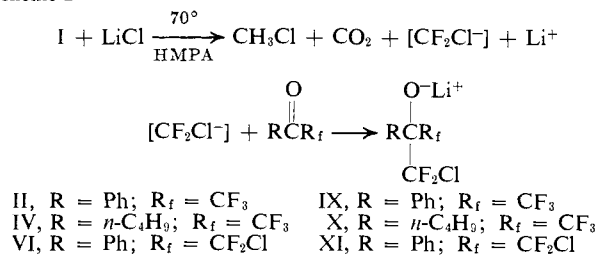
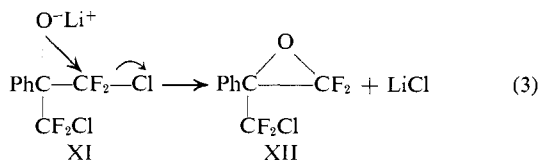


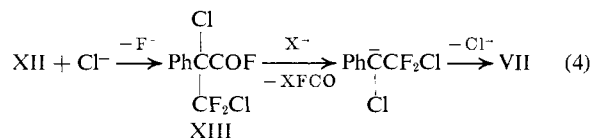
## Scheme I



XII, while IX and X are stable toward this intramolecular displacement and do not give oxiranes. In each case, protonation of the alcoholates IX, X, and XI upon steam distillation yields the corresponding alcohols. XII, in the presence of chloride ion, undergoes ring opening to form acid fluoride XIII which decomposes in

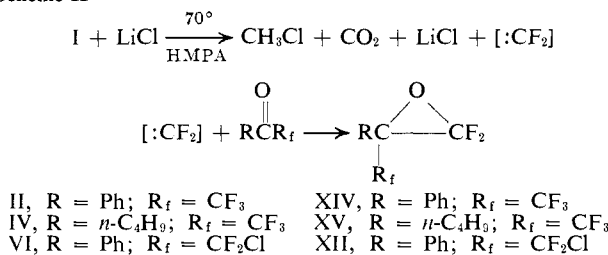


the presence of either chloride or fluoride ion<sup>14</sup> to yield the final product VII *via* displacement of chloride ion.



An alternate mechanism is the concerted decomposition of I to yield not the chlorodifluoromethide ion but difluorocarbene and chloride ion. Difluorocarbene then inserts into the carbon-oxygen double bond of the ketone to yield an oxirane directly (Scheme II). In

## Scheme II



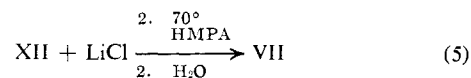
order to account for the observed products in eq 1 and 2, chloride ion must attack only at the difluoromethylene carbon of oxiranes XIV and XV to give alcoholates IX and X, but, in the case of oxirane XII, attack of chloride must occur at both the difluoromethylene carbon to give alcoholate XI and the benzylic carbon to give acid fluoride XIII.<sup>15</sup>

(14) Treatment of either XII or XIII with lithium chloride in HMPA gave a gas, which upon passage through methanol gave dimethylcarbonate (identified by glpc retention time). These observations were taken as evidence for the decomposition of XIII to the carbanion shown in eq 4 and either carbonyl fluoride (F<sub>2</sub>C=O) or carbonyl chlorofluoride (ClFC=O).

(15) Although a referee has suggested that the failure of alcohols III and V to form oxiranes under conditions in which VIII gives XII makes comparative predictions of the ring opening of XIV, XV, and XII somewhat tenuous, we believe it unlikely that such structurally similar oxiranes would exhibit such different ring opening behavior. However, additional experiments are required to settle this point unambiguously.

Preparation of alcohols III, V, and VIII was independently undertaken.<sup>16</sup> Subsequent treatment of these alcohols with aqueous potassium hydroxide resulted in oxirane formation only in the case of alcohol VIII, however.<sup>17</sup>

Ring-opening of XII by chloride ion under the same conditions as in eq 2 resulted in 95% glpc yield (46% isolated yield) of olefin VII. Alcohol VIII was not observed. Treatment of XII with lithium chloride at 0-10° resulted in formation of acid fluoride XIII in 68% glpc yield and VII in 30% glpc yield. XIII was then treated with lithium chloride in HMPA at 70° to give VII in quantitative yield.



The above observations are consistent with the mechanism depicted in Scheme I, involving chlorodifluoromethide ion formation and its subsequent attack at the carbonyl carbon atom. While the stabilities of alcoholates IX and X toward the intramolecular SN2 displacement reaction are not fully understood, the facts that (1) alcohol VIII is not formed by chloride ion ring-opening of XII and (2) no products derived from similar chloride ion ring opening of oxiranes XIV and XV were observed (eq 1) indicate that the reaction does not proceed *via* initial oxirane formation by insertion of difluorocarbene into the carbon-oxygen double bond of the ketones (Scheme II). This is believed to be the first report of successful trapping of a halodifluoromethide ion other than by protonation. Additional studies are now underway to further substantiate the existence of halodifluoromethide ions as reactive intermediates in organic reactions.

(16) The alcohols were prepared by addition of phenyl- or *n*-butyllithium to 4 F K or 5 F K at -70° in diethyl ether, followed by acidification with 6 N hydrochloric acid. The alcohols were then isolated by extraction followed by distillation at reduced pressure.

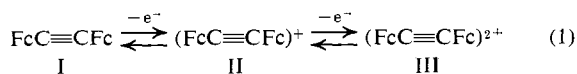
(17) This method has been used to prepare some polyfluorinated oxiranes including XII. See, for example, R. A. Bekker, G. V. Asratyan, B. L. Dyatkin, and I. L. Knunyants, *Dokl. Chem.*, **204**, 439 (1972).

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## Mixed-Valence Diferrocenylacetylene Cation

Sir:

We wish to report a new mixed-valence compound derived by one-electron oxidation of diferrocenylacetylene (eq 1) (where Fc = ferrocenyl). The resulting



mixed-valence compound (II) is unique in being the first example of a bridged biferrocene cation to exhibit an intervalence transfer transition in the near-infrared.<sup>1</sup>

The cyclic voltammogram of diferrocenylacetylene<sup>2</sup>

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

(2) Diferrocenylacetylene was prepared by the literature procedure: M. Rosenblum, N. Braun, J. Papenmeier, and M. Applebaum, *J. Organometal. Chem.*, **6**, 173 (1966). Ferrocenylacetylene was purchased from Wind River Chemicals.

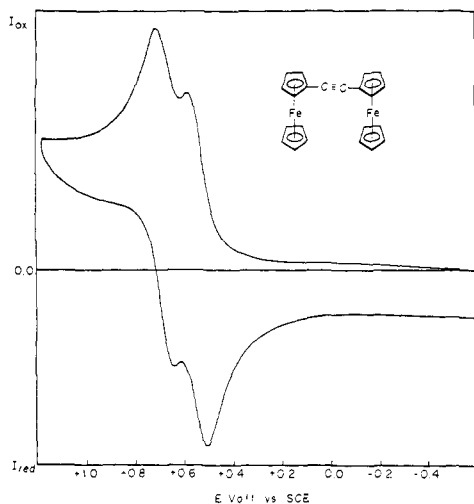
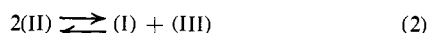


Figure 1. Cyclic voltammogram of differrocenylacetylene in  $\text{CH}_2\text{Cl}_2$  containing  $n\text{-Bu}_4\text{NBF}_4$  (0.2 M), sweep rate 200 mV/sec.

in methylene chloride is shown in Figure 1. In the anodic scan, two separate peaks are observed at 640 and 775 mV. Reduction peaks in the corresponding cathodic scan are found at 580 and 710 mV. The voltammogram is characteristic of a compound undergoing two reversible one-electron oxidations at close potentials, a feature which has been shown to be characteristic of weakly interacting bridged biferrocenes.<sup>3,4</sup>

Analysis of the voltammetric data (differences in peak potentials taken as representative of differences in redox potentials) indicates that a solution of II will disproportionate, as in eq 2. Approximately 90% of the



species in the equilibrium mixture at 25° are the mixed-valence monocations. This will probably preclude isolation of II, but the spectroscopic features can still be analyzed when the above ratios are taken into account.

To obtain absorption spectra of the cations of differrocenylacetylene,  $10^{-3}$  M solutions were generated electrochemically. Oxidation by precisely 1 F/mol yields a deep violet solution which was analyzed by polarography. Although separate waves are not obtained, the  $I_{\text{ox}}/I_{\text{red}}$  ratio was shown to be unity, indicating a current yield of 100%. Exhaustive coulometric oxidation resulted in the consumption of precisely 2 F/mol. Cyclic voltammetry and polarography clearly demonstrated the stability and identity of the resulting pale green dication (III). (Solutions are stable when protected from air and moisture.)

The visible-near-infrared spectra of differrocenylacetylene and its mono- and dications are shown in Figure 2. Absorptions in the visible at 545 nm ( $\epsilon$  2100) for the monocation and 720 nm ( $\epsilon$  1000)<sup>5</sup> for the dication are typical of ferrocenium ions and are assigned to the  ${}^2E_{2g} \rightarrow {}^2A_{1g}$  transition.<sup>6</sup> These bands are considerably shifted with respect to the unsubstituted ferrocenium ion ( $\lambda_{\text{max}}$  617 nm,  $\epsilon$  420).<sup>6</sup>

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

(4) W. H. Morrison, Jr., S. Krogsrud, and D. N. Hendrickson, *Inorg. Chem.*, **12**, 1998 (1973).

(5) The maximum at 545 nm in the spectrum of the dication is probably due to a small amount of monocationic impurity.

(6) R. Prins, *Chem. Commun.*, 280 (1970).

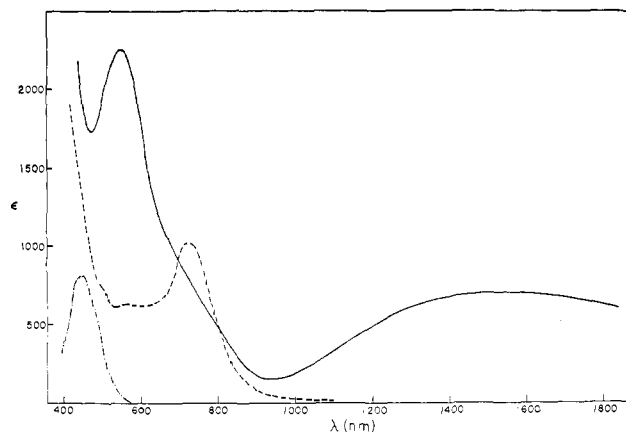
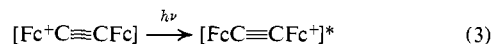


Figure 2. Visible and near-infrared spectra of differrocenylacetylene (---), the differrocenylacetylene monocation (—), and the differrocenylacetylene dication (- · -) in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M  $n\text{-Bu}_4\text{NBF}_4$ .

In addition, there is a broad band in the near-infrared spectrum of the mixed-valence monocation centered at 1560 nm ( $\epsilon$  670). This band is absent in both the neutral (I) and fully oxidized (III) species and is assigned to an intervalence transfer transition (eq 3).<sup>1,7</sup>



Intervalence transfer transitions in the near-infrared had previously been observed only in biferrocene-type molecules in which the ferrocene and ferrocenium portions are directly fused.<sup>1,8,9</sup> No corresponding low energy transitions have been observed for biferrocenes bridged by saturated groups.<sup>9-11</sup> The observation of a mixed-valence transition in the differrocenylacetylene monocation indicates that the intervalence electron transfer can occur exclusively through the ligand system, inasmuch as the iron-iron distance (estimated to be 6.5 Å in a cis conformation and 7.3 Å in a trans) is too large to involve direct metal-metal overlap.

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

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

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

(10) D. O. Cowan, P. Shu, and K. Bechgaard, unpublished results.

(11) W. H. Morrison, Jr., and D. N. Hendrickson, *Chem. Phys. Lett.*, **22**, 119 (1973).

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## Reactions of $\pi$ -2-Methallylnickel Bromide with Methylbenzoquinones. Evidence for Electron Transfer

Sir:

We recently reported the reaction between  $\pi$ -allylnickel bromide complexes and quinones to produce allylhydroquinones and speculated that it proceeded