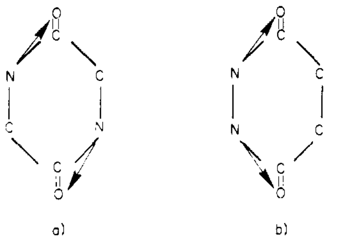

Figure 3. The arrangements of transition dipoles of peptide groups in diketopiperazines (a) and in diketopiperidazines (b).

The exciton splitting dominates both the uv spectra and the rotatory behavior, in contrast with the features exhibited by diketopiperazines.[4-6] Exciton theory[1] predicts no actual splitting of the π–π^* transition for dimers with parallel arrangements of transition dipoles, as is the case in diketopiperazines (Figure 3a). Rotatory strength in diketopiperazines consists, mainly, of contributions from a one-electron mechanism and a dipole–quadrupole coupling mechanism, both of which stress the importance of the n–π^* transition. Instead, a large splitting is predicted by the exciton theory for an oblique arrangement of transition dipoles[1] (Figure 3b). This situation is probably responsible for part of the high rotations which we observed for our cyclic compound.

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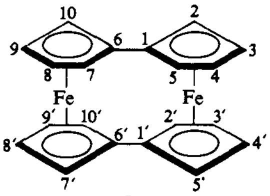
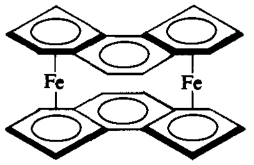
The Synthesis of 1,1′-Biferrocenylene

Sir:

Although the parent member of the novel 1,1′-biferrocenylene (I)[1] family has not been described, the synthesis of a homologous ferrocenophane, bis(*as*-indacenyliron) (II), has been reported.[2] In addition, mass spectral evidence has been reported for the formation of I during the reaction of cobalt(II) chloride with a mixture of lithiated ferrocenes, but the compound itself was not isolated.[3]



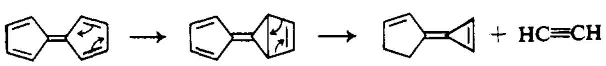
I



II

Because of internal strain resulting from the high degree of rigidity present in I, and the intramolecular repulsion of the nonbonding electrons of the iron atoms, it was thought that I might possess unusual physical and chemical properties.

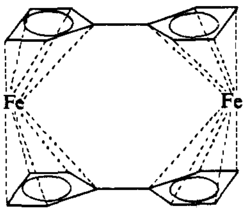
We wish to report the preparation of I by a modification of the Ullman coupling reaction which has been shown to be very effective in the ferrocene system.[4] 1,1′-Diiodoferrocene (99% purity by vpc) was heated at 140–160° for 3 hr in the presence of copper bronze using a large excess of either *n*-butylferrocene or diethylbenzene as solvent. The reaction mixture was filtered hot, and the product precipitated by the addition of the filtrate to a large volume of hexane. The crude product was recrystallized from benzene (solubility of I in cold benzene is approximately 0.2 mg/ml), yielding dark orange needles which exhibited both sublimation and decomposition >300°, with rapid decomposition occurring at 380°. *Anal.* Calcd for $C_{20}H_{16}Fe_2$: C, 65.54; H, 4.39; Fe, 30.16; mol wt, 367.9950. Found: C, 65.44, 65.46; H, 4.50, 4.44; Fe, 30.26, 30.33; mol wt (high-resolution mass spectroscopy), 367.9978. The fragmentation pattern observed in the mass spectrum of II at 70 V contained only three predominant peaks (amplitudes for each peak are given relative to 100 for the parent peak): *m/e* 56 (11.7), 128 (11.9), and 184 (13.4). The first two masses correspond to iron and fulvalene, respectively, from cleavage of the "sandwich" structure. The peak at *m/e* 184 may be assigned to a doubly charged parent species. An interesting feature of the mass spectral pattern is a small but significant peak at *m/e* 102 (3.8) which can be attributed to triafulvene, probably formed by a loss of acetylene from the fulvalene fragment as indicated below.



The infrared spectrum of I showed C–H stretch only in the ferrocene region (3090 cm^{-1}). Medium-weak absorption at 1100 cm^{-1} and medium-strong absorption at 997 cm^{-1} were also observed, analogous to absorptions in these regions reported in the infrared spectra of substituted biferrocenyls.[5] The electronic spectrum of a chloroform solution of I showed a maximum at 4660 Å (ε 255) and an inflection at 3600 Å (ε 562), while that of a cyclohexane solution revealed a shorter wavelength band at 2175 Å.

The low solubility of I in common solvents precluded any nmr studies at room temperature. Spectra were obtainable at elevated temperatures in benzene-d_6, however, and showed two triplets centered at 3.77 and 5.27 ppm from TMS. The signals appeared to be temperature independent in the range from 70 to 100°. By comparison, biferrocenyl, at 60° in benzene-d_6, shows a singlet at 3.97 ppm and two triplets centered at 4.08 and 4.30 ppm from TMS.

The unusually high- and low-field signals shown by I can be explained by structure III in which the iron atoms



III

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(1) The numbering system used for I is based upon that suggested for biferrocenyls by S. I. Goldberg and R. L. Matteson, *J. Org. Chem.*, **29**, 323 (1964).

(2) T. J. Katz and J. Schulman, *J. Am. Chem. Soc.*, **86**, 3169 (1964).

(3) I. J. Spilners and J. P. Pellegrini, Jr., *J. Org. Chem.*, 30, 3800 (1965).

(4) M. D. Rausch, *ibid.*, **26**, 1802 (1961).

(5) A. N. Nesmeyanov, V. N. Drozd, V. A. Sazonova, V. I. Romanenko, A. K. Prokof'ev, and L. A. Nikonova, *Izv. Akad. Nauk SSSR*, 667 (1693).

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 coworkers[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.

(6) M. Cais, J. J. Dannenberg, A. Eisenstadt, M. I. Levenberg, and J. H. Richards, *Tetrahedron Letters*, 1695 (1966).

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

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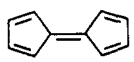
Organometallic π Complexes of Fulvalene[1,2]

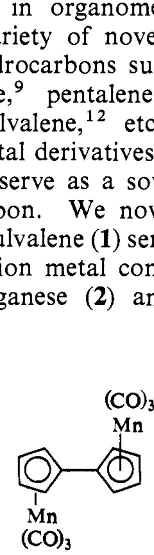
Sir:

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]

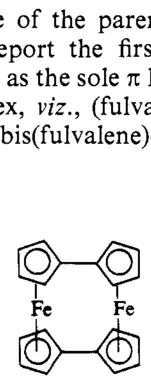
Recent advances in organometallic chemistry have indicated that a variety of novel but "unstable" unsaturated cyclic hydrocarbons such as cyclobutadiene,[9] benzocyclobutadiene,[9] pentalene,[10] benzopentalene,[11] calicene,[12] sesquifulvalene,[12] etc., can be isolated as stable transition metal derivatives, 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]



1



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).

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(3) R. D. Brown, *Trans. Faraday Soc.*, **45**, 296 (1949); **46**, 146 (1950); *Nature*, **165**, 566 (1950).

(4) For more recent theoretical discussions concerning the properties and structure predicted for fulvalene, see: (a) A. J. Silvestri, L. Goodman, and J. A. Dixon, *J. Chem. Phys.*, **36**, 148 (1962); (b) T. Nakajima and S. Katagira, *Bull. Chem. Soc. Japan*, **35**, 910 (1962); (c) A. Imamura and R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 5379 (1968).

(5) (a) E. C. Schreiber and E. I. Becker, *ibid.*, **76**, 3354, 6125 (1954); (b) P. L. Pauson and B. J. Williams, *J. Chem. Soc.*, 4153 (1961).

(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).

(7) (a) E. Matzner, Ph.D. Thesis, Yale University, Aug 1958; (b) W. von E. Doering, "Theoretical Organic Chemistry – The Kekulé Symposium," Butterworth and Co. (Publishers) Ltd., London, 1959, p 35; (c) W. B. DeMore, H. O. Pritchard, and N. Davidson, *J. Am. Chem. Soc.*, **81**, 5874 (1959); (d) E. M. Kosower and B. G. Ramsey, *ibid.*, **81**, 856 (1959); (e) K. V. Scherer, *ibid.*, **85**, 1550 (1963).

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(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).

(16) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, p 785.