We have now discovered a novel method of metal insertion into the porphyrin structure using metal carbonyls as metal sources and have succeeded in preparing a chromium mesoporphyrin IX dimethyl ester. Several other known metalloporphyrins have also been obtained by employing this new method. In the synthesis of the chromium porphyrins, mesoporphyrin IX dimethyl ester and an excess of chromium hexacarbonyl were heated in *n*-decane for 1.5 hr at a bath temperature of 170° under an atmosphere of nitrogen. After the reaction mixture[4a] was cooled to room temperature, solvent and unreacted chromium hexacarbonyl were evaporated and sublimed out under reduced pressure. The residue was dissolved in oxygen-free toluene and insoluble material, if any, was filtered off. The solution obtained was concentrated and reprecipitated by adding oxygen-free *n*-pentane, and the precipitate was collected by centrifugation. After drying for 8 hr at the boiling point of toluene, an apparently violet crystalline compound was obtained.[4b] *Anal.* Calcd for $C_{36}H_{40}O_4N_4Cr$: C, 67.06; H, 6.25; N, 8.69; Cr, 8.08. Found: C, 67.20; H, 6.11; N, 8.61; Cr, 7.88. The original N–H stretching vibration ($\sim$3300 cm^{-1}), N–H deformation ($\sim$1630 cm^{-1}), and N–H rocking vibration ($\sim$1100 cm^{-1}) of mesoporphyrin IX dimethyl ester disappeared from the infrared spectrum of this new complex. In addition, no absorption band of a carbonyl group bound to metal was observed, but the sharp single band ($\sim$1750 cm^{-1}) for an ester carbonyl group remained. The magnetic susceptibility of chromium mesoporphyrin IX dimethyl ester, measured by Gouy's method, was 2.84 BM.[5] These results indicate that the chromium ion in the new metalloporphyrin may be in the divalent state. Nickel protoporphyrin IX dimethyl ester and cobalt mesoporphyrin IX dimethyl ester were also prepared by the reaction of porphyrin with $Ni(CO)_4$ and $Co_2(CO)_8$, respectively. These two metalloporphyrins were identified by comparing their visible spectra with those of the authentic complexes.[6,7] Furthermore, iron insertion into protoporphyrin IX dimethyl ester was successful using iron pentacarbonyl and iodine in mesitylene for 4 hr at a bath temperature of 80° to form iron protoporphyrin IX dimethyl ester iodide. *Anal.* Calcd for $C_{36}H_{36}O_4N_4FeI$: Fe, 7.24. Found: Fe, 7.00.

During the investigation of the reaction between metal carbonyls and porphyrin as mentioned above, a significant observation has been made: the metal is oxidized and, in this oxidation state, the carbonyl groups do not remain. In 1965, Fitch and Lagowski[8] obtained ferrous acetylacetonate by the reaction of $Fe(CO)_5$ and acetylacetone under a nitrogen atmosphere. The reactions here described between metal carbonyls and porphyrins also gave the divalent metalloporphyrins except for the reaction between $Fe(CO)_5$ and protoporphyrin IX dimethyl ester in the presence of I_2 as an oxidizing agent. To accommodate the oxidation of the metal to the +2 state, the central imino hydrogens would seem the most likely reductants. Reduced porphyrin species, hydrogen, or formaldehyde would seem to be possible end products for these hydrogens. Chromium hexacarbonyl has six carbon monoxide molecules. A CO group occupies one coordinating site and is replaced by one monodentate ligand. Therefore, it is expected that two CO groups will remain on the chromium porphyrin because the ligand is quadridentate. However, chromium mesoporphyrin IX dimethyl ester has no CO group on it, as shown by the infrared spectrum. In chromium mesoporphyrin IX dimethyl ester it is probable that one electron, at least, occupies the d_{z^2} orbital because divalent chromium has four d electrons and the magnetic data show the presence of two unpaired electrons. The existence of a d_{z^2} electron weakens the bond between the metal and carbon monoxide perpendicular to the molecular plane because of the repulsion between the lone pair of electrons on C atom in CO and the d_{z^2} electron. This is perhaps one of the reasons that the bond between the metal and carbon atoms of CO in chromium porphyrin should be very weak even if it forms. Another possibility is to replace CO by another chromium mesoporphyrin IX dimethyl ester to form an association complex (as suggested by Elvidge and Lever[3]) for chromium(II) phthalocyanine. This point becomes apparent as a result of the investigation of the structure of the chromium porphyrin.

Acknowledgment. The authors wish to express their appreciation for financial support from the National Science Foundation.

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(4) (a) The visible absorption bands of the mixture at this stage of the reaction are 573 (α) and 535 mμ (β) in toluene, and the relative intensities of these two bands are $\alpha > \beta$. (b) This compound was sparingly soluble in toluene, but soluble in chloroform, methanol, and others. Both toluene and chloroform solutions showed a gradual change in their absorption spectra when they were kept in air. No variations, however, were observed in their absorption spectra after 24 hr. The initial and final absorption maxima and the order of intensity in toluene and chloroform solutions are as follows: λ(toluene, $I_{max} \sim 578$ mμ) < λ(toluene, $I_{max} \sim 546$ mμ), λ(toluene, $F_{max} \sim 573$ mμ) > λ(toluene, $F_{max} \sim 535$ mμ); λ(chloroform, $I_{max} \sim 573$ mμ) (ϵ 2.42×10^3)) < λ(chloroform, $I_{max} \sim 540$ mμ (ϵ 3.09×10^3)), λ(chloroform, $F_{max} \sim 575$ mμ (ϵ 3.0×10^3)) < λ(chloroform, $F_{max} \sim 545$ mμ (ϵ 4.7×10^3)); I_{max} is the initial maximum and F_{max} is the final maximum.

The reason for the different behavior of the compound in toluene and chloroform solutions, will be discussed in a forthcoming paper.

(5) We thank Professor Harry B. Gray for the use of his apparatus.

(6) J. E. Falk "Porphyrins and Metalloporphyrins," Elsevier Publishing Co., Inc., New York, N. Y., 1964, p. 244.

(7) A. Stern and M. Deželić, *Z. Physik. Chem.*, **180**, 131 (1937).

(8) J. W. Fitch, III, and J. J. Lagowski, *Inorg. Chem.*, 4, 910 (1965).

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The [1,1]Ferrocenophane System[1]

Sir:

In contrast to the active interest in cyclophane compounds generally, the [*m,n*]ferrocenophane system[1] has received little attention, the only compounds of this class which have been described being [4,4]ferrocenophane[2] and bis(*as*-indacenyliron).[3] We wish to report the synthesis and characterisation of 1,12-dimethyl[1,1]ferrocenophane (II).

Reduction of the bisfulvene (I)[4] with lithium aluminum hydride in tetrahydrofuran afforded a yellow

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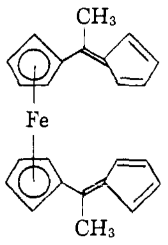
(1) The systematic nomenclature proposed by B. H. Smith in "Bridged Aromatic Compounds," Academic Press Inc., New York, N. Y., 1964, has been adopted throughout.

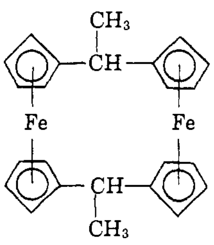
(2) A. Lüttringhaus and W. Kullick, *Angew. Chem.*, **70**, 438 (1958).

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

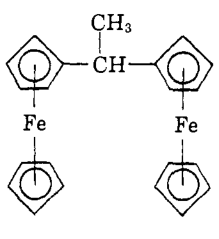
(4) M. Furdik, S. Toma, and J. Suchy, *Chem. Zvesti*, **15**, 547 (1961).



I



II



III

salt[5] which, on treatment with ferrous chloride, gave a mixture of products from which II was separated chromatographically in yields from 14 to 20%. The compound crystallized from ligroin in orange blades, mp 182–184° [*Anal.* Calcdf or $C_{24}H_{24}Fe_2$: C, 68.0; H, 5.7; mol wt, 424. Found: C, 68.1; H, 6.1; mol wt (mass spectrum), 424], and is assigned the structure II on the basis of the spectral characteristics summarized as follows.

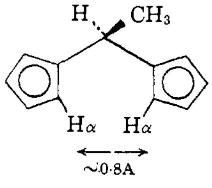
The infrared spectrum conforms to that expected of a heteroannularly substituted dialkylferrocene and, except for the absence of bands at 9 and 10 μ,[6] bears a close similarity to that of the related 1,1-diferrocenylethane (III).[7] As is generally the case with ferrocene derivatives,[8] the molecular ion peak in the mass spectrum is by far the most intense and establishes the molecular weight (for ^{56}Fe) to be 424, while the relative peak heights in the molecular ion group demonstrate the presence of two iron atoms. Two successive losses of methyl groups are indicated by the appearance of groups of peaks at $(M - 15)^+$ and $(M - 30)^+$ and confirmed by the presence of the appropriate metastable peaks, and these groups together with the M^+ group have doubly charged counterparts at $m/2e$ = 212, 204.5, and 197. The subsequent cracking pattern involves loss of a cyclopentadienyl group followed by general fragmentation.

The pmr spectrum (see Table I) comprises four groups of resonances in the ratio 4:12:2:6 (field increasing). The methyl and methine protons appear as a clean doublet centered at τ 8.90 and quadruplet centred at τ 6.33 (J = 7.5 cps), respectively, showing that the two methyl groups (and also the two methine protons) occupy equivalent molecular environments. The presence of two groups of cyclopentadienyl protons appearing as complex multiplets centered at τ 5.58 and 6.02, respectively, infers that the molecule is twisted in such a way that four of the 16 ring protons lie further from the iron atoms and are thus deshielded with respect to the remaining 12.[9,10] Such molecular distortion is to be expected since a geometry involving coplanarity of the rings in each hydrocarbon ligand in parallel planes "sandwiching" the iron atoms would lead to an impossibly severe steric interaction between H_α protons (see IV).

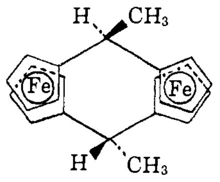
Table I. Pmr Spectra[a]

Compd	τ_{CH_3}	τ_{CH}	τ_{ring}
II	8.90	6.33	5.58 6.02
III	8.47	6.60	6.08

[a] In CS_2 solution at 40 Mcps against TMS.



IV



V

By comparison of the chemical shifts of the methyl and methine protons in II and III (see table), the ferrocenophane is tentatively assigned structure V, in which the methyl groups have the *exo* configuration. Although rotation of the ferrocenyl groups in III about the ring CH bonds would result in the chemical shift values of the methyl and methine protons, reflecting a time-averaged environment relative to the iron atoms, the upfield shift of the resonance of the methyl protons and the corresponding downfield shift of that of the methine protons in going from III to II can be best accommodated by structure V for the ferrocenophane.[11] Nonbonded interaction between methine protons render improbable the isomeric structure containing completely eclipsed ligands.

Both the fulvene route and other methods of preparation of related [1, 1]ferrocenophanes are being currently explored.

Acknowledgments. The author thanks Drs. P. Bladon and H. C. Hill for the determination of the pmr and mass spectra.

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[5] Analogous fulvene reductions have been described; *cf.* G. R. Knox, J. D. Munro, P. L. Pauson, G. H. Smith, and W. E. Watts, *J. Chem. Soc.*, 4619 (1961).

[6] *Cf.* M. Rosenblum, *Chem. Ind.* (London), 953 (1958).

[7] K. L. Rinehart, Jr., P. A. Kittle, and A. F. Ellis, *J. Am. Chem. Soc.*, **82**, 2082 (1960).

[8] D. J. Clancy and I. Spilners, *Anal. Chem.*, **34**, 1839 (1962).

[9] The shielding influence of the iron atom is well documented; *e.g.*, see K. L. Rinehart, Jr., D. E. Bublitz, and D. H. Gustafson, *J. Am. Chem. Soc.*, **85**, 970 (1963).

[10] Alternatively, it could be argued that the severe steric interaction between the two pairs of H_α protons (see IV) and their unique proximity to two cyclopentadienyl rings might cause them to be specifically deshielded. The deshielding of sterically compressed protons in polycyclic benzenoid compounds has been explained on such a basis; *cf.* C. Reid, *J. Am. Chem. Soc.*, **78**, 3226 (1956); *J. Mol. Spectry*, **1**, 18 (1957).

[11] Although the region close to the iron atom is known to be strongly shielding in nature,[9] protons located in the remaining volume between the planes of the rings are deshielded in accord with the molecular diamagnetic anisotropy defined by the susceptibility measurements of L. N. Mulay and M. E. Fox, *J. Am. Chem. Soc.*, **84**, 1308 (1962); *J. Chem. Phys.*, **38**, 760 (1963). An illustrative example is provided by M. Rosenblum in "Chemistry of the Iron Group Metallocenes," Part 1, Interscience Publishers, Inc., New York, N. Y., 1965, p 217.

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A Steroidal Analgesic

Sir:

We wish to report the synthesis of a new class of analgesic compounds having poly(lower alkoxy)estrane structures. These compounds, represented by the structure 2,3,4-trimethoxyestra-1,3,5(10)-trien-17β-ol (VI), are potent analgesics. In the "rat-tail flick" method of D'Amour and Smith[1] VI, by intravenous ad-

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[1] F. E. D'Amour and D. L. Smith, *J. Pharmacol.*, **72**, 74 (1941).