are located off-center in their respective ferrocenylene moieties. Such a distorted configuration of the molecule might be attained in order to relieve the intramolecular repulsion of the nonbonding electrons of the iron atoms. An analogous dislocation of the iron atom with respect to the substituted ring has been postulated by Cais and co-workers[6] in the case of α-ferrocenyl carbonium ions to explain the upfield shift of the 2 and 5 protons relative to the 3 and 4 protons. In the case of the α-ferrocenyl carbonium ions, displacement of the iron atom toward the C-2 and C-5 atoms increases the electron density and resultant shielding of the 2 and 5 protons, while decreasing the electron density around the C-3 and C-4 atoms, resulting in a deshielding of the 3 and 4 protons. According to those authors, however, the main influence of the displaced iron atom on the nmr spectrum is to effect a greater induced field in the vicinity of the 2 and 5 protons. A similar increased electron density in the iron–carbon bond and greater induced field should also apply to structure III, but in this case to the 3, 4, 8, and 9 protons, which we tentatively assign to the upfield positions. The corresponding deshielding effect upon the 2, 5, 7, and 10 protons would cause their signal to appear in the observed downfield positions.

Alternate syntheses of I, including the coupling of 1′,6′-dihalobiferrocenyls,[7] as well as the results of studies of the metalation and electrophilic substitution of I, will be reported in forthcoming papers.

Acknowledgment. We are grateful to Dr. Daniel Dyer of the Materials Physics Division, Air Force Materials Laboratory, for carrying out the high-temperature nmr study.

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(7) R. F. Kovar, F. L. Hedberg, and H. Rosenberg, unpublished studies.

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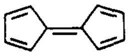
Organometallic π Complexes of Fulvalene[1,2]

Sir:

The cyclic unsaturated hydrocarbon fulvalene (bicyclopentadienylidene) (**1**) has been the subject of considerable theoretical and synthetic interest since 1949 when Brown[3,4] predicted the molecule to be a stable nonbenzenoid system. Since that time, a limited number of phenylated[5] and perhalogenated[6] fulvalenes have been described in the literature. Fulvalene itself has been detected only in dilute solutions, and the compound is apparently not sufficiently stable to permit isolation under normal conditions.[7,8]

Recent advances in organometallic chemistry have indicated that a variety of novel but "unstable" unsaturated cyclic hydrocarbons such as cyclobutadiene,[9] benzocyclobutadiene,[9] pentalene,[10] benzopentalene,[11] calicene,[12] sesquifulvalene,[12] etc., can be isolated as stable transition metal derivatives, and in certain instances[9] the latter can serve as a source of the parent unsaturated hydrocarbon. We now report the first two examples in which fulvalene (**1**) serves as the sole π ligand in an organotransition metal complex, *viz.*, (fulvalene)-hexacarbonyldimanganese (**2**) and bis(fulvalene)diiron (**3**).[13]



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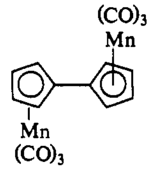
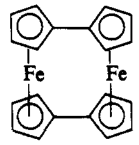


2



3

Initial attempts to extend the Ullmann biaryl reaction to iodocymantrene (**4**) were unsuccessful. A reaction between **4** and activated copper bronze[15] under nitrogen yielded only cymantrene, resulting from hydrogenation, as the product. When the procedure was modified using precipitated copper (zinc) powder,[16] however, **2** was obtained in 21% yield as air-stable yellow crystals, mp 142–143°. [*Anal.* Calcd for $C_{16}H_8Mn_2O_6$: C, 47.32; H, 1.99; Mn, 27.06; O, 23.64; mol wt, 406. Found: C, 47.24; H, 2.02; Mn, 27.23; O, 23.59; mol wt (osmometric in benzene) 403, (mass spectrometry) 406. The nmr spectrum of **2** in deuteriochloroform solution exhibited an A_2B_2 system, with two sets of apparent triplets centered at τ 5.04 and 5.26. These resonances are tentatively assigned to the four α protons and the four β protons, respectively. The infrared spectrum of **2** (KBr) exhibited strong absorptions at 2000 and 1925 cm^{-1} which may be assigned to terminal carbonyl stretching frequencies.

The mass spectrum of solid **2** was obtained at 60° and is

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(1) Organometallic π Complexes. XVII. For part XVI see M. D. Rausch and A. Siegel, *J. Org. Chem.*, **34**, 468 (1969).

(2) Presented in part at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 9–13, 1968, Abstracts, INOR-088.

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(6) (a) V. Mark, *Tetrahedron Letters*, 333 (1961); (b) A. E. Ginsburg, R. Paatz, and F. Korte, *ibid.*, 779 (1962); (c) P. T. Kwitowski and R. West, *J. Am. Chem. Soc.*, **88**, 4541 (1966); (d) R. West and P. T. Kwitowski, *ibid.*, **90**, 4697 (1968).

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(8) The topic of fulvalene chemistry has recently been reviewed: E. D. Bergmann, *Chem. Rev.*, **68**, 41 (1968).

(9) G. F. Emerson, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 131 (1965).

(10) T. J. Katz and M. Rosenberger, *ibid.*, **85**, 2030 (1963); T. J. Katz and J. Mrowca, *ibid.*, **89**, 1105 (1967).

(11) M. Cais, A. Modiano, and A. Raveh, *ibid.*, **87**, 5607 (1965).

(12) M. Cais and A. Eisenstadt, *ibid.*, **89**, 5468 (1967).

(13) These new complexes may likewise be named, according to currently adopted metallocene nomenclature, as bicymantrenyl[14] and 1,1′-biferrocenylene, respectively. Biferrocenyl[15] can also be regarded as a complex containing both fulvalene and π-cyclopentadienyl ligands, *i.e.*, fulvalenebis(π-cyclopentadienyliron).

(14) N. Tirosh, A. Modiano, and M. Cais, *J. Organometal. Chem.*, **5**, 357 (1966).

(15) M. D. Rausch, *J. Am. Chem. Soc.*, **82**, 2080 (1960); *J. Org. Chem.*, **26**, 1802 (1961).

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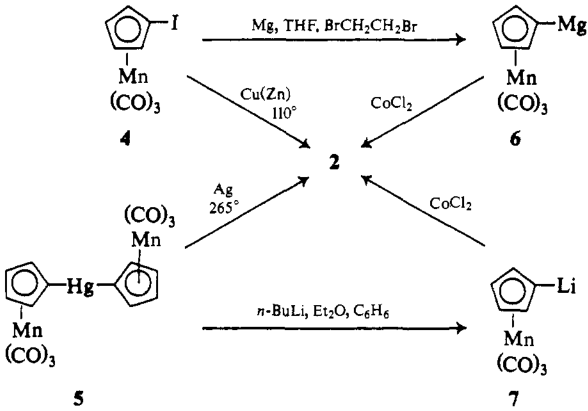
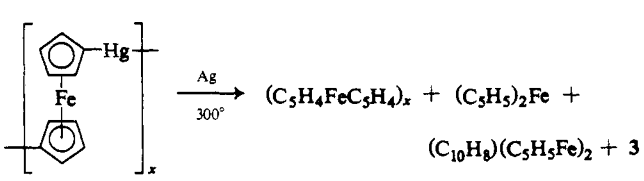
completely consistent with the proposed structure. In addition to the parent peak at *m/e* 406, other lines corresponding to successive loss of carbonyl groups are seen at *m/e* 322, 294, 266, and 238. The fulvalene–manganese bond appears to be quite stable, as no separation of the organic ligand occurs prior to loss of the carbonyl groups. Furthermore, the lines corresponding to $Mn_2(C_{10}H_8)^+$, $Mn(C_{10}H_8)^+$, and $Mn_2(C_{10}H_8)^{2+}$ all have significant intensities. In fact, $Mn_2(C_{10}H_8)^+$ exhibits the most intense line in the spectrum, exclusive of Mn^+ and CO^+. Also of interest is the fact that the fulvalene system may be released from manganese without structural rearrangement, since an ion with *m/e* 128 is observable. By comparison, the cyclopentadienyl ring does not appear to be released from manganese without fragmentation.[17]

Several other routes to **2** are also available. Thus, the pyrolysis of dicymantrenylmercury (**5**) in the presence of powdered silver at 265° for 15 hr resulted in the formation of **2** in 67% yield. The reaction of either cymantrenylmagnesium iodide (**6**) or cymantrenyllithium (**7**) with cobalt(II) chloride afforded **2** in yields of 15 and 13%, respectively. Incidentally, **6** and **7** represent the only known organometallic derivatives of cymantrene other than mercury reagents such as **5**, and their formation and reactions should prove to be very useful in developing the chemistry of cymantrene.[18] The various routes leading to the fulvalene complex **2** are summarized below.



As reported earlier by one of us,[19] the pyrolysis of polymercuriferrocenylene (**8**) produces polyferrocenylene, together with small amounts of ferrocene, biferrocenyl, and an orange-red crystalline product which analyzed for $(C_{10}H_8Fe)_x$ but which was not further identified at that time. Molecular weight determinations on the latter substance were not successful, owing to its extremely limited solubility in organic solvents. A reinvestigation of this product by means of mass spectrometry has now clearly established its structure as the bis(fulvalene) complex **3**.[19a]



8

The very limited solubility of **3** in organic solvents and the unusually high thermal stability of this substance (mp >375°) are remarkable in view of the corresponding properties of biferrocenyl.[15] Hedberg and Rosenberg, who have independently isolated **3** from the reaction of 1,1′-diiodoferrocene and copper powder in butylferrocene,[20] have noted similar physical properties for **3**. Indeed, it was a consideration of the solubility properties of **3** as first observed and communicated to us by these workers which prompted our reinvestigation of the orange-red product from the polymercuriferrocenylene pyrolysis reaction. By means of more extensive extraction of the pyrolysate from the latter reaction, we have been able to increase the yield of **3** from *ca.* 2 to 8%, based on **8**.

The mass spectrum of solid **3** was obtained at 240–280°; the solid sublimed completely under these conditions and left no detectable residue. The above-mentioned thermodynamic stability of **3** is further manifested in the nature of the ions formed upon electron bombardment, as the most intense line in the mass spectrum, besides that of Fe^+, corresponds to the parent $^{56}Fe_2(C_{10}H_8)_2{}^+$. A similar observation with ferrocene was noted some time ago.[21] Even $^{56}Fe_2(C_{10}H_8)_2{}^{2+}$ is a fairly abundant ion. One of the most intense lines in the spectrum of **3** is that at *m/e* 128 and may correspond to the fulvalene cation. Otherwise, the spectrum of **3** is quite complicated and will be discussed in detail in a future publication.

Ring substitution reactions of both **2** and **3** are of considerable interest, since they should permit a comparison of the relative reactivities of these new fulvalene complexes with their well-known π-cyclopentadienyl analogs, cymantrene and ferrocene. Initial studies indicate that **2** is readily converted to a 3-acetyl derivative upon treatment with acetyl chloride and aluminum chloride in dichloromethane solution, and that **3** undergoes Friedel–Crafts benzoylation to form a mixture of benzoylated derivatives in an analogous manner. These reactions are of additional interest in that the products may conceivably serve as important intermediates in the synthesis of a variety of new substituted fulvalenes. We are currently investigating additional ring substitution reactions of **2** and **3**, the conversion of **2** and **3** to other transition metal complexes of fulvalene, and the potential generation of fulvalenes from their transition metal derivatives.

Acknowledgments. The authors wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant in support of this research, and the National Science Foundation for funds used to purchase the mass spectrometer used in the study. We are also indebted to Mr. Charles Meade of the University of Massachusetts Microanalytical Laboratory for the determination of oxygen in **2**, to Mr. John Conville

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(17) R. E. Winters and R. W. Kiser, *J. Organometal. Chem.*, **4**, 190 (1965).

(18) For example, carbonation of **6** and **7** gives the expected product, cymantrenoic acid, $(\pi\text{-}C_5H_4COOH)(CO)_3Mn$, in yields of 31–33 and 32–37%, respectively (R. F. Kovar and M. D. Rausch, unpublished studies).

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

(19a) NOTE ADDED IN PROOF. An X-ray crystallographic study of **3** has been completed and is in complete agreement with the "double sandwich" structure indicated. The two five-membered ring portions of each fulvalene ligand are essentially coplanar. The fulvalene ligands are essentially coparallel, and their respective carbon atoms are fully eclipsed. The iron–iron distance is *ca.* 4.0 Å (M. R. Churchill and J. Wormald, unpublished work).

(20) F. M. Hedberg and H. Rosenberg, *J. Am. Chem. Soc.*, **91**, 1258 (1969).

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of Lehigh University for assistance in obtaining the mass spectra, to Dr. T. H. Coffield of the Ethyl Corporation for a generous gift of cymantrene, and to Drs. Hedberg and Rosenberg for their communication of results prior to publication.

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Received October 23, 1968

Ruthenium Nitrosyl Complexes from Solutions of Ruthenium(III) Ammines in Dilute Perchloric Acid

Sir:

Unknown brown-black solutions have been reported when dilute perchloric acid reacts with the chloropentaammineruthenium(III) cation.[1] We now find that nitrosyl complexes of ruthenium may be isolated from such solutions, the NO group being readily identified by its characteristic infrared absorption spectrum.

At steam-bath temperatures, reaction between the metal complex (concentration $\sim 10^{-3}$ *M*) and 0.1 *M* perchloric acid is evident by the marked color development after approximately 10 min. After a further 2 hr deep purple solutions are obtained, and by slow (48 hr) fractional crystallization on the steam bath both purple-black and yellow solids may be isolated. The infrared spectrum of the yellow product in potassium bromide has the following bands (cm^{-1}) for which assignments are given in parentheses: 3500 br s (H_2O), 3220 s, 3120 s (N–H), 1850 s (N–O), 1620 br w (N–H, H_2O), 1300 m (N–H), 1140 s, 1120 s, 1080 s, 940 w (ClO_4^-), 840 br m (N–H) (br = broad; s = strong; m = medium; w = weak). This spectrum agrees with that reported for the $[RuOH(NH_3)_4NO]^{2+}$ cation with the inclusion of the ClO_4^- modes.[2,3] The less-soluble purple-black fractions showed a strong absorption at 1925 cm^{-1} in addition to the above list. This is attributed to the presence of some $[RuH_2O(NH_3)_4NO](ClO_4)_3$ for which frequencies are expected in the 1910–1920-cm^{-1} region, the exact location depending upon the counterion.[4] The intense dark colors of the solutions and certain of the solids isolated are no doubt due to chloronitrosyl complexes. Thus, from the more soluble fractions, solids having strong additional absorption at 1880 cm^{-1} are obtained. Also, decomposition of the purple solids with sodium hydroxide followed by acidification and treatment with silver nitrate shows the presence of chloride ion.

When a chloride-free preparation of $[RuH_2O(NH_3)_5](ClO_4)_3$ is used in these experiments, chloride ion may be detected among the reaction products. Hexaammineruthenium(III) chloride also reacts with 0.1 *M* perchloric acid when heated in solution on the steam bath to yield nitrosyl complexes. For similar concentrations of reagents, the reaction is distinctly slower than for the pentaammine complexes, suggesting that coordination of ClO_4^- may be the initial step in this unusual reaction.

Acknowledgment. Financial support for this research by Hercules, Inc., is gratefully acknowledged.

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(1) J. A. Broomhead, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **3**, 826 (1964).

(2) E. E. Mercer, W. A. McAllister, and J. R. Durig, *ibid.*, **5**, 1884 (1966).

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(4) M. B. Fairey and R. J. Irving, *Spectrochim. Acta*, **22**, 359 (1966).

(5) On sabbatical leave from the Australian National University, Canberra, Australia.

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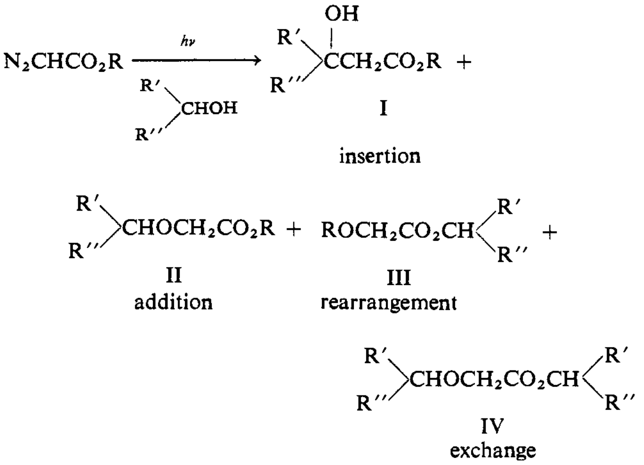
Received December 9, 1968

Photochemistry of Diazo Esters. II. A Novel Reaction Path

Sir:

Photolysis of diazo compounds is generally assumed to proceed by a carbene mechanism.[1-3] Our current study on a series of diazoacetates in alcohols, however, indicates a novel reaction path not involving carbene intermediates.



Products I, II, and III have been rationalized in terms of carbalkoxymethylene reactions.[2-4] The formation of IV, with a net exchange of the alcohol moiety, is the main concern of the present communication. The reaction is quite general since exchange products were found in each system studied (Table I), and the exchanged alcohol could also be detected. The efficiency of exchange varies with respect to substituents in the order PhO ≃ MeO > EtO > *i*-PrO ≃ AllylO ≃ *t*-BuO, and with respect to the solvent, Me < Et < *i*-Pr < *t*-Bu alcohol. Evidently steric effects are not important, and all esters exchange freely in *t*-butyl alcohol; moreover, the *t*-butyl ester solvolyzes as readily as its isopropyl and allyl analogs.

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