Mixed Valence Cations. Chemistry of π-Bridged Analogues of Biferrocene and Biferrocenylene

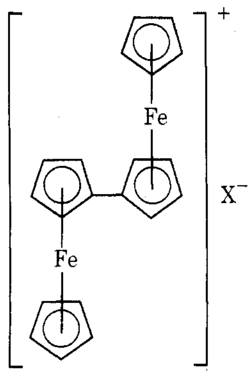
Carole Levanda, Klaus Bechgaard, and Dwaine O. Cowan*

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

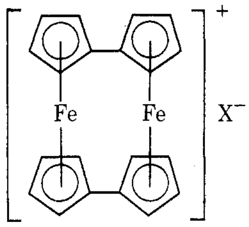
Received December 15, 1975

Solutions of the mono- and dications of acetylene bridged analogues of biferrocene and biferrocenylene were generated electrochemically in order to investigate their ESR and absorption spectra. The visible and near-infrared spectra of the mono- and dications of diferrocenylacetylene and diferrocenylbutadiyne show features similar to biferrocene cations. Moderately intense bands in the near-infrared spectra of the diferrocenylacetylene monocation (λ 1560 nm, ε 670) and the diferrocenylbutadiyne monocation (λ 1180 nm, ε 570) are assigned to intervalence transfer transitions. The energy of the bands increases as the iron–iron distance increases. A corresponding decrease in the intensity of the bands, and $\Delta E_{1/2}$, the separation in half-wave potentials, is observed. The opposite effect of frequency and intensity as a function of metal–metal distance is noted in the spectra of the ferrocenophane cations. The monocation of [2.2]ferrocenophane-1,13-diyne (FDA) has a near-infrared band (λ 1760 nm, ε 2100) at lower energy and higher intensity than the biferrocenylene (BFD) monocation. The ESR spectrum of FDA (2,3) has a rhombic *g* tensor and sharp lines, and bears strong resemblance to that of BFD (2,3). The electrochemical and spectral results suggest that FDA (2,3) is a delocalized analogue of the BFD cation.

The mixed valence monocations of biferrocene (I) and biferrocenylene (II) (bisfulvalenediiron, BFD) have been characterized by a variety of physical measurements.[1,2] A general property of mixed valence monocations is the appearance of low-energy transitions not found in either the neutral or dicationic species.[3,4] For both biferrocene (2,3) and BFD (2,3) salts,[5] such transitions are observed in the near infrared.[6,7,8] The similarity between these compounds, however, ends here. It has been shown that the relatively small structural change in going from biferrocene to biferrocenylene produces a drastic difference in the physical properties of the ions.



I

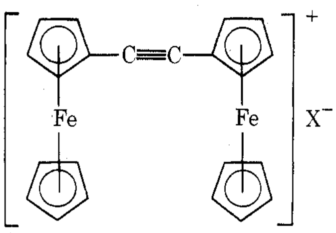


II (BFD)

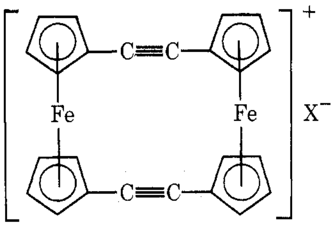
The biferrocene (2,3) ion has been described as a system in which there is only weak interaction between the two halves (i.e., the two iron atoms) in the ground state. Electron transfer is sufficiently slow to allow detection of signals ascribable to the ferrocene and ferrocenium portions of the molecule in Mossbauer[9] and ESCA[10] experiments. Likewise, the magnetic properties of I are reasonably well explained in terms of a perturbed ferrocenium ion.[11]

The BFD (2,3), however, defies these descriptions. Mossbauer and ESCA results[12] must be interpreted in terms of a fully delocalized system in which both iron atoms are equivalent. Because of this essential difference, it is likely that the near-infrared transition observed for BFD (2,3) cannot be explained by the simple model which has been applied successfully to the weakly interacting biferrocenes.[6,13] The question remains as to whether the delocalized nature of BFD (2,3) results from greater metal–metal interaction due to the proximity of the iron atoms in the forced cis conformation, or from interactions through the π system of the fused fulvalene ligands. In this study, an attempt is made to evaluate these factors.

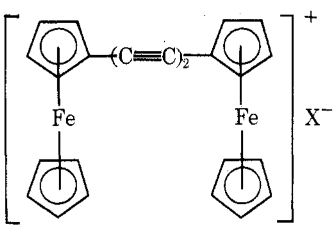
The cations of biferrocenes bridged by acetylene linkages, such as compounds III–V, provide a conjugated ligand system in which iron–iron distances (estimated to be 6.5 Å in IV) are too large to allow substantial direct metal–metal interaction. We recently reported[14] that the diferrocenylacetylene cation (III) exhibits a low-energy transition not observed in the (2,3) and (3,3) compounds. This intervalence transfer transition and the "ferrocenium" transition in the visible have energies and intensities on the order of those observed for biferrocene (2,3) cations.[13] If the metal centers in mixed valence ions can interact solely through the π system of planar ligands, we might expect the bisacetylene bridged ferrocenophane cation [FDA (2,3), IV] to be a fully delocalized analogue of BFD (2,3). Herein we wish to report the results of electrochemical, ESR,



III



IV (FDA)



V

and electronic absorption studies which have bearing on this question.

Experimental Section

Materials. The neutral compounds, diferrocenylacetylene,[15] [2.2]ferrocenophane-1,13-diyne (FDA),[16] and 1,4-diferrocenylbutadiyne,[17] were synthesized by literature procedures. The preparations of the biferrocene (2,3) cation[6] and the BFD (2,3) cation[7,8] have been described. Ferrocenylacetylene was purchased from Wind River Chemicals. Spectrograde CH$_2$Cl$_2$ (Burdick and Jackson) was dried by passage through an alumina column (Woelm, activity I Basic), purged with argon, and stored in a sealed siphon bottle until used. The electrolyte, n-Bu$_4$NBF$_4$, was prepared[18] from n-Bu$_4$NHSO$_4$ (Aldrich) and vacuum dried.

Electrochemistry. Cyclic voltammograms were obtained using a PAR 175 Universal Programmer and a PAR 173 potentiostat combined with a standard three-electrode configuration. The working electrode, a platinum button (Beckman), and the reference, a saturated calomel electrode, were connected via a salt bridge containing n-Bu$_4$NBF$_4$ (0.2 M) in CH$_2$Cl$_2$. All electrochemical experiments were performed under argon. The current function, $[i_p/(V^{1/2}C)]$,[19] was constant over a wide range of sweep rates (25–300 mV/s), and a 1:1 relationship of the anodic and cathodic peak currents was observed. Together, these indicate the electrochemical reversibility of the couples. The half-wave potentials given in Table I were calculated from peak potentials.[19]

In preparative runs, 0.05 mmol of substrate was oxidized on a platinum basket in a cell holding 50–100 ml of solvent (0.1 M inelectrolyte). Owing to the sparing solubility of neutral FDA, solutions of its cations were generated by controlled potential oxidation. The greater solubility of diferrocenylacetylene and diferrocenylbutadiyne permitted preparation of the cations by constant current oxidation. Samples for absorption spectra were transferred from the electrolysis cell through 2-mm Teflon tubing to a 1-cm quartz flow cell which was thoroughly rinsed with the electrolysis solution and then sealed by pinching the Teflon tubing. Visible and near-infrared spectra were recorded on a Cary 14 spectrophotometer within 15 min of sample preparation.

The FDA dication can be generated in CH$_2$Cl$_2$, but it is only slightly soluble. Attempts to record its spectrum in CH$_2$Cl$_2$/CH$_3$CN mixtures were unsuccessful owing to rapid decomposition to the monocation.

ESR. Samples for ESR measurements were transferred from the electrolysis cell to thin-walled Pyrex tubes. The solutions were degassed on a vacuum line by ten freeze–thaw cycles and sealed off. ESR spectra were recorded on a Varian E-12 spectrometer with 100-kHz modulation. The field was standardized by use of diphenyl picrylhydrazil at two different microwave frequencies.

Results and Discussion

Electrochemistry. Polyferrocenes and ferrocenophanes, like ferrocene itself, generally undergo reversible one-electron oxidations with the number of waves being determined by the number of ferrocenyl units.[20,21] The half-wave potentials of the redox processes and the separation between consecutive waves vary over a wide range depending on the nature of the compound. The half-wave potentials for formation of I–V as determined by cyclic voltammetry in CH$_2$Cl$_2$ containing n-Bu$_4$NBF$_4$ are given in Table I. The neutral compounds are reasonably soluble in this solvent/electrolyte system and the electrochemically generated mono- and dications are relatively stable.

The neutral compounds corresponding to I–V all undergo two successive reversible one-electron oxidations to yield the mono- and dications, respectively (eq 1)

$$\mathrm{Fc{-}X{-}Fc} \overset{-e}{\rightleftarrows} [\mathrm{Fc{-}X{-}Fc}]^{+} \overset{-e}{\rightleftarrows} [\mathrm{Fc{-}X{-}Fc}]^{2+} \tag{1}$$

(where Fc represents a ferrocenyl unit and X can be one or more bridging groups). Biferrocene, BFD, and FDA exhibit well-resolved one-electron waves. Diferrocenylacetylene and diferrocenylbutadiyne, however, owing to a relatively small difference ($\Delta E_{1/2}$) between the first and second half-wave potentials, show cyclic voltammograms characteristic of superimposed one-electron waves.[22] There is sufficient resolution in Fc—C≡C—Fc to assign peak potentials. For Fc(—C≡C—)$_2$Fc, these values are estimated, since only an inflection in the wave can be detected. That the butadiyne undergoes two one-electron processes, rather than a two-electron oxidation, is demonstrated by the difference in peak potentials (140 mV) of the oxidative and reductive peaks. For a two-electron oxidation, a difference of 30 mV is expected.[19]

Table I. Half-Wave Potentials[a] in CH$_2$Cl$_2$[b]

Compd	$E_{1/2}(1)^c$	$E_{1/2}(2)^c$	$\Delta E_{1/2}{}^d$
Fc—C≡C—Fc	0.625	0.755	0.130
FDA	0.620	0.975	0.355
Fc(—C≡C—)$_2$Fc	~0.58	~0.68	~0.10
Biferrocene	0.435	0.785	0.350
BFD	0.265	0.855	0.590

[a] Calculated from peak potentials. [b] Containing n-Bu$_4$NBF$_4$ (0.2 M). [c] Volts vs. SCE at 100 mV/s (platinum disk electrode). [d] $\Delta E_{1/2} = E_{1/2}(2) - E_{1/2}(1)$.

The monocations III–V were generated from the neutral compounds by passage of precisely 1 F/mol. Exhaustive coulometric oxidation resulted in consumption of 2 F/mol and yielded the dications. Voltammetric and polarographic analyses of the resulting solutions indicated a current yield of 100%. Solutions of the monocations were stable for several days when protected from air and moisture. The dications, however, reverted to the monocations within a few hours.

Owing to the small difference between the first and second half-wave potentials of diferrocenylacetylene and diferrocenylbutadiyne, discrete solutions of the monocations III and V do not exist. An equilibrium mixture of three species is formed, as in eq 2:

$$2(2,3)^{+} \rightleftarrows (2,2) + (3,3)^{2+} \tag{2}$$

When a solution of diferrocenylacetylene is oxidized by 1 F/mol, it is calculated, by use of the Nernst equation, that 90% of the species in the equilibrium mixture are the (2,3) monocations. For the butadiyne, with an estimated difference in half-wave potentials of 100 mV, only 70% of the species are the monocations V. This will probably preclude the isolation of the pure monocationic salts III and V, but their spectral properties can still be analyzed when the above ratios are taken into account.

A mixed valence compound can be characterized by an interaction parameter (α), which is proportional to the intensity of the intervalence transfer transitions, and reflects the extent of delocalization between iron centers in the ground state. Another measure of the degree of interaction between the halves of a biferrocene-type compound is $\Delta E_{1/2}$, the difference in half-wave potentials (Table I). It is tempting to try to correlate these parameters. Within a small series of structurally similar compounds, such as the acetylenes (III, V), such a correlation may be useful (vide infra). For the accumulated data on mixed valence biferrocenes with gross structural differences, however, no clear-cut interrelation between the magnitude of $\Delta E_{1/2}$ and the presence or absence of a low-energy band is substantiated. This can be seen from the following examples.

No intervalence transfer transitions have been observed in the near infrared for mixed valence biferrocenes bridged by sp^3 carbons. Such compounds are characterized by small $\Delta E_{1/2}$ values (0.17 V for -CH$_2$- and 0.0 V for -CH$_2$CH$_2$-).[23] For selenium bridged biferrocenes, however, substantially larger potential differences are observed (0.22 V for -Se- and 0.14 V for -SeSe-), but again no low-energy transitions are found in the monocations.[24] The acetylene bridged cations III and

Table II. ***g* Values for Mixed Valence Biferrocenyl Cations**

Registry no.	Compd	Solvent	Temp, K	g_1	g_2	g_3
59187-96-1	FDA (2,3) BF_4	CH_2Cl_2[a]	77	1.88	1.98	2.57
39333-81-8	BFD (2,3) BF_4[b]	EtOH/ CH_2Cl_2	160	1.87	2.00	2.27
				$g_\perp$	$g_\parallel$	
	FDA (2,3) BF_4	Solid[a]	77	1.94	2.70	
11108-35-3	Biferrocene (2,3) picrate[c]	Acetone	77	1.85	3.53	

[a] Containing n-Bu_4NBF_4. [b] Reference 2. [c] Reference 11.

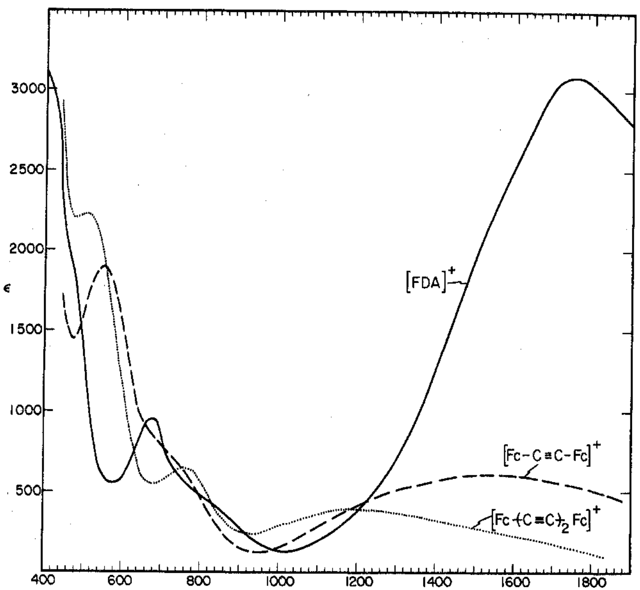


Figure 1. Visible and near-infrared spectra of the FDA monocation (IV) (—), the diferrocenylacetylene monocation (III) (- - -), and the diferrocenylbutadiyne cation (V) (· · ·) in CH_2Cl_2 containing 0.1 M n-Bu_4NBF_4.

V, on the other hand, have rather intense intervalence transfer bands and small $\Delta E_{1/2}$ values.

One trend that has been noted previously[21,23] is the increase in $\Delta E_{1/2}$ in doubly bridged ferrocenophanes as compared to the singly bridged derivatives. The size of $\Delta E_{1/2}$ approximately doubles when biferrocene is compared to BFD, diferrocenylacetylene to FDA, and diferrocenylmethane to [1.1]-ferrocenophane.[21] The exact cause of this increase in half-wave separation is unclear and may be due to elusive factors such as solvation energies, molecular size, and geometry, as well as orbital overlap between the two halves of the ferrocene molecule. At the present state of investigation, we find that intervalence transfer transitions occur only in biferrocenes that are directly fused or bridged by π-unsaturated groups, and occur regardless of $\Delta E_{1/2}$ values.

ESR. ESR spectra of ferrocenium ions have been interpreted in terms of an axial g tensor.[25] The spectra are characterized by large anisotropies and fast relaxation; the signals are detectable only at very low temperatures. The spectrum of mixed valence biferrocene (2,3) picrate showed similar features and was analyzed as a slightly perturbed ferrocenium ion.[11]

The spectrum of the BFD (2,3) ion, however, is quite different. The solid triiodide salt was found to have a rhombic g tensor and a relatively small anisotropy.[23] Furthermore, well-resolved spectra of the fluoroborate and picrate salts in glasses were obtained at temperatures higher than those suitable for substituted ferrocenium ions.[2] Exchange narrowing[23] and/or lower effective symmetry could give rise to the observed narrow lines.

The ESR spectrum of the FDA (2,3) cation has been measured in a methylene chloride glass at 77 K. Having a rhombic g tensor, and sharp lines, it bears strong resemblance to that of the BFD cation.[2] The g values are listed in Table II. The resolution of the glass spectrum is affected by trace amounts of oxygen, but reproducible results were obtained by careful degassing. Interestingly, the spectrum of solid FDA (2,3) BF_4 diluted in n-Bu_4NBF_4 (prepared by the evaporation of solvent from the electrolysis solution) shows axial symmetry, indicating that the solid may not be magnetically dilute.

Two different types of mixed valence biferrocenes have been distinguished by their magnetic properties: the weakly interacting biferrocene (2,3) cation, and the delocalized BFD (2,3) ion. Magnetically, the FDA (2,3) ion resembles the latter, which strongly suggests that FDA (2,3) should also be treated as a fully delocalized system. ESCA and Mossbauer experiments are necessary to verify this conclusion. It is, however, in accordance with the spectral similarities of the two compounds, as discussed below.

An attempt was made to obtain an ESR spectrum of the diferrocenylacetylene cation (III) under the experimental conditions described above. Only a very weak signal centered around $g = 2.00$ could be detected. We anticipated difficulty in obtaining the spectrum in light of the electrochemical results. The equilibrium mixture contains the dication which, if strongly paramagnetic, could affect the resolution drastically. No attempt was made to obtain the spectrum of V.

Visible and Near-Infrared Absorption Spectra. The monocations I–V have low-energy transitions in the near infrared that are not found in their (2,2) and (3,3) derivatives. In addition, transitions in the visible are observed, similar to that found at 600 nm for the ferrocenium ion.[26,27] The visible and near-infrared spectra of cations III–V are shown in Figure 1. Table III lists the absorption maxima and intensities of the visible and near-infrared bands for several mono- and dicationic biferrocenes.

The 1800-nm band in biferrocene (2,3) has been assigned to an intervalence transfer transition[1] by which a vibrationally excited valence isomer is formed:

$$[\mathrm{Fe(II)\text{-}Fe(III)}] \xrightarrow{h\nu} [\mathrm{Fe(III)\text{-}Fe(II)}]^* \qquad (3)$$

A simple model for intervalence transfer transitions has been proposed by Hush.[3] The usefulness of this model in interpreting the results in a series of substituted biferrocenyl cations has been demonstrated.[13] The spectral results of the singly bridged acetylene cations III and V also appear to be consistent with this model.

In substituted biferrocenyl cations, the intensity of intervalence transfer transitions was shown to be dependent upon the overlap of π orbitals in the fulvalene ligand.[13] Mayoh and Day[29] have shown that in the absence of direct metal–metal overlap, the metal centers in mixed valence compounds can interact via ligand π and π^* orbitals. We might expect this mode of interaction to predominate in acetylene bridged biferrocene cations, owing to the large iron–iron distances. The intensities of the near-infrared bands in III and V are on the order of those observed for substituted biferrocenes. This gives some indication that similar processes of valence transfer might be involved in both the directly fused and acetylene bridged biferrocene cations.

In comparing the quantitative features of the near-infrared bands of I, III, and V, we find that the intensity decreases as the distance between the metal centers increases. Since the bandwidths are greater in both III and V (about 5000 cm^{-1})

Table III. Spectral Data

Registry no.	Compd	Solvent	λ_{max}, nm (ϵ)[a] Monocations	Dications
12098-14-5	Fc—C≡C—Fc	CH_2Cl_2[b]	545 (2100),[c] 720 (s), 1560 (670)[c]	500 (s), 720 (1000)
1273-18-3	Fc(—C≡C—)$_2$Fc	CH_2Cl_2[b]	510 (2220), 760 (670), 1180 (570)[c]	580 (s), 760 (1260)
59187-97-2	FDA	CH_2Cl_2[b]	670 (960), 840 (s), 1760 (3100)	
1287-38-3	Biferrocene[d]	CH_3CN[e]	545 (2160), 680 (s), 1800 (750)	480 (920), 660 (1000)
11105-90-1	BFD[f]	CH_3CN	600 (370), 1550 (2100)	465 (2755)
1271-47-2	FcC≡CH	CH_2Cl_2[b]	480 (s), 565 (300), 700 (310)	

[a] Reproducible within 5%. s = shoulder. [b] Containing n-Bu_4NBF_4 (0.1 M). [c] The experimentally determined ϵ has been corrected for % monocation in the equilibrium mixture (see electrochemistry discussion). [d] Reference 13. [e] Containing Et_4NClO_4 (0.1 M). [f] References 8 and 28.

than in I (about 3200 cm^{-1}), however, the oscillator strengths for the near-infrared transitions of all three are comparable. The interaction parameter can be estimated by eq 4

$$\alpha^2 \cong \frac{4.6 \times 10^{-9}\, \epsilon_{max}\Delta_{1/2}}{\bar{\nu} r^2} \qquad (4)$$

where ϵ_{max} is the molar absorptivity, $\Delta_{1/2}$ is the band width in cm^{-1}, $\bar{\nu}$ is the frequency in cm^{-1}, and r is the donor–acceptor distance. The interaction parameter, therefore, is largest in the biferrocene cation and decreases with greater donor–acceptor distance.[1]

Intuitively, we expect electronic and inductive effects to diminish as the distance between metal centers increases. For compounds I, III, and V, this is reflected in the cyclic voltammetric results. As the iron–iron distance increases, $\Delta E_{1/2}$, the separation in half-wave potentials, decreases. For this small series of mixed valence biferrocenes there appears to be a correlation between α and $\Delta E_{1/2}$.

The energy of the near-infrared band increases in going from the biferrocene cation (I) to the acetylene (III) to the butadiyne (V). Shifts to higher energy comparable to that of the butadiyne have been observed in the biferrocene series, but only for unsymmetrically substituted compounds.[30] According to the Hush model,[3] the energy (E_{op}) of the Frank–Condon transition for a one-electron transfer in a symmetrical compound is four times that needed to form a symmetrical transition state in the corresponding thermal exchange process (E_{th}). In principle, E_{th} can be calculated in terms of metal–ligand force constants and the difference in metal–ring bond lengths and stretching frequencies in the ferrocene and ferrocenium portions of the molecule. Within a series of biferrocenyl cations, the relative size of E_{th} (and the corresponding energy of the intervalence transfer band) gives a measure of the structural similarity between the ferrocene and ferrocenium halves of the mixed valence ion. In compounds I, III, and V, more reorganizational energy is required for electron transfer as the iron–iron distance increases.[31] From the data on the frequency and intensity of the near-infrared bands, it follows that less reorganizational energy is needed in the electron transfer process as the amount of delocalization in the ground state increases.

The opposite effect of frequency and intensity as a function of metal–metal distance is noted in the spectra of the mixed valence ferrocenophanes II and IV. The FDA ion has a near-infrared band at lower energy and higher intensity than the BFD ion. The ESR and electrochemical results suggest that FDA (2,3) may be a fully delocalized analogue of the BFD cation. If so, the results for neither ion can be interpreted in terms of the Hush model, for which a prerequisite of weak interaction prevails.

The similarity found in the ESR spectra of the FDA and BFD ions is corroborated by the qualitative features of their electronic spectra. Most conspicuous are the greater intensities of the near-infrared bands and lower intensities of the visible bands of the ferrocenophanes as compared to their singly fused derivatives. There is, however, one important difference. When the near-infrared spectrum of the BFD ion is plotted in the linear frequency representation, its resolution into two bands is apparent.[8] The combined bandwidth is roughly 4800 cm^{-1}. Two bands are not observed for the FDA ion in a similar representation. Owing to solvent absorption, however, extinction coefficients in the 1680–1780-nm region must be interpolated, and so the exact shape of the curve could not be determined. The band for FDA (2,3) is narrower; a bandwidth of 2800 cm^{-1} is estimated.

The 600-nm band of the ferrocenium ion has been assigned to the $^2E_{2g} \rightarrow {}^2E_{2u}$ ligand-to-metal transition.[26,27,32] This assignment was based, in part, on the effect of ring substituents on the energy of the band. Inductively, an acetylene group is electron withdrawing. This is reflected in the half-wave potential of ferrocenylacetylene (FcC≡CH) which is some 180 mV higher than that of ferrocene in methylene chloride. A corresponding increase in energy of the "ferrocenium" transition is expected for acetylene substituted ions.

The situation, however, is somewhat more complicated. At least three bands are observed in the visible spectrum of the ferrocenylacetylene cation. These bands may result from separate ligand to metal transitions from the substituted and unsubstituted cyclopentadienyl rings. A similar suggestion was made for substituted biferrocenyl cations.[13]

In the visible spectra of the mixed valence acetylenes III–V, at least two bands are observed. Since we expect weak iron–iron interactions in ions III and V, we assume that these bands are due to typical transitions of substituted ferrocenium ions as found for other substituted biferrocene monocations. The spectra of the dications of III and V show features similar to those of the biferrocene dication.[13]

If the FDA monocation is a fully delocalized system, we would not expect to see transitions due to either of the constituent halves. In the FDA ion (IV), as in the BFD ion, the visible transitions are of lower intensity and energy than those of the corresponding singly bridged cations.

Conclusions

It has previously been demonstrated[1] that the biferrocene cation is a class II mixed valence compound under the categories defined by Day.[4] On the basis of the electrochemical results and the visible and near-infrared absorption spectra, the singly bridged acetylene cations III and V also appear to be members of this class. The spectral data on the near-infrared bands can be interpreted in terms of the Hush model for intervalence transfer transitions.

It has also been shown[2] that BFD (2,3) has properties that are quite different from biferrocene (2,3), and ion II may, in fact, be a class III mixed valence compound. The electrochemistry, ESR, and electronic absorption spectra of FDA

(2,3) closely resemble those of BFD (2,3). Based on these observations, we conclude that the π-bridged FDA (2,3) ion is a fully delocalized analogue of BFD (2,3). The question remains as to why BFD (2,3) is a delocalized ion while biferrocene (2,3) is not. Two possible contributing factors in the case of BFD have been cited: the proximity of the iron atoms and the fused π-ligand system. This study shows the importance of the latter.

Acknowledgment. The authors wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Advanced Research Projects Agency for grant support of this research.

References and Notes

(1) D. O. Cowan, C. LeVanda, J. Park, and F. Kaufman, *Acc. Chem. Res.*, **6**, 1 (1973).
(2) C. LeVanda, D. O. Cowan, K. Bechgaard, U. T. Mueller-Westerhoff, P. Eilbracht, G. A. Candela, and R. L. Collins, *J. Am. Chem. Soc.*, **98**, 3181 (1976).
(3) N. S. Hush, *Prog. Inorg. Chem.*, **8**, 391 (1967).
(4) M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, **10**, 247 (1967).
(5) The notation (2,3) is used for the mixed valence monocations. Similarly, (2,2) and (3,3) refer to the neutral molecule and dication, respectively.
(6) F. Kaufman and D. O. Cowan, *J. Am. Chem. Soc.*, **92**, 6198 (1970).
(7) D. O. Cowan and C. LeVanda, *J. Am. Chem. Soc.*, **94**, 9271 (1972).
(8) U. T. Mueller-Westerhoff and P. Eilbracht, *J. Am. Chem. Soc.*, **94**, 9272 (1972).
(9) D. O. Cowan, R. L. Collins, and F. Kaufman, *J. Phys. Chem.*, **75**, 2026 (1971).
(10) D. O. Cowan, J. Park, M. Barber, and P. Swift, *Chem. Commun.*, 1444 (1971).
(11) D. O. Cowan, G. A. Candela, and F. Kaufman, *J. Am. Chem. Soc.*, **93**, 3889 (1971).
(12) D. O. Cowan, C. LeVanda, R. L. Collins, G. A. Candela, U. T. Mueller-Westerhoff, and P. Eilbracht, *J. Chem. Soc., Chem. Commun.*, 329 (1973).
(13) C. LeVanda, D. O. Cowan, and K. Bechgaard, *J. Am. Chem. Soc.*, in press.
(14) C. LeVanda, D. O. Cowan, C. Leitch, and K. Bechgaard, *J. Am. Chem. Soc.*, **96**, 6788 (1974).
(15) M. Rosenblum, N. Brawn, J. Papenmeier, and M. Applebaum, *J. Organomet. Chem.*, **6**, 173 (1966).
(16) M. Rosenblum, N. M. Brawn, D. Ciappenelli, and J. Tancrede, *J. Organomet. Chem.*, **24**, 469 (1970).
(17) K. Schlogl and H. Egger, *Monatsh. Chem.*, **94**, 376 (1963).
(18) V. D. Parker, unpublished results.
(19) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).
(20) G. M. Brown, T. J. Meyer, D. O. Cowan, C. LeVanda, F. Kaufman, P. V. Roling, and M. D. Rausch, *Inorg. Chem.*, **14**, 507 (1975).
(21) J. E. Gorton, H. L. Lentzner, and W. E. Watts, *Tetrahedron*, **27**, 4353 (1971).
(22) (a) F. Ammar and J. M. Saveant, *J. Electroanal. Chem. Interfacial Electrochem.*, **47**, 215 (1973); (b) D. S. Polcyn and I. Shain, *Anal. Chem.*, **38**, 370 (1966).
(23) W. H. Morrison, Jr., S. Krogsrud, and D. N. Hendrickson, *Inorg. Chem.*, **12**, 1998 (1973).
(24) D. O. Cowan, P. Shu, and K. Bechgaard, unpublished results.
(25) R. Prins, *Mol. Phys.*, **19**, 603 (1970).
(26) R. Prins, *Chem. Commun.*, 280 (1970).
(27) Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *J. Am. Chem. Soc.*, **93**, 3603 (1971).
(28) U. T. Mueller-Westerhoff and P. Eilbracht, *Tetrahedron Lett.*, 1855 (1973).
(29) (a) B. Mayoh and P. Day, *Inorg. Chem.*, **13**, 2273 (1974); (b) B. Mayoh and P. Day, *J. Chem. Soc., Dalton Trans.*, 846 (1974).
(30) C. LeVanda, D. O. Cowan, K. Bechgaard, and M. D. Rausch, to be submitted for publication.
(31) Results in diruthenium ammine complexes show a similar dependence of band energy and intensity as a function of metal–metal distance: R. W. Callahan, G. M. Brown, and T. J. Meyer, *J. Am. Chem. Soc.*, **96**, 7829 (1974).
(32) In ref 14, an incorrect assignment was inadvertently written.

Halogen–Metal Exchange in Esters of Haloaryl Acids[1]

William E. Parham* and Lawrence D. Jones

Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706

Received January 21, 1976

n-Butyllithium reacts selectively at −100 °C in THF–hexane with *tert*-butyl *p*-bromobenzoate by halogen–metal exchange; the resulting *tert*-butyl *p*-lithiobenzoate is stable at −100 °C and can be elaborated in high yield to give para-substituted *tert*-butylbenzoates by reactions with electrophiles. The less hindered isopropyl esters are not stable to aryllithium at −100 °C unless further hindered by ortho substitution.

Considerable progress has been made recently in developing improved procedures for the elaboration of aromatic acids utilizing derived aryllithium reagents. The method of Meyers[2] involving direct ortho metalation of oxazolines derived from aromatic acids would appear to be the method of choice for symmetrically substituted 2-aryloxazolines, since the ortho-substituted aryl halide corresponding to the position of lithiation is not a required intermediate as in halogen–metal exchange reactions. The alternative procedure,[3a] developed in our laboratory, involving direct halogen–metal exchange of the lithium salts of bromoarylcarboxylic acids at very low temperature (−100 °C) affords good yields of elaborated acids, subsequent to reaction with E^+. In addition, the process is positionally selective at the site occupied by bromine in the starting acid and is applicable to *o*-, *m*-, or *p*-bromobenzoic acids, as is the complementary procedure employing oxazolines to mask carboxyl functions to Grignard reagents.[4]

It has been shown that stable aryllithium reagents can be prepared at −100 °C with a variety of aryl bromides containing reactive functional groups (COO^-,[3] CN,[5] CH_2Cl,[6] CH_2CH_2Br,[6] *o*-NO_2[7]); however, similar reactions[8] with aryl halides containing methyl ester functions are of limited synthetic utility since the derived aryllithium reagents either self-condense or react with unchanged bromoaryl ester at low temperature (−78 → −100 °C) to give high yields of methyl benzoylbenzoates. In order to further define the limitations for synthetic reactions of aryllithium reagents containing ester functions, we have examined, as model compounds, halogen–metal exchange with *tert*-butyl *p*-bromobenzoate, isopropyl p-bromobenzoate, and isopropyl *o*-bromobenzoate. In all cases, progress of halogen–metal exchange was followed by quenching aliquots with water and determining (by NMR, GLC, and isolation of products) the ratio of starting bromoaryl ester to ester derived by replacing bromine with hydrogen.

While reaction of *tert*-butyl *p*-bromobenzoate (**1a**)[9] with *n*-propyllithium in ether at −40 °C is reported to involve preferential addition of alkyllithium to the ester function, the reaction of **1a** with *n*-butyllithium in THF–hexane at −100 °C involves selective halogen–metal exchange to give only **2a.** Reaction was complete after 5 min at −100 °C, and good yields (isolated) of elaborated aryl esters were obtained by reaction of **2a** with suitable electrophiles as shown in Scheme I.