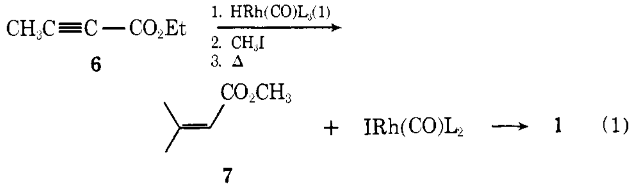
trally and by elemental analysis and which was recycled, in 86% yield, overall, to $HRh(CO)L_3$ (**1**).

We believe that the C–C coupling step is a concerted one. The formation of trisubstituted olefin with greater than 98% cis stereochemistry from the *cis*-methylvinylrhodium(III) complex **3** indicates that the coupling step does not proceed through free radcals.[14]

The scope of the Rh(I) based coupling reaction is not limited to the choice of metal hydride, acetylene, and alkyl group discussed in detail herein. In preliminary studies, we have shown that L_4RhH reacts readily with DADC to yield **2** after carbonylation. We have also observed that ethyl iodide reacts smoothly with **2** to yield, upon gentle heating at 80°, ethyl-substituted cis- and trans-trisubstituted olefins.[15] Finally, initial studies show that $HRh(CO)L_3$ reacts with ethyl tetrolate (**6**) to give an isolable Rh(I) complex which, upon treatment with methyl iodide, yields ethyl β,β-dimethylacrylate (**7**) (see eq 1), at room temperature.



(1)

We are now examining the effect of varying metal ligands upon the metal hydride addition reaction. We are also studying the (C=C) isomerization reaction for Rh(III) complexes in order to produce trans-trisubstituted olefins from acetylenes with greater stereoselectivity than is now possible. The detailed results of these studies will be reported in the near future.

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(14) For similar reasoning ruling out free-radical coupling of vinyl groups arising from the thermal decomposition of vinylcopper(I) species, see ref 8.

(15) Thus far, product yields of up to 72%, based on DADC, have been observed.

Jeffrey Schwartz,* Donald W. Hart, John L. Holden
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

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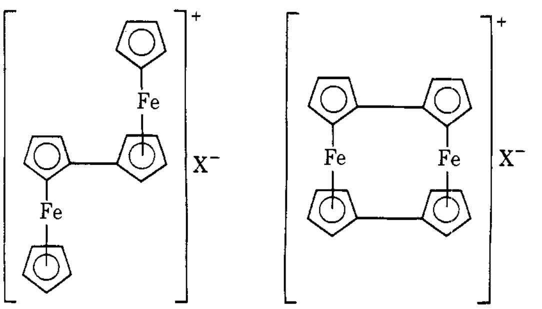
1,1′-Biferrocenylene[Fe(II)Fe(III)] Salts[1]

Sir:

The interesting properties recently observed for the mixed valence compound biferrocene[Fe(II)Fe(III)] picrate (**1**)[2] prompted us to prepare mixed valence salts of 1,1′-biferrocenylene: 1,1′-biferrocenylene[Fe(II)Fe(III)] picrate (**2**) and 1,1′-biferrocenylene[Fe(II)Fe(III)] $(TCNQ)_2^-$ (TCNQ = tetracyano-*p*-quinodimethane) (**3**). The rigid geometry of the 1,1′-biferrocenylene



1, X = picrate **2**, X = picrate
3, X = $(TCNQ)_2^-$

could allow greater through-bond and through-space interaction of the two component parts.[3] As a result of this increased interaction the properties of **2** and **3** should be different from those of **1**.

The biferrocenylene was prepared by a modification of the method of Hedberg and Rosenberg.[4] Inasmuch as the yield in the coupling reaction of 1,1′-diiodoferrocene in the presence of copper bronze depends upon the purity[5] of the low-melting 1,1′-diiodoferrocene and this compound is extremely difficult to purify, the 1,1′-diiodoferrocene was replaced with the more easily purified 1,1′-dibromoferrocene.[6] When the coupling reaction was performed with 1,1′-dibromoferrocene in biphenyl at 190° an 18% yield of the red crystalline 1,1′-biferrocenylene was obtained. The properties of this compound are identical with those previously reported.[4,7] Oxidation of 1,1′-biferrocenylene with benzoquinone in the presence of picric acid (benzene solvent)[8] gave **2** while **3** was obtained by the TCNQ oxidation of 1,1′-biferrocenylene in acetonitrile.

Anal. Calcd for **2**, $C_{26}H_{18}N_3O_7Fe_2$: C, 52.38; H, 3.04; N, 7.05. Found: C, 52.20; H, 3.05; N, 6.71. Calcd for **3**, $C_{44}H_{24}N_8Fe_2$: C, 68.07; H, 3.11; N, 14.42. Found: C, 67.96; H, 3.22; N, 14.21.

The infrared spectrum of **2** measured in a KBr pellet was what would be expected based on the infrared spectra of 1,1′-biferrocenylene and biferrocene[Fe(II)-Fe(III)] picrate[8] (for example, three transitions were observed in the far-infrared ring-tilt, stretch region: 350, 458, and 492 cm^{-1}). The infrared spectrum of **3** measured in a KBr pellet indicated similar but very weak transitions on a background of almost total absorption or reflection from 4000 to 400 cm^{-1}. Compound **2** had two overlapping absorptions of approximately equal intensity in the cyclopentadienyl C–H out-of-plane bending region[9] (835 and 842 cm^{-1}). Ferricenium ions exhibit absorption in the 840–870-cm^{-1} region while ferrocenes have the corresponding absorption at 810–835 cm^{-1}. This suggests that the two ferrocenyl rings are not identical.[10]

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(1) The Organic Solid State. X. For part IX see J. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. H. Perlstein, *J. Amer. Chem. Soc.*, in press.

(2) (a) D. O. Cowan and F. Kaufman, *ibid.*, **92**, 219 (1970); (b) F. Kaufman and D. O. Cowan, *ibid.*, **92**, 6198 (1970).

(3) D. O. Cowan, C. LeVanda, J. Park, and F. Kaufman, *Accounts Chem. Res.*, **6**, 1 (1973).

(4) F. L. Hedberg and H. Rosenberg, *J. Amer. Chem. Soc.*, **91**, 1258 (1969).

(5) F. L. Hedberg, personal communication and unpublished data of C. LeVanda.

(6) R. F. Kovar, M. D. Rausch, and H. Rosenberg, *Organometal. Chem. Syn.*, **1**, 173 (1971).

(7) M. D. Rausch, R. F. Kovar, and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **91**, 1259 (1969).

(8) D. O. Cowan, R. L. Collins, and F. Kaufman, *J. Phys. Chem.*, **75**, 2025 (1971).

(9) C. U. Pittman, Jr., J. C. Lai, D. P. Vanderpool, M. Good, and R. Prado, *Macromolecules*, **3**, 746 (1970).

The uv–visible absorption spectra are consistent with the structural formulations of **2** and **3**.[11] In addition to the normal uv–visible absorptions, near-infrared transitions are observed at 1500 nm (ϵ 1.8 × 10^3 for **2** in acetonitrile; ϵ 1.6 × 10^3 for **3** in DMF[12]) for the mixed valence compounds **2** and **3**. A similar transition in biferrocene[Fe(II)Fe(III)] picrate **1** (1900 nm (ϵ 551)) was assigned to a photon-assisted intramolecular intervalence exchange (mixed valence transition). Based on the Hush model[2b,13,14] the energy (λ) of the mixed valence transition is dependent upon differences in geometry and bond lengths in the donor and acceptor portions of the molecule but is not very dependent upon the extent of delocalization (interaction, α) in the ground state or upon the distance separating the donor and acceptor portions of the molecule. This suggests that there is a greater geometrical change upon the partial oxidation of 1,1′-biferrocenylene than upon the partial oxidation of biferrocene. However, the intensity of the allowed transition is proportional to the probability of finding the electron on the acceptor portion in the ground state (α^2) and upon the square of the distance between the two moieties. The interaction parameter α can be approximately evaluated using the following equation[3,13]

$$\alpha^2 = \frac{4.5 \times 10^{-4}\epsilon_{\max}\Delta_{1/2}}{(\bar{\nu})(r^2)}$$

where r is the distance separating the donor and acceptor in ångströms, $\epsilon_{\max}$ is the molar absorptivity at the band maximum, $\Delta_{1/2}$ is the band half-width in wave numbers, and $\bar{\nu}$ is the frequency in wave numbers. Using the equation α^2 is calculated to be 9×10^{-3} ($\alpha = 0.095$) for biferrocene[Fe(II)Fe(III)] picrate **1**, and 4.5–5.1 × 10^{-2} (α = 0.21–0.23) for 1,1′-biferrocenylene[Fe(II)-Fe(III)] picrate or $(TCNQ)_2^-$. Based on α^2 there is about five–six times more interaction in compounds **2** and **3** than in compound **1**. The value of α for compounds **2** and **3** indicates that they are class II compounds with trapped valences ($\alpha < 0.25$).[3,15] However, it is possible that changes of phase or changes in the counterion could alter the value of α enough so that the valences would no longer be trapped.

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Dwaine O. Cowan,* Carole LeVanda
Chemistry Department, The Johns Hopkins University
Baltimore, Maryland 21218
Received September 21, 1972

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(10) Preliminary ESCA and Mössbauer measurements indicate that the two iron atoms may be in fractional oxidation states.

(11) For compound **3** the ratio of the intensity of the 395:842 nm bands is 1.8 as observed for other $(TCNQ)_2^-$ salts: L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Amer. Chem. Soc.*, **84**, 3374 (1962).

(12) Spectra of DMF solutions were taken immediately after preparation, as ferricenium salts are known to decompose slowly in DMF: R. Prins, A. R. Korswafen, and A. G. T. G. Kortbeek, *J. Organometal. Chem.*, 39, 335 (1972).

(13) N. S. Hush, *Progr. Inorg. Chem.*, **8**, 391 (1967).

(14) B. Mayoh and P. Day, *J. Amer. Chem. Soc.*, **94**, 2885 (1972).

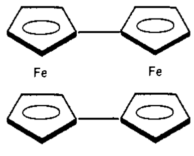
(15) When the resonance interaction (β) between the donor (i) and acceptor (j) components of the mixed valence system is as large as the thermal barrier to electron hopping (E_{th}) then complete delocalization exists. From the Hush model the thermal activation energy for electron hopping (E_{th}) is one-quarter of the activation energy for the optical electron transfer transition (E_{op}). Since the resonance interaction (β) between the i and j components is given by[14] $\beta = \alpha(E_{op})$, then α must be less than 0.25 to have trapped valences, where α is defined by the following equation.

$$\Psi_G = \sqrt{1 - \alpha^2}\phi_i + \alpha\phi_j$$

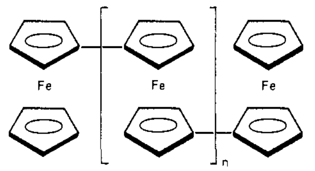
Bisfulvalenediiron and Its Iron(II–III) Mixed Valence System

Sir:

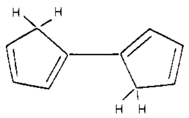
A new and convenient synthesis of [0.0]ferrocenophane (bisfulvalenediiron, "BFD") (**1**) and a description of the iron(II)–iron(III) mixed valence system derived therefrom are the subject of this communication. We were prompted to investigate the preparation of **1** *via* dihydrofulvalene **2** and fulvalene dianion **3**, because this approach, starting from simple materials and capable of being carried out without the isolation of any intermediates, seemed temptingly rational and more efficient than the two previously reported syntheses[1,2] of **1** from substituted ferrocenes.



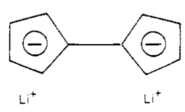
1, "BFD"



4, n = 0,1,2 . . .



2



3

Sodium cyclopentadienide (CpNa) was converted to **2** according to the procedure given by Doering and Matzner.[3] This reaction was found to proceed with approximately 70–80% conversion[4] to **2**. Subsequent addition of n-butyllithium afforded **3**, contaminated chiefly by cyclopentadienide.[5] Addition of ferrous chloride[6] in THF produced **1** together with polyferrocenylenes **4** (n = 0, 1, 2. . .), of which we separated only the first four.[7] BFD is known[1,2] to be only sparingly soluble in all common organic solvents, and was purified by repeated extraction (Soxhlet apparatus with

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(1) The pyrolysis of polymercuriferrocenylene affords 2–8% of BFD: M. D. Rausch, R. F. Kovar, and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **91**, 1259 (1969).

(2) F. L. Hedberg and H. Rosenberg, *ibid.*, **91**, 1258 (1969). These authors obtained **1** in unspecified yield from the Ullmann coupling reaction of 1,1′-diiodoferrocene.

(3) (a) W. v. E. Doering, "Theoretical Organic Chemistry—The Kekule Symposium," Butterworths, London, 1959; (b) E. A. Matzner, Ph.D. Thesis, Yale University, 1958.

(4) The per cent conversion to **2** was estimated from the ratio of ferrocene products.

(5) The first step of this reaction presumably involves the initial formation of 5-iodocyclopentadiene, which was recently described (R. Breslow and J. M. Hoffman, Jr., *J. Amer. Chem. Soc.*, **94**, 2110 (1972)) as being surprisingly stable. We considered that the (inverse) addition of CpNa to iodine in our first reaction step might lead to a more complete conversion to **2**. However, no major change in the final product distribution was noted in this case.

(6) Used as its stable bis-THF complex: S. Herzog, K. Gustav, E. Krüger, H. Oberender, and R. Schuster, *Z. Chem.*, **3**, 428 (1963).

(7) These ferrocenes were recently described by P. V. Roling and M. D. Rausch, *J. Org. Chem.*, 37, 729 (1972).