about the Mn-S band. Presumably, however, this barrier is less than 0.8 kcal mol^{-1} or else the preferred isomer should have been "frozen out" sufficiently for some intensity change to be detected spectroscopically. Why the barrier for rotation about an Mn-S band is lower than that about an Fe-Si band may result from the lower steric interaction between the groups attached to the S atom than in the case of the Si atom.

Registry No. π-$C_5H_5Mn(CO)_2SMe_2$, 40674-63-3; π-$C_5H_5Mn(CO)_2SEt_2$, 40674-64-4; π-$C_5H_5Mn(CO)_2S(n\text{-}Pr)_2$, 40674-65-5; π-$C_5H_5Mn(CO)_2S(n\text{-}Bu)_2$, 40674-66-6; π-$C_5H_5Mn(CO)_2THT$, 40674-67-7.

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Polarographic and Magnetic Susceptibility Study of Various Biferrocene Compounds

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Biferrocene, a series of five bridged biferrocenes (bridge = $-CH_2-$, $-CH_2CH_2-$, $-C(CH_3)_2C(CH_3)_2-$, -Hg-, and $-CH=CHC_6H_4CH=CH-$ (1,4)), and biferrocenylene were studied polarographically using a rotating platinum electrode. The $-C(CH_3)_2C(CH_3)_2-$, -Hg-, and $-CH=CHC_6H_4CH=CH-$ (1,4) bridged biferrocenes exhibited one irreversible two-electron half-wave. The methylene-bridged biferrocene showed two one-electron waves (0.39 and 0.56 V *vs.* sce), as did biferrocene (0.31 and 0.64 V *vs.* sce) and biferrocenylene (0.13 and 0.72 V *vs.* sce). Both of the half-waves for these compounds were found to be quasireversible. Variable-temperature (4.2-290°K) magnetic susceptibility data were presented for the dioxidized hexafluorophosphate salts of the $-CH_2-$ and $-C(CH_3)_2C(CH_3)_2-$ bridged biferrocenes. No *intra*molecular exchange interactions were detected; however, *inter*molecular exchange interactions were inferred by a comparison with magnetic data for ferricenium triiodide and by computer fitting of the data to a theoretical model. Susceptibility data were also presented for the salts resulting from the reaction of DDQ (2,3-dichloro-5,6-dicyanobenzoquinone) with cobaltocene, ferrocene, biferrocene, and biferrocenylene. In each case the anion resultant from DDQ is diamagnetic and in the case of $[(C_5H_4)_2Fe(C_5H_4)_2Fe^{2+}](DDQ^-)_2$ the Fe(III) complex is diamagnetic. The esr spectrum of monooxidized biferrocenylene and the above results are discussed in relation to the mixed-valence character found in some biferrocenes.

Introduction

Ferrocene has played an important role in developing a knowledge of electronic structure in organometallic chemistry.[1,2] Interest has been directed recently toward biferrocene (I), the ring-fused ferrocene dimer $(C_5H_5)Fe(C_5H_4)$-$(C_5H_4)Fe(C_5H_5)$, which was first observed[3] as a reaction byproduct in 1959. Oxidation of biferrocene either can lead to a monooxidized compound, as first reported by Spilners,[4] or can lead with a strong oxidizing agent to the dioxidized product. These materials are proving to have interesting properties.

Very recently Cowan, *et al.*,[5-10] and Mueller-Westerhoff and Eilbracht[11] prepared and investigated the physical properties of some biferrocene and biferrocenylene salts. The monooxidized biferrocene salt was formulated as a mixed-valence $Fe^{II}Fe^{III}$ compound. The mixed-valence character was established in part by observing, in the 77°K iron Mossbauer spectrum, separate quadrupole-split doublets for the two different iron atoms. The mixed-valence biferrocene compound was also characterized by an electronic transition in the near-ir spectrum; this feature is absent in the $Fe^{II}Fe^{II}$ and $Fe^{III}Fe^{III}$ compounds and was assigned by Cowan as an $Fe^{II}Fe'^{III} \rightarrow Fe^{III}Fe'^{II}$ transition.

In this paper we report on polarographic studies of various biferrocenes and biferrocenylene and discuss the results in reference to the compound's potential as mixed-valence compounds. Variable-temperature magnetic susceptibility data for two dioxidized bridged biferrocene compounds and for dioxidized biferrocenylene are also presented and analyzed.

Experimental Section

Compound Preparation. Samples of phenylferrocene, diferrocenylmethane, 1,2-diferrocenyl-1,1,2,2-tetramethylethane, and 1,2-diferrocenylethane were generously provided by Professor K. L. Rinehart. Analyses were performed by the University of Illinois School of Chemical Sciences microanalytical laboratory.

Biferrocene, $(C_5H_5)Fe(C_5H_4)$-$(C_5H_4)Fe(C_5H_5)$, was prepared as previously reported.[12] *Anal.* Calcd for $C_{20}H_{18}Fe_2$: C, 64.91; H, 4.90. Found: C, 64.73; H, 5.18. Diferrocenylmercury, $[(C_5H_5)(C_5H_4)Fe]_2Hg$, was made according to directions given by Rausch, *et al.*[13] *Anal.* Calcd for $C_{20}H_{18}Fe_2Hg$: C, 42.10; H, 3.18. Found: C, 42.77; H, 3.13. Biferrocenylene, $(C_5H_4)_2Fe(C_5H_4)_2Fe$, was prepared according to Rausch.[14] *Anal.* Calcd for $C_{20}H_{16}Fe_2$: C, 65.27; H, 4.38. Found: C, 65.12; H, 4.18. A sample of 1,4-bis(β-ferrocenylvinyl)benzene was purchased from Aldrich and recrystallized twice from absolute ethanol.

A sample of $[1,1\text{-}(CH_2)Fe_2(C_5H_5)_2(C_5H_4)_2](PF_6)_2$ was prepared

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(1) Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *J. Amer. Chem. Soc.*, 93, 3603 (1971).

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(7) D. O. Cowan, G. A. Candela, and F. Kaufman, *J. Amer. Chem. Soc.*, 93, 3889 (1971).

(8) D. O. Cowan, J. Park, M. Barber, and P. Swift, *Chem. Commun.*, 1444 (1971).

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

(10) D. O. Cowan and C. LeVanda, *J. Amer. Chem. Soc.*, 94, 9271 (1972).

(11) U. T. Mueller-Westerhoff and P. Eilbracht, *J. Amer. Chem. Soc.*, 94, 9272 (1972).

(12) M. D. Rausch, *J. Org. Chem.*, 26, 1802 (1961).

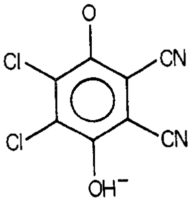
(13) M. D. Rausch, M. Vogel, and H. Rosenberg, *J. Org. Chem.*, 22, 900 (1957).

(14) M. D. Rausch, *J. Org. Chem.*, 28, 3337 (1963).

by adding ~100 mg of diferrocenylmethane to ~1 ml of concentrated H_2SO_4. This mixture was allowed to stand at room temperature for 15 min; then it was cooled in ice and slowly diluted to a volume of 10 ml with cold water. To the resulting cold aqueous solution of the Fe(III) cation was added an aqueous solution of NH_4PF_6. The blue precipitate was filtered and washed with cold water and dried *in vacuo* over P_2O_5. *Anal.* Calcd for $(C_{21}H_{20}Fe_2)(PF_6)_2$: C, 37.43; H, 2.97. Found: C, 36.91; H, 2.90. A sample of $[1,1\text{-}[(CH_3)_2CC(CH_3)_2]Fe_2(C_5H_5)_2(C_5H_4)_2](PF_6)_2$ was prepared by the same procedure. *Anal.* Calcd for $(C_{26}H_{30}Fe_2)(PF_6)_2$: C, 41.96; H, 4.06; Fe, 15.01. Found: C, 41.37; H, 4.10; Fe, 14.32.

A sample of $[Fe_2(C_5H_4)_4]I_3$ was prepared by reaction of biferrocenylene with iodine as previously indicated.[15] *Anal.* Calcd for $[Fe_2(C_5H_4)_4]I_3$: C, 32.08; H, 2.15; Fe, 14.91. Found: C, 32.89; H, 2.20; Fe, 15.04.

The oxidizing agent 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) is very useful for preparing salts of various ferrocenes. Samples of $[Co(C_5H_5)_2{}^+](DDQH^-)$, $[Fe(C_5H_5)_2{}^+](DDQH^-)$, $[Fe_2(C_5H_5)_2(C_5H_4)_2{}^{2+}](DDQH^-)_2$, and $[Fe_2(C_5H_4)_4{}^{2+}](DDQH^-)_2$ were prepared by the method of Brandon.[16] As will be discussed in the Results, we have found that the anion in these materials is *not* a radical as was believed but is probably the hydroquinone anion ($DDQH^-$)

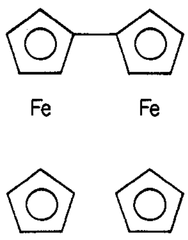


Anal. Calcd for $(C_{10}H_{10}Co^+)(C_8HN_2O_2Cl_2{}^-)$: C, 51.83; H, 2.66; Co, 14.13. Found: C, 51.73; H, 2.36; Co, 14.26. Calcd for $(C_{10}H_{10}Fe^+)(C_8HN_2O_2Cl_2{}^-)$: C, 52.22; H, 2.68; Fe, 13.49. Found: C, 52.85; H, 2.54; Fe, 13.43. Calcd for $(C_{20}H_{18}Fe_2{}^{2+})(C_8HN_2O_2Cl_2{}^-)_2$: C, 52.34; H, 2.44; Fe, 13.52. Found: C, 52.91; H, 2.23; Fe, 13.46. Calcd for $(C_{20}H_{16}Fe_2{}^{2+})(C_8HN_2O_2Cl_2{}^-)_2$: C, 52.47; H, 2.20; Fe, 13.55. Found: C, 53.62; H, 2.16; Fe, 13.88.

Physical Measurements. Variable-temperature (4.2-290°K) magnetic susceptibilities were measured with a Princeton Applied Research Model 150A (superconducting magnet with $H = 54.3$ kG) vibrating-sample magnetometer. A calibrated gallium arsenide diode was used to determine the sample temperature and $CuSO_4 \cdot 5H_2O$ was used as a standard in the magnetic susceptibility measurements. Corrections for the diamagnetism of the sample container and background were applied at all temperatures. Duplicate runs were made on samples over the entire temperature range. Pascal constants were used to correct for the diamagnetism of the compounds.

Polarographic measurements were carried out with a Princeton Applied Research Model 174 polarograph. Polarograms of the various biferrocenes were run at a rotating platinum electrode and a dropping mercury electrode (dme). Cyclic voltammetry was performed with a stationary Pt electrode employing a PAR Model 173 potentiostat and a homemade function generator; the electrode was cleaned after each run. Duplicate runs were made on each sample. Polarograms of methylene-bridged biferrocene, phenylferrocene, and ferrocene were run on 1×10^{-3} M acetonitrile solutions with 0.1 M $(C_2H_5)_4NClO_4$ as supporting electrolyte. Biferrocene, tetramethylethylene-bridged biferrocene, and 1,4-bis(β-ferrocenylvinyl)benzene were studied at 5×10^{-4} M in acetonitrile with the same electrolyte. Insolubility necessitated running biferrocenylene and biferrocenylmercury at low concentrations (2×10^{-5} and 1×10^{-5} M, respectively). Degassing with nitrogen prefaced each run. Background ir voltages were taken into account in the treatment of the data. The potentials quoted in this work are referred to a saturated aqueous calomel electrode at 27°.

Results and Discussion



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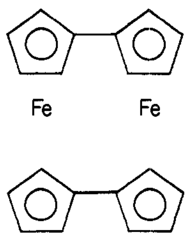

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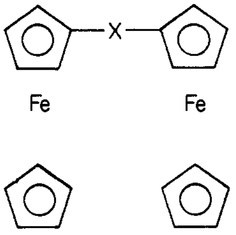

III

Electrochemistry. Samples of biferrocene (I), biferrocenylene (II), and a series of bridged biferrocenes (III), with the bridging group X = $-CH_2-$, $-CH_2CH_2-$, $-(CH_3)_2CC(CH_3)_2-$, -Hg-, and $-CH{=}CHC_6H_4CH{=}CH-$ (1,4), were prepared and studied polarographically. The polarographic data for these compounds, as well as those for some other relevant ferrocenes, are given in Table I. In most cases the data in Table I were collected for acetonitrile solutions with 0.1 M tetraethylammonium perchlorate electrolyte using a rotating platinum electrode. The $E_{1/2}$ values are referenced to the sce and the numbers of electrons (n) were determined by comparing limiting currents with that obtained for a given solution of ferrocene.

From the data in Table I it can be seen that in the case of the bridged biferrocenes where X = -Hg-, $-CH_2CH_2-$, $-(CH_3)_2CC(CH_3)_2-$, and $-CH{=}CHC_6H_4CH{=}CH-$ (1,4) only one oxidation wave is detected. In each case the wave corresponds to a two-electron process. Apparently both iron atoms in these biferrocenes are oxidized at the same potential; oxidation of the first iron does not affect the ease with which the second iron is oxidized. Diferrocenylmethane, however, exhibits two oxidation waves, as was noted by Watts,[17] at 0.39 and 0.56 V *vs.* sce. The first wave is close to that for ferrocene (0.41 V *vs.* sce). The dc polarogram of diferrocenylmethane is reproduced in Figure 1C; the two waves are barely discernible in this dc polarogram. Differential pulse polarography with a stationary platinum electrode (see Figure 2) clearly resolves the two waves in diferrocenylmethane. The differential pulse work on 1,2-diferrocenylethane also shows there are two waves; however, in this case the two waves are even closer than those for diferrocenylmethane.

The effect of oxidation of one iron atom in a biferrocene-like molecule on the oxidation potential of the second is increased for the directly fused compounds biferrocene (I) and biferrocenylene (II). Biferrocene in acetonitrile shows two waves at 0.31 and 0.64 V *vs.* sce and biferrocenylene two waves at 0.13 and 0.72 V *vs.* sce. The dc polarograms of biferrocene and biferrocenylene are reproduced in Figure 1.

Biferrocene, the four bridged biferrocenes, and biferrocenylene were also investigated at a dme. Differential pulsed polarograms for these compounds show clearly resolved half-waves before the onset of mercury discharge and peak positions are given in Table I. The second half-waves of biferrocene, biferrocenylene, and methylene-bridged bi-

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(15) D. N. Hendrickson, Y. S. Sohn, and H. B. Gray, *Inorg. Chem.*, **10**, 1559 (1971).

(16) R. L. Brandon, J. H. Osiecki, and A. Ottenberg, *J. Org. Chem.*, 31, 1214 (1966).

(17) J. E. Gorton, H. L. Lentzner, and W. E. Watts, *Tetrahedron*, **27**, 4353 (1971).

Table I. Polarographic Data for Various Biferrocenes and Biferrocenylene

Compd	$E_{1/2}$,[a] V Rotating platinum	Diff pulse dme	n	Slope[b] of E *vs.* log $(i/(i_d - i))$
$[Fe(C_5H_5)(C_5H_4)]_2Hg$	0.28	0.24	2	0.081
$[Fe(C_5H_5)(C_5H_4)]_2$-$[(CH_3)_2CC(CH_3)_2]$	0.36	0.34	2	0.090
$[Fe(C_5H_5)(C_5H_4)]_2$-$[-CH{=}CHC_6H_4CH{=}CH-]$	0.40	0.41	2	0.081
$Fe[(C_5H_5)(C_5H_4)]_2[C_2H_4]$	0.37	0.33 0.37	2	0.086
$[Fe(C_5H_5)(C_5H_4)]_2[CH_2]$	0.39 0.56	0.33	1 1	0.067 0.097
$[Fe(C_5H_5)(C_5H_4)]_2$	0.31 0.64	0.31	1 1	0.067 0.074
$[Fe(C_5H_4)_2]_2$	0.13 0.72	0.12	1 1	0.064 0.083
$[Fe(C_5H_5)(C_5H_4)(C_6H_5)]$	0.42		1	0.074
$Fe(C_5H_5)_2$	0.41		1	0.081

[a] All half-wave potentials are referred to the sce. [b] Determined at a rotating Pt electrode.

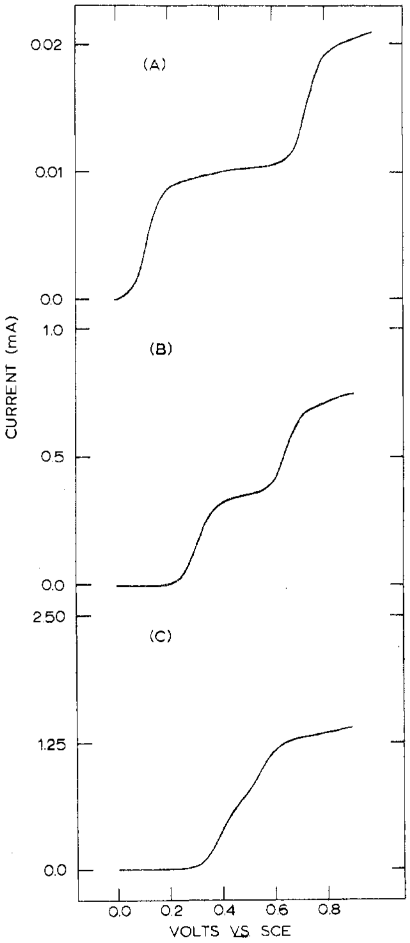

Figure 1. Dc polarograms at a rotating Pt electrode of three biferrocenes, all dissolved in acetonitrile with 10^{-1} M $(C_2H_5)_4NClO_4$ as electrolyte: (A) biferrocenylene (2×10^{-5} M), (B) biferrocene (5×10^{-4} M), and (C) diferrocenylmethane (10^{-3} M).

ferrocene could not be seen before discharge. The dme potentials are essentially the same as those found with the rotating platinum electrode.

Chemical oxidation of these biferrocenes was studied. Iodine oxidation, concentrated sulfuric acid oxidation, and oxidation by trichloroacetic acid in the presence of oxygen were tried, because they are methods commonly used to

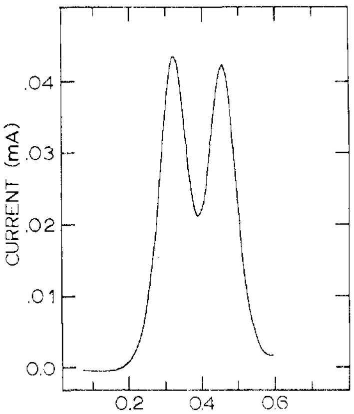

Figure 2. Differential pulsed polarogram of diferrocenylmethane (10^{-3} M) in acetonitrile, employing a stationary Pt electrode and 10^{-1} M $(C_2H_5)_4NClO_4$ electrolyte.

prepare ferricenium salts. With 1,2-diferrocenyltetramethylethane and 1,4-bis(β-ferrocenylvinyl)benzene, oxidation resulted in dioxidized salts. The mercury-bridged biferrocene is not stable in the presence of acids and inconclusive results were obtained with iodine. In the case of diferrocenylmethane, oxidation also resulted in dioxidized salts. Biferrocene and biferrocenylene gave only monooxidized compounds with the above oxidizing agents except the concentrated H_2SO_4 oxidation of biferrocenylene which gave a dioxidized product. The chemical oxidation results are in qualitative agreement with the electrochemistry data.

It is well known[18] that many species are characterized by irreversibility when studied at a solid electrode such as was used in this work. The oxidation of ferrocene at a dme and rotating Pt electrode has been shown[19] to be reversible and as such we have compared in Table I the slope of the E *vs.* log $(i/(i_d - i))$ curve for ferrocene at a rotating platinum electrode with the corresponding slopes for the various biferrocenes and biferrocenylene. From this comparison we can infer that the two-electron waves seen for four of the compounds are probably irreversible because their slopes are comparable to or exceed the slope of ferrocene (a two-electron wave should have a slope equal to half that of a one-electron wave). Alternatively, there could be two closely spaced one-electron waves or the characteristics of adsorption or charge transfer between the electrode surface and the electroactive species could be different for these four molecules than for ferrocene. The three systems (excluding 1,2-diferrocenylethane where the waves are too close) studied in this work that show two one-electron waves have slopes for both waves that are not too different from that for ferrocene; in each case the slope for the second wave (higher potential) is larger, possibly indicating a greater degree of irreversibility in the second wave. This is substantiated, in part, by the cyclic voltammograms of these three systems taken in acetonitrile employing a stationary platinum electrode. For example, the cyclic voltammogram of biferrocene is reproduced in Figure 3 and this shows that the second oxidation wave is totally irreversible as indicated by a lack of any reduction current following oxidation. All in all, the above data give us a good determination of $E_{1/2}$ values for a series of biferrocenes under similar conditions, but the necessity of a solid electrode obscures to a certain

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(18) R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York, N. Y., 1969.

(19) S. P. Gubin, S. A. Smirnova, L. I. Denisovich, and A. A. Lubovich, *J. Organometal. Chem.*, 30, 243 (1971).

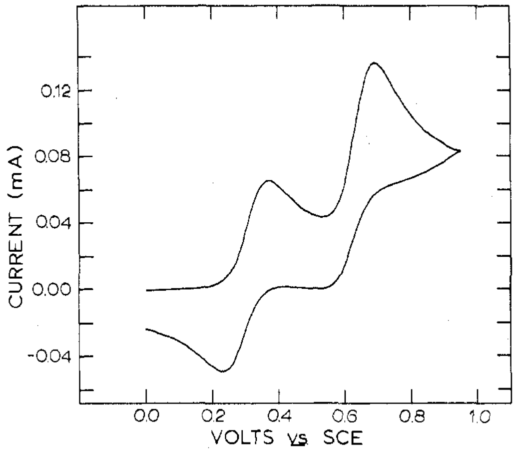
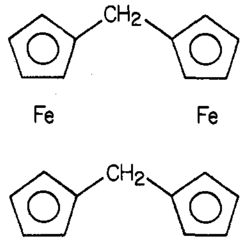


Figure 3. Cyclic voltammogram of biferrocene (5×10^{-4} *M*) in acetonitrile at a stationary platinum electrode (sweep rate 100 mV/sec).

degree the determination of the reversibilities of the various waves.

Bonding Considerations from the Electrochemistry Data. In the bridged biferrocenes there are two possible types of interaction, as previously stated by Watts, *et al.*,[17] between the two ferrocene moieties: (a) interaction propagated through the bridge and (b) direct iron–iron interaction. The above series of biferrocenes was selected in an attempt to ascertain the relative importance (in respect to separation between the two half-waves) of these two interactions (if possible) and to ascertain what factors determine whether or not a mixed-valence biferrocene compound will form. Watts assesed the relative importance of the two interactions by comparing the separation of the two waves for diferrocenylmethane with that for [1.1]ferrocenophane (IV).



IV

He found that the separation between half-waves was about twice as large (0.19 V) for the difused molecule IV than that (0.10 V) for diferrocenylmethane and concluded that a substantial part of the difference was due to a direct Fe-Fe "electrostatic field interaction" which raises the second potential of the [1.1]ferrocenophane.

A similar comparison can be made between biferrocene and biferrocenylene using the data in Table I. Again the separation between the two half-waves almost doubles in going from the singly fused to the difused system. An analysis shows that more than half of the doubling, however, results from a lowering of the first oxidation potential and *not* from a raising of the second oxidation potential. Similar comments can be made concerning the change in half-wave separations observed by Watts. It is our contention that the change in half-wave separation upon difusing is probably due to a summation of three effects: an increase in bridge-propagated interaction due to the additional bridge, a through-space electric field effect on the second oxidation potential resulting from having one iron atom oxidized, and a direct electron exchange between the two iron centers. The second effect would seemingly only operate on the second oxidation wave to increase it upon difusing, whereas the first and third effects could influence both of the oxidation potentials. It is, of course, very difficult to assess the relative importance of the three effects; however, it is possible to identify which effects are important in determining whether a mixed-valence compound is obtained.

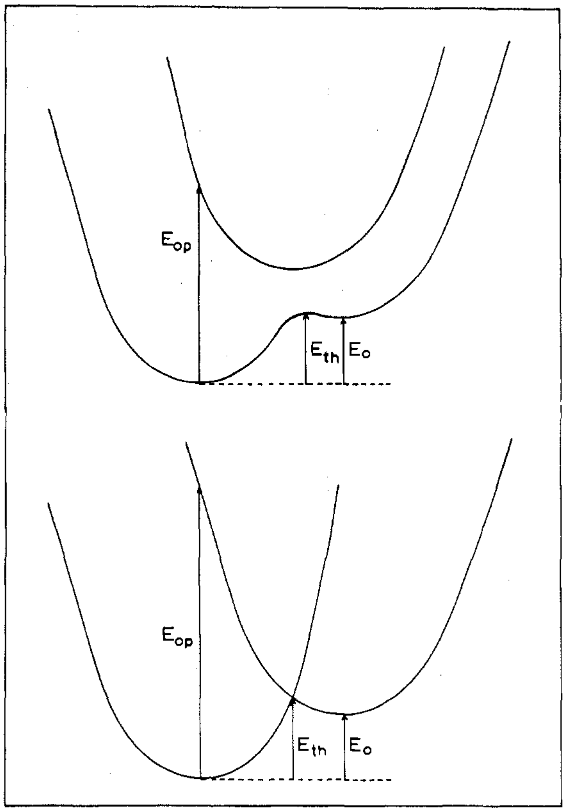


Figure 4. The potential well diagrams for the mixed-valence system $Fe^{II}Fe'^{III}$: bottom, the case where the halves of the system are "noninteracting"; top, the case where there is an interaction and thermal intervalence transfer is possible.

Hush[20] has presented a review on mixed-valence compounds in which he has developed a simple theoretical model for intervalence transfer

$$Fe^{II}Fe'^{III} \xrightarrow{\Delta} Fe^{III}Fe'^{II}$$

If the halves of the molecule $Fe^{II}Fe'^{III}$ do *not* interact, then the potential wells for the intervalence transfer appear as the two crossing wells in Figure 4. In this case the left well is the well for $Fe^{II}Fe'^{III}$, the right well is for $Fe^{III}Fe'^{II}$, and the displacement along the horizontal axis is a measure of the difference in normal coordinates of the two states of the molecule. With crossing wells there can be no thermal intervalence transfer. If the halves of the molecule interact, then the two wells will be noncrossing as depicted in Figure 4 and it is possible to have a thermal intervalence transfer. The electron hopping (*i.e.*, intervalence transfer) can be effected by either direct Fe-Fe electron exchange or superexchange propagated through the bridge. Both of these exchange terms result from electron-electron repulsion in conjunction with an antisymmetric wave function.

Three effects (bridge-propagated interactions, direct Fe-Fe electron exchange, and through-space electric field effects) determine whether a certain biferrocene can be monooxidized, while the rate of intervalence transfer (that is, does a mixed-

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[20] N. S. Hush, *Progr. Inorg. Chem.*, 8, 391 (1967).

valence compound exist?) is determined (at room temperatures) by the extent of electron exchange (direct or superexchange) between the two metal centers. Cowan[5-8] has reported that the picrate salt of monooxidized biferrocene is mixed valence on the iron Mossbauer time scale (rate $< 10^7$ sec^{-1}) and we have verified this for the triiodide monooxidized biferrocene salt. Very recently we reported[21] that the triiodide salt of monooxidized biferrocenylene gives an iron Mossbauer spectrum with only *one* quadrupole-split doublet; thus, the monooxidized biferrocenylene molecule has an intervalence transfer rate $>10^7$ sec^{-1}.

It would be desirable to have some direct evidence to gauge the extent of electron exchange in the oxidized salts of biferrocene and biferrocenylene and it is with this in mind that we turn to the variable-temperature magnetic susceptibility and esr results.

Magnetic Susceptibility. We studied the variable-temperature (4.2-290°K) magnetic susceptibility of three oxidized biferrocene and bridged biferrocene salts and of a salt of dioxidized biferrocenylene. Magnetic susceptibility measurements on $[1,1\text{-}(CH_2)Fe_2(C_5H_5)_2(C_5H_4)_2](PF_6)_2$ and $[1,1\text{-}[(CH_3)_2CC(CH_3)_2]Fe_2(C_5H_5)_2(C_5H_4)_2](PF_6)_2$ resulted in the data given in Table II and depicted in Figure 5. Both of the μ_{eff} *vs.* temperature curves are typical of ferricenium μ_{eff} curves; that is, there is no indication of an *intra*molecular exchange interaction. This can be seen by comparison with the susceptibility data for $[Fe(C_5H_5)_2]I_3$, which are also given in Table II. The solid lines in Figure 5 are theoretical least-squares fits to the data.

The $^2E_{2g}$ ferricenium ground state has been shown to be split into two Kramers doublets by a combination of spin-orbit interaction (gauged by the magnitude of the orbital reduction parameter k') and low-symmetry crystal field distortion (gauged by the parameter δ). Furthermore, the presence of a low-lying $^2A_{2g}$ state has been noted ($\Delta E = E(^2A_{2g}) - E(^2E_{2g})$). With these considerations the molar paramagnetic susceptibility (per iron atom) of a ferricenium system is

$$\chi = 1/3(\chi_{\parallel} + 2\chi_{\perp})$$

where

$$\chi_\alpha = \frac{\chi_\alpha[\psi_\pm{}^a(^2E_{2g})] + e^{-\Delta E/kT}\chi_\alpha(^2A_{1g})}{1 + e^{-\Delta E/kT}}$$

Here χ_α is either the parallel or perpendicular component of the susceptibility tensor; $\psi_\pm{}^a(^2E_{2g})$ is the lower energy Kramers doublet of the $^2E_{2g}$ ground state. The various χ_α expressions for the two electronic states have been given in a previous paper.[15] In an attempt to account for possible *inter*molecular interactions we have modified the reported χ_α expressions for the two states by replacing T by $T - \Theta$, Θ acting as a Curie-Weiss constant. Ginsberg[22] has shown that a Θ constant is equivalent to an exchange term between molecules.

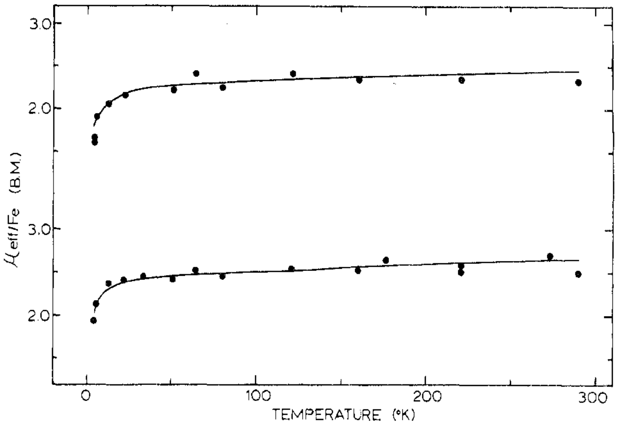

Figure 5. The effective magnetic moments (μ_{eff}) per iron atom as a function of temperature for two dioxidized bridged biferrocenes: top, $1,1\text{-}[(CH_3)_2CC(CH_3)_2]Fe_2(C_5H_5)_2(C_5H_4)_2(PF_6)_2$; bottom, $[1,1\text{-}(CH_2)Fe_2(C_5H_5)_2(C_5H_4)_2](PF_6)_2$. The solid lines are least-squares fit theoretical lines (see text).

Table II. Variable-Temperature Magnetic Susceptibility Data for $[1,1\text{-}(CH_2)Fe_2(C_5H_5)_2(C_5H_4)_2][PF_6]_2$ (A), $[1,1\text{-}[(CH_3)_2CC(CH_3)_2]Fe_2(C_5H_5)_2(C_5H_4)_2][PF_6]_2$ (B), and $Fe(C_5H_5)_2I_3$ (C)

$10^3\chi_M{}^{\text{cor},a}$ cgsu				$10^3\chi_M{}^{\text{cor},a}$ cgsu			
A	B	C	T, °K	A	B	C	T, °K
5.41	4.68	2.87	290	18.9	15.8	11.5	80
6.66			273	24.9	22.5	14.3	64.5
		3.35	255	28.8	24.2	17.7	51.0
7.15, 7.60	6.24	3.85	221	44.6		27.7	33.5
		4.49	191	66.2	53.2		22.0
9.94			176	109	81.1	64.4	13.0
9.98	8.54	5.37	160	200	160		5.7
13.5	12.0	6.87	121	223	167, 152	123	4.2

[a] Molar paramagnetic susceptibilities are corrected for background and for diamagnetism of the compound. Compound diamagnetism is from Pascal's constants and the values are (A) -302.0×10^{-6}, (B) -332.0×10^{-6}, (C) 264.5×10^{-6} cgsu/mol.

Fitting the susceptibility data in Table II for $[Fe(C_5H_5)_2]I_3$ to the above expression gave $\delta = 117$ cm^{-1}, $k' = 0.80$, $\Delta E = 2317$ cm^{-1}, and $\Theta = -1.33°$. The negative Θ value indicates that there is an *inter*molecular antiferromagnetic interaction. The data for the dioxidized salt of diferrocenylmethane give, upon least-squares fitting, $\delta = 311$ cm^{-1}, $k' = 0.87$, $\Delta E = 4240$ cm^{-1}, and $\Theta = -1.99°$. Likewise, the data for the dioxidized 1,2-diferrocenyltetramethylethane give $\delta = 453$ cm^{-1}, $k' = 0.84$, $\Delta E = 3140$ cm^{-1}, and $\Theta = -2.64°$. Thus a comparison of the parameters for these two dioxidized biferrocenes with those for ferricenium triiodide shows that there is no indication of *intra*molecular exchange interaction in the molecules.

Cowan, *et al.*,[7] reported the magnetic susceptibility of dioxidized biferrocene tetrafluoroborate, $[Fe_2(C_5H_5)_2(C_5H_4)_2](BF_4)_2$, in the range of 2-300°K. A sharp increase in effective magnetic moment at lower temperatures (<50°K) was detected. This was explained by proposing that the dioxidized cation is highly distorted at elevated temperatures and that at lower temperatures the distortion is reduced. The effective magnetic moment of the ferricenium ion has been shown[15] to be sensitive to distortions, that is, crystal fields of symmetry lower than D_5. It was of interest to see if a different salt of dioxidized biferrocene would show the same effect.

The compound 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) has been reported to dioxidize biferrocene; apparently, the magnetism of the dioxidized biferrocene $(DDQ^-)_2$ salt has not been studied due to anticipated complexities associated with the DDQ^- anion, which has been reported[23] to be a radical anion. We prepared $[Co(C_5H_5)_2{}^+](DDQ^-)$ and $[Fe(C_5H_5)_2{}^+](DDQ^-)$.

The esr of the cobalticenium salt did show an organic free

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Table III. Variable-Temperature Magnetic Susceptibility Data for the DDQH Salts of Biferricenium (A) and Ferricenium (B)

$10^3 \chi_M{}^{cor,a}$, cgsu			$10^3 \chi_M{}^{cor,a}$, cgsu		
A	B	T, °K	A	B	T, °K
5.94	2.51	290	27.4	10.7	64.5
6.79	2.86	255	33.7	12.9	51.0
7.61	3.30	221	52.3	19.2	33.5
8.85	3.67	191	121	40.0	13.0
10.7	4.42	160	171	54.0	8.0
13.9	5.68	121	225	70.6	4.2
22.2	8.76	80			

[a] Molar paramagnetic susceptibilities are corrected for background and for diamagnetism of the compound. Compound diamagnetism is from Pascal's constants and the values are (A) -429.2×10^{-6} and (B) -217.5×10^{-6} cgsu/mol.

radical signal; however, the magnetic susceptibility of the salt indicated that there was less than 0.2% radical anion. In short, the anion in the oxidation product of cobaltocene with DDQ is *not* a free radical, but probably a hydroquinone DDQH$^-$. The diamagnetism of the DDQ anion was further substantiated by magnetic susceptibility data for $[Fe(C_5H_5)_2{}^+](DDQH^-)$, which are given in Table III and depicted in Figure 6. The 290°K μ_{eff} value of 2.41 BM is on the low side of the μ_{eff} range reported[15] for ferricenium systems, indicating that there is very little unpaired spin on the anion. Fitting of the $[Fe(C_5H_5)_2{}^+](DDQH^-)$ data in Table III to the theoretical expression gave $\delta = 436$ cm^{-1}, $k' = 0.84$, $\Delta E = 3380$ cm^{-1}, and $\Theta = -4.23°$. These parameters are very reasonable for a ferricenium compound as judged by the parameters for $[Fe(C_5H_5)_2]I_3$.

With the DDQ anion characterized as above, the magnetic susceptibility of the dioxidized biferrocene (DDQH$^-$)$_2$ salt was determined in the range 4.2-290°K. The data are given in Table III and depicted in Figure 6. It can be seen that the appearance of the μ_{eff} *vs.* temperature curve for $[Fe_2(C_5H_5)_2(C_5H_4)_2](DDQH)_2$ is very similar to that of $[Fe(C_5H_5)_2](DDQH)$ as well as other ferricenium curves. Fitting of the susceptibility data for this dioxidized biferrocene salt yields $\delta = 258$ cm^{-1}, $k' = 0.88$, $\Delta E = 3120$ cm^{-1}, and $\Theta = -1.87°$. The Θ value is again small and as such the conclusion is that there is no appreciable *intra*molecular exchange interaction between the two Fe(III) atoms in this dioxidized biferrocene salt. Mossbauer spectroscopy[5,21] has indicated that monooxidized biferrocene is a "trapped-valence" system in agreement with our findings that the dioxidized biferrocene system possesses negligible exchange interaction.

In contrast, monooxidized biferrocenylene was shown by Mossbauer[21] to be an average valence system, which implies an appreciable electron exchange between the two iron centers in the molecule. We prepared the dioxidized salt of biferrocenylene using DDQ and found that this salt is *diamagnetic* in the range of 4.2-290°K.[24] In terms of an effective spin Hamiltonian $JS_1 \cdot S_2$, where J is the "exchange integral," this means that the ground state of dioxidized biferrocenylene is the $S' = 0$ diamagnetic state and that there is very little population in the $S' = 1$ triplet state, that is, $J \gg \sim 400$ cm^{-1}. It is clear why the monooxidized biferrocenylene is an average-valence system, if, indeed, an exchange interaction of such a magnitude is operative. An antiferromagnetic interaction between the two iron centers is, of course, synonymous with a bonding interaction. The question (rhetorical?) that remains is whether this intramolecular Fe-Fe interaction would be classed as a "chemical bond." The Fe-Fe distance in biferrocenylene has been determined[25] to be 3.98 Å, and if, as seems reasonable, this distance is not dramatically ($\Delta < 0.1$ Å) changed in the conversion to the dioxidized molecule, it would appear that this interaction would *not* be classed as a "chemical bond." In passing we should note that the exchange interaction operative in the dioxidized biferrocenylene molecule is most likely a direct iron-iron electron exchange and *not* a ring-propagated superexchange interaction. The same superexchange mechanism would be operational, in part, in dioxidized biferrocene, whereas, the magnetic susceptibility for this system did not show any indications of such an interaction.

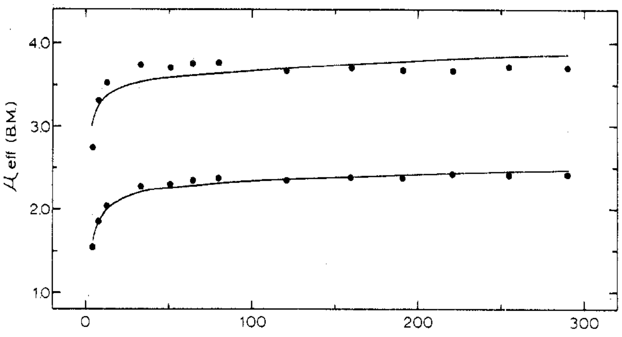

Figure 6. The effective moment (μ_{eff}) *vs.* temperature curves for two DDQ oxidation compounds: bottom, $[Fe(C_5H_5)_2](DDQH^-)$; top, $[Fe_2(C_5H_5)_2(C_5H_4)_2](DDQH^-)_2$. Note that latter compound is dioxidized and that μ_{eff} is given for the molecule, *not* per iron atom as in Figure 4. The solid lines are least-squares-fit theoretical lines (see text).

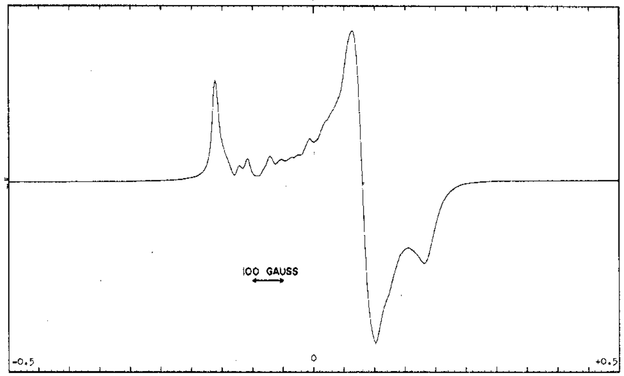

Figure 7. The liquid nitrogen esr spectrum of $[Fe_2(C_5H_4)_4{}^+](I_3{}^-)$. The center of the spectrum is 3100 G and the frequency is 9.097 GHz.

Evidence for the presence of electron-exchange interactions in monooxidized biferrocenylene is readily apparent in the 77°K esr spectrum of a solid sample of $[Fe_2(C_5H_4)_4]I_3$, which is reproduced in Figure 7. This is an unusual "ferricenium" esr spectrum in that the peaks are relatively sharp (peak widths are 3-10 times sharper than those reported[5] for monooxidized biferricenium picrate). A sharpening of this nature is indication of exchange narrowing. The resolution in this esr spectrum is so good that it is possible to detect nonaxial character in the spectrum as well as some weak hyperfine structure, which is possibly due to coupling with the ring protons. This esr spectrum is characterized with $g_z = 2.34$, $g_y = 1.99$, and $g_x = 1.88$. Ferricenium and biferricenium systems have been reported[7,26] to have $g_\parallel$ in the range of 3.2-4.35 and $g_\perp$ in the range of 1.91-1.26.

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(24) The magnetic susceptibility of the compound indicated there was about 12 wt % monooxidized biferrocenylene. This is in agreement with the analysis of the compound, as well as with what would be expected considering the oxidation potential of DDQ.

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The g_y and g_x values found for the spectrum in Figure 7 are close to the $g_\perp$ range, but the g_z is seemingly way out of the $g_\parallel$ range. It must be remembered, however, that the unpaired electron in $Fe_2(C_5H_4)_4^+$ is rapidly exchanging between the two iron centers, which is a unique situation compared to all other ferricenium systems. The room-temperature spectrum of the solid, as well as the acetonitrile solution spectra (300 and 77°K), is very similar to that reproduced in Figure 7, except the resolution is somewhat poorer.[27]

Registry No. $[Fe(C_5H_5)(C_5H_4)]_2Hg$, 1274-09-5; $[Fe(C_5H_5)(C_5H_4)]_2[(CH_3)_2CC(CH_3)_2]$, 12610-01-4; $[Fe(C_5H_5)(C_5H_4)]_2[CHCHC_6H_4CHCH]$, 12094-51-8; $[Fe(C_5H_5)(C_5H_4)]_2[C_2H_4]$, 12156-05-7; $[Fe(C_5H_5)(C_5H_4)]_2[CH_2]$, 1317-11-9; $[Fe(C_5H_5)(C_5H_4)]_2$, 1287-38-3; $[Fe(C_5H_4)_2]_2$, 11105-90-1; $[Fe(C_5H_5)(C_5H_4)(C_6H_5)]$, 1287-25-8; $Fe(C_5H_5)_2$, 102-54-5; $[1,1\text{-}(CH_2)Fe(C_2H_5)_2(C_5H_4)_2][PF_6]_2$, 39291-61-7; $[1,1\text{-}[(CH_3)_2CC(CH_3)_2]Fe_2(C_5H_5)_2(C_5H_4)_2][PF_6]_2$, 39291-62-8; $Fe(C_5H_5)_2I_3$, 1291-35-6; $[Co(C_5H_5)_2](DDQH)$, 39291-56-0; $[Fe(C_5H_5)_2](DDQH)$, 39291-57-1; $[Fe_2(C_5H_5)_2(C_5H_4)_2](DDQH)_2$, 39291-60-6; $[Fe_2(C_5H_4)_4](DDQH)_2$, 39291-59-3.

Acknowledgment. We are grateful for support from NIH Grant HL 13652.

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[27] Note Added in Proof. Professor W. E. Watts has pointed out to us (and we have verified this by proton nmr) that the compound labeled as $-C(CH_3)_2C(CH_3)_2-$ bridged biferrocene is (for our sample) a mixture of 80% $-C(CH_3)_2CH{=}C(CH_3)-$ bridged and 20% $-C(CH_3)CH_2C({=}CH_2)-$ bridged biferrocene, a fact that in no way detracts from the conclusions of our work.

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Mono- and Disubstituted Derivatives of Benzo[*c*]cinnolinebis(tricarbonyliron)

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The preparations of benzo[*c*]cinnolinebis(tricarbonyliron) derivatives containing phosphine, phosphite, cyclohexyl isocyanide, triphenylarsine, or triphenylstibine ligands are reported. Depending upon both the ligand and the reaction conditions, mono- or disubstituted products are obtained. Trisubstitution has not been observed. Infrared, mass spectroscopic, pmr, and cmr data indicate that the preferred substitution site is that trans to the metal–metal bond. A close similarity is noted between these complexes and the corresponding derivatives of bis-μ-mercapto-bis(tricarbonyliron) complexes.

Introduction

A variety of ligand-bridged hexacarbonyldiiron complexes is known. Bridging ligands include sulfur[1] and halogens[2] as well as phosphorus-,[3,4] arsenic-,[4] sulfur-,[5] selenium-,[6] tellurium-,[6] and nitrogen-donor[7] moieties. Although carbon monoxide displacement from mercapto-bridged complexes by phosphines and other soft ligands has been extensively studied,[8] only scattered observations of such substitutions have been made for complexes in which the bridging moiety involves a phosphorus-,[9] arsenic-,[9] or nitrogen-donor[10,11] ligand. This paper reports the preparation and characterization of a number of mono- and disubstituted derivatives of benzo[*c*]cinnolinebis(tricarbonyliron) containing phosphine, phosphite, cyclohexyl isocyanide, and triphenylarsine ligands. A triphenylstibine derivative was identified by infrared spectroscopy but was not isolated.

Experimental Section

Benzo[*c*]cinnolinebis(tricarbonyliron) and its substituted derivatives are remarkably air-stable, even in solution. Nevertheless, all reactions were carried out under a nitrogen atmosphere, and subsequent work-up procedures involved only short periods of exposure to atmospheric oxygen. All microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Materials. Phosphines, phosphites, and iron pentacarbonyl were obtained from commercial sources and were used as received. Commercially obtained triphenylarsine was recrystallized from methanol before use. Cyclohexyl isocyanide was prepared by dehydration of *N*-cyclohexylformamide according to the procedure of Hertler and Corey.[12] Benzo[*c*]cinnoline was prepared by $LiAlH_4$ reduction of 2,2′-dinitrobiphenyl following the description of Badger,[13] and benzo[*c*]cinnolinebis(tricarbonyliron) was prepared from iron pentacarbonyl and benzo[*c*]cinnoline as described by Bennett.[11]

Preparation of Derivatives of Benzo[*c*]cinnolinebis(tricarbonyliron). General Procedure. Disubstituted derivatives were formed with smooth evolution of 2 equiv of carbon monoxide when a slight excess of tri-*n*-butylphosphine, diphenylphosphine, trimethyl phosphite, or cyclohexyl isocyanide was allowed to react with $Fe_2(CO)_6(C_{12}H_8N_2)$ in toluene solution at ambient temperatures. With ethyldiphenylphosphine, triphenyl phosphite, and triphenylphosphine the monosubstituted derivatives were formed under these conditions. The monosubstituted tri-*n*-butylphosphine derivative, $Fe_2(CO)_5(C_{12}H_8N_2)P(n\text{-}C_4H_9)_3$, was obtained from reactions involving equimolar reagents. The disubstituted triphenylphosphine derivative, $Fe_2(CO)_4(C_{12}H_8N_2)[P(C_6H_5)_3]_2$, was produced under more vigorous reaction conditions (100° for 48 hr). Similar conditions (100° for 72 hr) were required to achieve complete monosubstitution with triphenylarsine. Infrared spectra of crude products clearly demonstrated the formation of the monosubstituted triphenylstibine derivative, $Fe_2(CO)_5(C_{12}H_8N_2)Sb(C_6H_5)_3$. However, this substitution was less than 50% complete after 100 hr at 100°. This product was not obtained in a pure state.

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