyl- and 3-hexylthiophene was chosen for study because it was soluble in CH_2Cl_2 and also because it possessed good mechanical properties. In our hands poly(3-methylthiophene) was too insoluble and poly(3-hexylthiophene) was too soft and rubbery. Copolymer **1** was prepared by the nickel-catalyzed Grignard coupling of 2,5-dibromo-3-methylthiophene and 2,5-dibromo-3-hexylthiophene in the ratio 1:1 following a procedure similar to that reported for the synthesis of polythiophene.[2b,4] The molecular weight of this copolymer is estimated[5] to be about 2000 (i.e., 15 rings) on the basis of elemental analysis of the residual bromo terminal groups. The material is dark red and is soluble at room temperature in common organic solvents such as tetrahydrofuran, $CHCl_3$, and CH_2Cl_2. It was pressed into a thin disk at room temperature which exhibited low conductivity.[6,7] Exposure of the disk to I_2 vapor increased the conductivity to $\sigma = 5\text{–}10\ \Omega^{-1}\ cm^{-1}$ which then decreased steadily upon standing consistent with the reported behavior of other polythiophenes.[7] Copolymer **1** was treated with **2** (3:1 ratio) under N_2 atmosphere in refluxing CH_2Cl_2 for 80 min following a procedure similar to that reported[8] to give thiophene complexes. The residue upon evaporation of the CH_2Cl_2 was washed with methanol and dried under vacuum to give brown-black **3**. The conductivity of disks

Scheme I



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[1] (a) Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem. Rev.* **1988,** *88,* 183. (b) Kaner, R. B.; MacDiarmid, A. G. *Sci. Am.* **1988,** *258,* 106.

[2] (a) Furlani, A.; Napoletano, C.; Paoless, R.; Russo, M. W. *Synth. Met.* **1987,** *21,* 337. (b) Yamamoto, T.; Sanechika, K.; Yamamoto, A. J. *Polym. Sci., Polym. Lett. Ed.* **1980,** *18,* 9. (c) Jen, K. Y.; Miller, G. G.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1986,** 1346. (d) Bocchi, V.; Gardini, G. P. *J. Chem. Soc., Chem. Commun.* **1986,** 148.

[3] Shaver, A.; Gao, G. P.; Butler, I. S. *Appl. Organomet. Chem.* **1988,** *2,* 9 and references therein.

[4] Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M. *Tetrahedron* **1982,** *38,* 3347.

[5] Amer, A.; Zimmer, H.; Mulligan K. J.; Mark, H. B., Jr.; Pons, S.; McAleer, J. F. *J. Polym. Sci., Polym. Lett. Ed.* **1984,** *22,* 77.

[6] The conductivity of samples pressed into thin disks was measured via the four-probe method using a Harrison 6516A DC power supply and a Keithley 169 multimeter. The instrumentation was sensitive to conductivity values as low as $10^{-6}\ \Omega^{-1}\ cm^{-1}$ which sets an upper limit for the value for **1**. However, poly(2,5-thiophene) prepared in the same manner is reported[7] to have conductivity values in the range $10^{-10}\text{–}10^{-11}\ \Omega^{-1}\ cm^{-1}$.

[7] (a) Yamamoto, T.; Sanechika, K.; Yamamoto, T. *Chem. Lett.* **1981,** 1079. (b) Lin, J. W.-P.; Dudek, L. P. *J. Polym. Sci., Polym. Chem. Ed.* **1980,** *18,* 2869.

[8] Goodrich, J. D.; Nickias, P. N.; Selegue, J. P. *Inorg. Chem.* **1987,** *26,* 3424.

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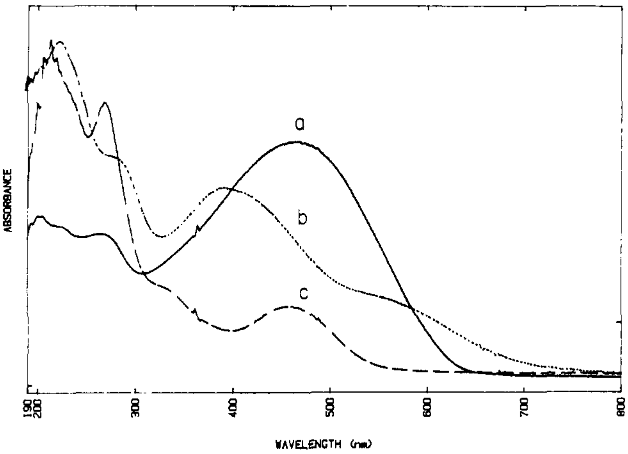

Figure 1. The UV-visible spectra of (a) **1**, (b) **3**, and (c) $[CpFe(CO)_2(3\text{-methylthiophene})]BF_4$ (**6**).

pressed from this material was of the order of 10^{-3} Ω^{-1} cm^{-1}.

The new material exhibits two strong bands in the carbonyl stretching region of its IR spectrum consistent with the presence of the $[CpFe(CO)_2]^+$ residue.[8,9a,10] Integration of the aryl and alkyl regions of the NMR spectrum[9b] of **3** relative to that of the Cp region suggests that 7% of the thiophene rings are attached to the organoiron cation. Treatment of **3** in CH_2Cl_2 with NaI gave, upon evaporation of solvent, a nonconducting residue whose NMR spectrum ($CDCl_3$) and IR spectrum in the carbonyl stretching region was characteristic[3] of $CpFe(CO)_2I$ (**4**),[9c] embedded in **1**. Heating solid **3** to 100 °C gave a nonconducting material whose IR spectrum was characteristic of $[CpFe(CO)_3]BF_4$ (**5**),[9d] in the carbonyl stretching region; consistent with the reported[8] behavior of $[CpFe(CO)_2(\text{thiophene})]BF_4$. In both cases the dark red color of the original **1** had returned. The preparation of **3** and its subsequent transformations are depicted in Scheme I. The similarity of the NMR and infrared spectra and reactivity of **3** to that of model compounds such as $[CpFe(CO)_2(\text{thiophene})]BF_4$ and $[CpFe(CO)_2(3\text{-methylthiophene})]BF_4$ (**6**)[10] leads to the conclusion that $[CpFe(CO)_2]^+$ residues bind to the sulfur atoms of some of the thiophene rings of the polymer backbone of **3**.

Changing the ratio of **1** and **2** in the preparation of **3** changes the percentage of iron-functionalized thiophene rings; however, the conductivity reaches its maximum value at quite low loadings (10^{-4} Ω^{-1} cm^{-1} at 1%, $10^{-3}/\Omega^{-1}$ cm^{-1} at 3–20% loadings). The conductivity is constant for over 2 months when samples were stored in vacuo and increased slightly when stored in air. Comparison of the UV–visible spectra of **1**, **3**, and $[CpFe(CO)_2(3\text{-methylthiophene})]BF_4$ (**6**) (Figure 1) reveals that the single broad band at 470 nm observed for **1** is split into two bands at 400 nm and approximately 570 nm upon complexation (i.e., **3**). It is important to note here that disks composed of pure **2** or **6** or a "solid solution"[3] of **6** in **1** are nonconducting ($<10^{-6}$ Ω^{-1} cm^{-1}).[11,12] Clearly the covalent attachment of the organoiron cation to **1** perturbs the electronic configuration of the polymer.[1a]

The $[CpFe(CO)_2]^+$ residue may be regarded as mimicking the action of I_2 on **1** by introducing charge anomalies in the conjugated system leading to improved electrical conduction. However, **3** may also be viewed as a collection of complexes connected by long conjugated ligands which fulfil the requirement for inner-sphere electron transfer.[13] Since **3** is a polythiophene matrix, each "ligand" is in intimate contact with several other ligands, thus fulfilling the requirement for outer-sphere electron transfer. Conduction could occur via a combination of inner- and outer-sphere redox reactions[14] involving the Fe(II)/Fe(III) couple. The implications of these concepts are under study.

Acknowledgment. This work was supported by the National Sciences and Engineering Council of Canada and the Quebec Department of Education. J.P.G. acknowledges the award of a McGill University predoctoral fellowship and support from the Laboratory for Inorganic Materials (Concordia University).

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[9] (a) **3**: IR (solid state) $\nu(CO)$ 2065, 2021 cm^{-1}; IR (CH_2Cl_2) 2071, 2025 cm^{-1}. (b) **3**: ^1H NMR ($CDCl_3$) [δ, (multiplicity, relative intensity, assignment)] 7.1–6.7 (s, 2, CH); 5.5–5.0 (br, 0.6–1.0, C_5H_5); 2.8–2.2 (m, 5, alkyl); 1.67–0.96 (m, 11, alkyl). (c) **4**: IR (solid state) $\nu(CO)$ 2036, 1933 cm^{-1}. (d) **5**: IR (solid state) $\nu(CO)$ 2123, 2068, 2006 cm^{-1}.

[10] Compound **2** was similarly treated with 3-methylthiophene to give $[CpFe(CO)_2(3\text{-methylthiophene})]BF_4$ (**6**). **6**: IR (solid state) $\nu(CO)$ 2069, 2016 cm^{-1}; IR (CH_2Cl_2) 2072, 2031 cm^{-1}.

[11] The failure of the solid solution of **6** in **1** to conduct and the persistence of the conductivity of **3** under DC conditions rules out ionic conduction[12] as the source of the improved conductivity.

[12] Pollock, D. D. In *Electrical Conduction In Solids: An Introduction*; American Society for Metals: Metals Park, Ohio, 1985; p 265.

[13] Cotton, F. A.; Wilkinson, T. In *Advanced Inorganic Chemistry*, 5th ed.; Wiley-Interscience: Toronto, 1988; pp 1307–1316.

[14] Thus a Fe(III) center generated near the anode could be propogated to the cathode by intra- and interchain electron transfer. Such a process would be a type of "electron hopping" mechanism (Böltger, H.; Bryskin, V. V. In *Hopping Conduction in Solids*; VCH Verlagsgesellschaft: Akademie-Verlag, Berlin, 1985; Chapter 1).

A Homogeneous Iron(II) System Capable of Selectively Catalyzing the Reduction of Terminal Alkynes to Alkenes and Buta-1,3-dienes

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Received April 12, 1989

Summary: Terminal alkynes are selectively hydrogenated to alkenes by the iron(II) catalyst precursors $[(PP_3)FeH(N_2)]BPh_4$ and $[(PP_3)FeH(H_2)]BPh_4$ in THF under very mild conditions [$PP_3 = P(CH_2CH_2PPh_3)_3$]. The catalytic reductive dimerization of $HC{\equiv}CSiMe_3$ to 1,4-bis(trimethylsilyl)butadiene prevails over alkene formation at reflux temperature.

Few iron complexes have been reported to be efficient hydrogenation catalysts.[1] We describe here a homogeneous iron(II) system which brings about the selective reduction of terminal alkynes to the corresponding alkenes under mild conditions and at good rates. Interestingly, by an appropriate choice of the alkyne substituent, the reductive dimerization to 1,4-disubstituted butadienes can be made to prevail over hydrogenation.

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[1] Spencer, A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1987; Vol. 6, p 231.