In summary, the present results provide the first unambiguous example of a thiophenic moiety functioning as a sulfur donor ligand. Although the Ru–S interaction is obviously influenced by the geometric constraints imposed by the chelate ring, our findings indicate that stable complexes of nonchelating S-bound thiophene ligands are feasible.[18]

Acknowledgment. This work was supported by the National Science Foundation and the Illinois Coal Research Board. T.B.R. is a fellow of the Camille and Henry Dreyfus and Alfred P. Sloan Foundations. Mass spectra were obtained in the Mass Spectrometry Laboratory, University of Illinois, supported in part by the National Institute of General Medical Sciences (GM 27029). 360-MHz NMR spectra were measured at the University of Illinois NSF Regional NMR Facility.

Registry No. **1a**, 91281-15-1; **1b**, 91281-16-2; **2a**, 91281-17-3; **2b**·2-$(CH_3)_2CO$, 91310-93-9; Ph_2PCl, 1079-66-9; (*p*-tol)$_2$PCl, 1019-71-2; 4-lithiodibenzothiophene, 75288-58-3.

Supplementary Material Available: Structure factor tables for $RuCl_2(tol_2P(DBT))_2 \cdot 2(CH_3)_2CO$, positional and thermal parameters, and bond distances and angles (24 pages). Ordering information is given on any current masthead page.

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[1.1]Ferrocenophanes as Effective Catalysts in the Photoelectrochemical Hydrogen Evolution from Acidic Aqueous Media

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We wish to report the successful application of a new type of catalyst in the photoelectrochemical production of hydrogen from aqueous media in an electrolytic cell where the externally applied potential is reduced by a photogenerated potential, thus leading to a conversion of light to electrical and consequently chemical energy in the form of hydrogen gas. In such a cell, the photoreduction of hydrogen on a semiconductor photocathode such as p-type silicon is thermodynamically allowed, but it is kinetically inhibited: silicon and many other semiconductors show a high overvoltage for hydrogen evolution, which means that additional energy must be supplied to overcome this barrier. Previous work[1-7] in this area has remedied this problem in a temporary way through a variety of schemes. Our recent investigations of the synthesis[8] and properties[9,10] of the binuclear metallocene [1.1]ferrocenophane (**1**, "FCP") have now led us to a novel and useful polymeric material, with which p-type semiconductor electrodes can be modified in such a way that they continuously and over extended periods of time liberate hydrogen when irradiated by visible light. At this time, we have been concerned only with this part of the water splitting reaction, ignoring for the moment the need to improve the efficiency of oxygen generation at a suitable photoanode.

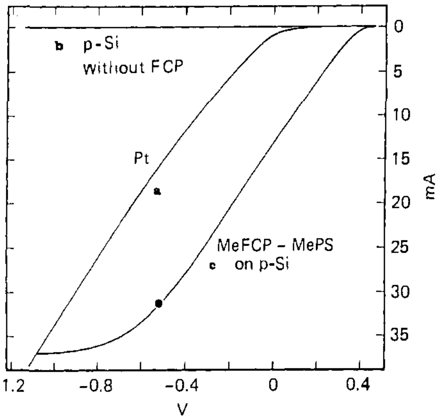
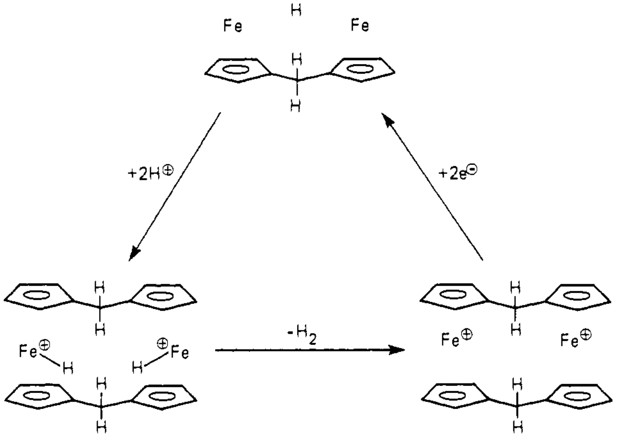


Figure 1. Current/voltage (vs. SCE) plots in neat HBF_3OH at scan rates of 50 mV/s of (a) a Pt cathode with the same surface area as that of the electrode in (b) and (c); (b) a p-Si photocathode in the absence of FCP, whether illuminated or in the dark; the same curve is obtained when a modified electrode is not illuminated; (c) illuminated MeFCP–polymer coated p-Si cathode. The same Pt anode was used in all cases. Note especially that no hydrogen evolution is observed (i.e., a flat line at 0 mA is shown in the *I*/*V* curve) within the above range for two cases: when a nonmodified p-type Si cathode is illuminated or when a modified cathode is kept in the dark.

FCP readily dissolves in strong, nonoxidizing acids such as boron trifluoride hydrate (HBF_3OH) with liberation of hydrogen. Quantitative studies in this laboratory have confirmed an earlier observation[11] that exactly 1 mol of hydrogen is evolved per mol of FCP. The dication **2** resulting from the reaction $2H^+ + FCP \rightarrow H_2 + FCP^{2+}$ can be converted back to neutral FCP by various reducing agents, such as $TiCl_2$ or $SnCl_2$. Because of the low basicity[12,13] of ferrocenes, no hydrogen evolution is observed from more dilute HBF_3OH or other aqueous acids.



The reduction of **2** to **1** can also be effected electrochemically and photoelectrochemically so that **1** can serve as a means to partially eliminate the overpotential problems. Effective photoelectrochemical catalysis of hydrogen production by FCP in solution was demonstrated by the following experiments: the onset

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[9] Hydride abstraction from FCP produces a bridge carbocation, which is stabilized by the adjacent ferrocenes: Mueller-Westerhoff, U. T.; Nazzal, A.; Proessdorf, W.; Mayerle, J. J.; Collins, R. L., *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 293; *Angew. Chem. Suppl.* **1982**, 686.

[10] Proton abstraction from FCP by butyl lithium in THF leads to a bridge carbanion, containing an intramolecular hydrogen bond between the carbon atoms of the bridge: Mueller-Westerhoff, U. T.; Nazzal, A.; Proessdorf, W. *J. Am. Chem. Soc.* **1981**, *103*, 7678.

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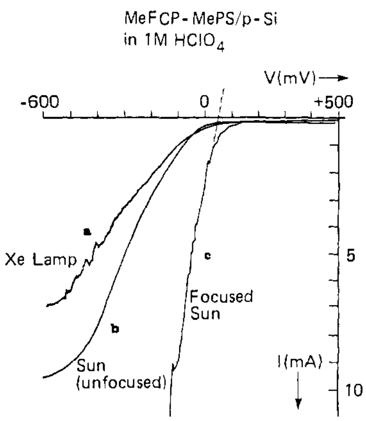

Figure 2. Current/voltage plots (vs. SCE) of an irradiated MeFCP–MePS modified p-Si photocathode (Pt anode, scan rate 50 mV/s). The illumination conditions are only qualitatively defined: (a) a Xe are lamp, (b) diffuse sunlight, and (c) sunlight focused through a magnifying glass.

of hydrogen liberation at a Pt electrode in HBF_3OH containing FCP occurs at −100 mV vs. SCE; at an irradiated p-type silicon cathode,[14] hydrogen is produced at +200 mV vs. SCE; a gain of 300 mV.

A much more efficient way of using FCP as a hydrogen generation catalyst in a liquid junction solar cell would be to cover the photocathode surface with a FCP containing polymer, which not only achieves very high concentrations of FCP at the surface but also provides the very desirable protection of the electrode against attack by the electrolyte. To prepare such a polymer bound FCP, we made use of our recent finding that FCP and its bridge-methylated derivatives 1-MeFCP (**3**) and 1,12-Me_2FCP can be cleanly deprotonated to produce bridge carbanions.[10] Reaction of the carbanion of **3** with commercial poly(chloromethyl)styrene) produced polymer-bound 1-MeFCP.[16] A solution of this methylferrocenophane–(methylpolystyrene) polymer ("MeFCP–MePS") in THF was used to deposit a film of polymer on either the $\langle 100 \rangle$ or $\langle 111 \rangle$ face of p-type silicon electrodes. With 870 mW/cm^2 Xe light, a MeFCP–MePS-modified p-type silicon electrode (resistivity 1 Ω cm, $\langle 111 \rangle$ face exposed) of 0.16-cm^2 area operated with a maximum underpotential of 450 mV (Figure 1), where "underpotential" refers to the difference in potential between this electrode and a shiny platinum electrode at equal currents under these conditions.[17] At 31.0 mA and −540 mV (the point marked in Figure 1), the underpotential was 400 mV. At more negative potentials, a saturation current of 37 mA was reached. The electrode maintained this excellent performance throughout 5 days.

We were concerned that the low metal basicity of the ferrocenophanes would restrict us to HBF_3OH as the electrolyte, but we subsequently found that hydrogen evolution occurs readily and at underpotentials of 250–350 mV on illuminated MeFCP–MePS-modified p-type silicon electrodes even in dilute acid media such as 1 M $HClO_4$, 1 M HBF_4, and 1 M HCl. Irradiating a MeFCP–MePS-coated p-Si electrode by a Xe arc lamp or by sunlight in a cell containing 1 M $HClO_4$ as the electrolyte lead to rapid hydrogen evolution at potentials negative of 0 mV vs. SCE, corresponding to an underpotential of approximately 250 mV compared to the standard potential of hydrogen. Simply focusing the sunlight onto the electrode through a magnifying glass held in front of the cell increased the underpotential to 300 mV and, as expected, led to a much steeper rise in current. These results are shown in Figure 2.

If the same mechanism of double protonation and hydrogen elimination applies for FCP in solution and in surface-confined FCP, we need to explain why we see this hydrogen evolution from dilute acids although we know that only the strongest acids can protonated metallocenes. The concentration of FCP in the surface layer at the photocathode is several orders of magnitude higher in the MeFCP–MePS film (approximately 2 M) than in the experiments with FCP in solution (around 10^{-3} M). We thus may simply be looking at the effect of concentration on a continuously shifting equilibrium, which depends on the FCP concentration and the square of the proton concentration. Using dilute acids, this equilibrium will be largely on the side of the nonprotonated FCP unless its concentration is increased dramatically—as we are doing in the case of MeFCP–MePS.

The above results demonstrate the usefulness of ferrocenophane derivatives in photoelectrochemical hydrogen generation. We are currently exploring structurally related materials[19,20] and binuclear compounds of higher metal basicity.

Acknowledgment. Eda Easton deserves our gratitude for advice on the right choice of wax and for donating some of her casting wax. We acknowledge many discussions with Drs. Gordon (San Jose) and Rusling (Storrs) concerning the electrochemical aspects of this work.

Registry No. 1, 1294-39-9; HBF_3OH, 16903-52-9; $HClO_4$, 7601-90-3; Si, 7440-21-3.

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[14] Our cathodes are boron-doped p-type silicon (ρ = 1–10 Ωcm, $\langle 100 \rangle$ or $\langle 111 \rangle$ face exposed) with 5000 Å Al sintered on the back. The flattened end of a copper lead was attached to the back with silver epoxy; the wire was covered with Teflon tubing (1 mm inner diameter). The back and the sides of the electrode were covered with wax.

[15] The commerical poly((chloromethyl)styrene) (poly(vinylbenzyl chloride), Aldrich) is a 60/40 mixture of ortho and para isomers.

[16] Elemental analysis of the resulting polymer-bound FCP (calculated for a 1:1 MeFCP–poly(methylstyrene) ($C_{32}H_{31}Fe_2$): C, 72.89; H, 5.93; Fe, 21.18%. Found: C, 67.87; H, 5.50; Fe, 19.20; Cl, 1.80%) shows that some of the chloromethyl groups still are present (1.8% chlorine remains), but approximately 75% of the reactive polymer sites now carry a MeFCP group.

[17] This cell does not represent an independent solar energy device, because we are supplying an external potential in addition to the light-generated one. The amount of external energy needed for a given process is reduced by the energy converted by the photocathode. To assign a conversion efficiency to this light-to-chemical-energy process is without much merit. In related work[18] on InP photocathodes, a "net power density gain" of 12% was defined. Using the same approach, our Si cathode has a gain of 9%. This number is given for calibration purposes only. The same authors also referred to the term "underpotential" which we use here.

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Pulse Radiolysis Generation of Sulfur Radical Cations Stabilized by Neighboring Carboxylate and Alcohol Groups

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Radical cations derived from dialkyl thioethers are transient species that undergo diverse reactions.[1-3] Their stability and ease of formation are dramatically enhanced by electron-rich neighboring groups with favorable geometries which facilitate sulfur-sulfur or sulfur–heteroatom p-orbital overlap.[4] Since such sulfur-centered radicals have recently gained prominence as possible

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