

and C-15 lines are straightforward and they can be readily used in our investigation.

It is evident that the mobility of the π electrons allows for extensive delocalization of the positive charge. This mobility proved equally efficient in the case of complexation of the imine with SO_2 where we observed similar shifts as upon protonation. This is to be expected since SO_2 is known to act as a Lewis acid with amines.

For a nuclear magnetic resonance signal to be an acceptable indicator of protonation and perturbation by the protein, it must be in a region relatively free from protein signals. C-14 is likely to be the most informative since it absorbs at about 120 ppm downfield from TMS in the protonated *all-trans*-imine. C-14 in the 11-*cis* protonated imine should not differ by more than one or two parts per million from that of the *all-trans* isomer.¹⁰ The protein is expected to contribute 32 to 47 ^{13}C resonances in the region 115 to 125 ppm.¹¹ Recent work with ribonuclease-S indicates that the line broadening of protonated carbons in macromolecules will not be prohibitive for ^{13}C NMR studies.¹² If C-14 is enriched to 90% ^{13}C and we consider the expected spread of protein signals, we foresee no difficulty in obtaining useful spectra.

On the basis of the results reported here we are synthesizing 11-*cis*-retinal ^{13}C -labeled at C-14. This will be complexed with natural opsin obtained by bleaching bovine rhodopsin. Further labeling of C-13 and C-15 is also being undertaken.

In the ^{13}C -labeled rhodopsin we expect to establish that the Schiff base linkage is indeed protonated. In addition we

expect to obtain useful data for the characterization of the effect of the protein environment in the visual chromophore.

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References and Notes

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- (11) For amino acid ^{13}C NMR data see E. Oldfield and A. Allerhand, *J. Am. Chem. Soc.*, **97**, 221 (1975); W. Horsley, H. Steinlicht, and J. S. Cohen, *ibid.*, **92**, 680 (1970).
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Organometallic Chemistry of the Transition Metals. XXXII. Some Reactions of Iron Carbonyls with Dimethylenecyclobutane Derivatives^{1,2}

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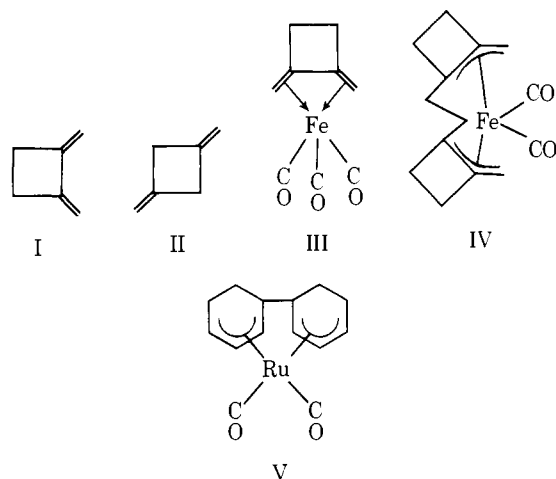
Abstract: 1,2-Dimethylenecyclobutane reacts with $\text{Fe}_3(\text{CO})_{12}$ in boiling benzene to give both yellow-orange liquid $\text{C}_6\text{H}_8\text{Fe}(\text{CO})_3$ in which the 1,2-dimethylenecyclobutane functions as a 1,3-diene ligand in the usual manner and yellow crystalline $\text{C}_{12}\text{H}_{16}\text{Fe}(\text{CO})_2$ in which two 1,2-dimethylenecyclobutane units couple to form a symmetrical bis(η^3 -allylic) $\text{C}_{12}\text{H}_{16}$ ligand. 3,4-Dimethylenecyclobutene reacts with $\text{Fe}_2(\text{CO})_9$ in tetrahydrofuran at room temperature to give an unstable yellow liquid $\text{C}_6\text{H}_6\text{Fe}(\text{CO})_4$ in which the cyclobutene double bond is bonded to the $\text{Fe}(\text{CO})_4$ unit. Mild warming of this complex results in conversion to the shift isomer $\text{C}_6\text{H}_6\text{Fe}(\text{CO})_4$ in which one of the exocyclic double bonds is bonded to the $\text{Fe}(\text{CO})_4$ unit. Bicyclo[3.2.0]hepta-1,4,6-triene reacts with $\text{Fe}_3(\text{CO})_{12}$ in boiling benzene to give a yellow-orange liquid $\text{C}_7\text{H}_6\text{Fe}(\text{CO})_3$ containing a novel bicyclic cyclobutadiene ligand formed by hydrogen migration.

The thermal dimerization of allene is well known⁴ to give a mixture of ~85% 1,2-dimethylenecyclobutane (I) and ~15% 1,3-dimethylenecyclobutane (II). In 1962 one of us (R.B.K.) first observed the reaction of this allene dimer with $\text{Fe}_3(\text{CO})_{12}$ to give yellow crystals of stoichiometry $\text{C}_{12}\text{H}_{16}\text{Fe}(\text{CO})_2$. This apparent (diene)₂ $\text{Fe}(\text{CO})_2$ stoichiometry was totally different from both the known (diene) $\text{Fe}(\text{CO})_3$ stoichiometry of iron carbonyl complexes of other 1,3-dienes⁵⁻⁷ and the (diene)₂ FeCO stoichiometry predictable in 1962 from effective atomic number considerations and subsequently demonstrated for butadiene⁸ and 1,3-cyclohexadiene⁹ complexes. However, the available

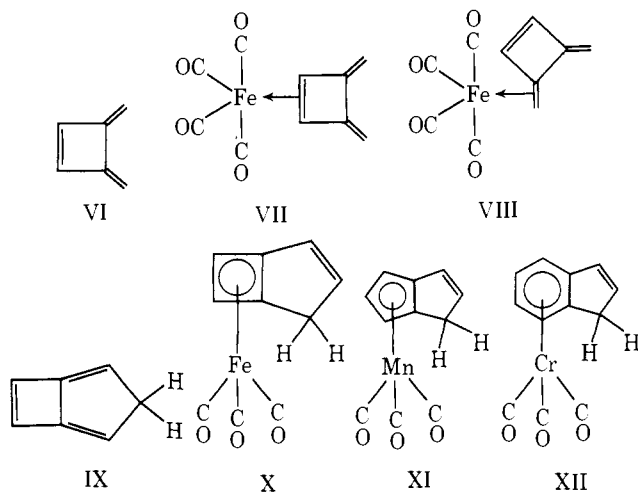
spectroscopic data on this $\text{C}_{12}\text{H}_{16}\text{Fe}(\text{CO})_2$ complex, including even the proton NMR spectrum, gave no clue at that time concerning possible structures. Even though this $\text{C}_{12}\text{H}_{16}\text{Fe}(\text{CO})_2$ complex was subsequently also characterized mass spectrometrically^{10,11} its structure remained a mystery until the start of this work in 1974.

The availability of pulsed Fourier transform carbon-13 NMR spectroscopy provided a new technique of potential value for elucidation of the structure of this apparently anomalous $\text{C}_{12}\text{H}_{16}\text{Fe}(\text{CO})_2$ complex. Accordingly, we repeated the reaction between allene dimer and $\text{Fe}_3(\text{CO})_{12}$ in order to obtain some $\text{C}_{12}\text{H}_{16}\text{Fe}(\text{CO})_2$ for carbon-13 NMR

spectroscopy. From this reaction we obtained both the desired $C_{12}H_{16}Fe(CO)_2$ and the recently reported¹² diene-iron tricarbonyl $C_6H_8Fe(CO)_3$ (III). The carbon-13 NMR spectra suggested that $C_{12}H_{16}Fe(CO)_2$ had the unusual structure IV containing a new type of chelating bis(η^3 -allylic) ligand. A ruthenium carbonyl complex V with a similar chelating bis(η^3 -allylic) ligand was recently obtained from $Ru_3(CO)_{12}$ and 1,3-cyclohexadiene.¹³



The new structure type IV obtained from 1,2-dimethylenecyclobutane and $Fe_3(CO)_{12}$ made of interest some reactions of other dimethylenecyclobutane derivatives with iron carbonyls. The reaction of 3,4-dimethylenecyclobutene (VI)¹⁴ with $Fe_2(CO)_9$ under mild conditions was shown to give both possible isomeric (olefin) $Fe(CO)_4$ type products VII and VIII with the more symmetrical isomer VII undergoing thermal isomerization into the less symmetrical isomer VIII. The reaction of bicyclo[3.2.0]hepta-1,4,6-triene (IX)¹⁵ with $Fe_3(CO)_{12}$ was shown to proceed in a completely different manner with a hydrogen migration to give the complex X containing a bicyclic cyclobutadiene ligand analogous to the dihydropentalenyl ligand in $C_8H_7Mn(CO)_3$ (XI)¹⁶ and the indene ligand in $C_9H_8Cr(CO)_3$ (XII).¹⁷



This paper describes in detail our work on the preparations and properties of these unusual iron carbonyl complexes.

Experimental Section

Microanalyses and molecular weight determinations by vapor pressure osmometry were performed by Atlantic Microlab, Inc., Atlanta, Ga., and by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Infrared spectra were taken in hexane solutions

and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Proton NMR spectra were taken in $CDCl_3$ solutions and recorded on a Varian T-60 spectrometer at 60 MHz or a Varian HA-100 spectrometer at 100 MHz. Melting points were taken in capillaries and are uncorrected.

The carbon-13 NMR spectra were taken in $CDCl_3$ solutions using a Jeolco PFT-100 spectrometer operating at 25.0336 MHz in the Fourier transform mode with proton decoupling and a deuterium lock. A pulse angle of 45° and a pulse interval of 3 s were used. Carbon-13 chemical shifts (δ) are reported in parts per million downfield from internal tetramethylsilane. The multiplicities of the carbon-13 resonances, as determined by off-resonance decoupling experiments, are given in parentheses.

The mass spectra were taken at 70 eV on the University of Georgia Perkin-Elmer Hitachi RMU-6 mass spectrometer using a chamber temperature of 210° and the indicated sample temperatures. Intensities relative to 100 for the strongest metal-containing ion are given in parentheses.

Allene dimer⁴ was prepared by passing commercial allene (PCR Inc., Gainesville, Fla.) through a 2 × 40 cm glass tube filled with glass beads heated to 500 ± 10°. The product was collected in a -30° trap and unreacted allene in successive traps at -80°. Recycling the unreacted allene several times through the hot tube followed by atmospheric pressure distillation of the crude allene dimer gave a ~20% yield of product, bp 73°, shown by its proton NMR spectrum to consist of the expected⁴ mixture of ~85% 1,2-dimethylenecyclobutane and ~15% 1,3-dimethylenecyclobutane.

3,4-Dimethylenecyclobutene (VI) was prepared by a similar pyrolysis of commercial 1,5-hexadiene (Farchan Chemical Co., Willoughby, Ohio) in a single pass at 350°.¹⁴ The bicyclo[3.2.0]hepta-1,4,6-triene (IX) was prepared from methyl vinyl ketone and chloroacetone by the published sequence of reactions.¹⁵ The iron carbonyls $Fe_2(CO)_9$ ¹⁸ and $Fe_3(CO)_{12}$ ¹⁹ were prepared from commercial $Fe(CO)_5$ (GAF Corp., New York, N.Y.) by the cited published procedures.

A nitrogen atmosphere was routinely provided for handling air-sensitive organometallic compounds. Alcoa F-20 alumina from Bauxite, Ark., or commercial Florisil was used for chromatography as indicated.

Reaction of Allene Dimer with $Fe_3(CO)_{12}$. A mixture of 2.0 g (25 mmol) of allene dimer, 10.0 g (20 mmol) of $Fe_3(CO)_{12}$, and 100 ml of benzene was boiled under reflux for 16 h. After removal of solvent at ~35° (35 mm), the reaction mixture was chromatographed on a 2 × 100 cm alumina column in pentane solution. The two yellow to yellow-orange bands which separated were each eluted with pentane. Evaporation of the first eluate gave 1.3 g (24% yield) of yellow liquid $C_6H_8Fe(CO)_3$ which could be purified by evaporative distillation at 40° (0.01 mm). Evaporation of the second eluate followed by low-temperature crystallization from pentane gave 0.8 g (25% yield) of $C_{12}H_{16}Fe(CO)_2$.

Reaction of Allene Dimer with $Fe_2(CO)_9$. A mixture of 1.0 g (12.5 mmol) of allene dimer, 5.0 g (13.7 mmol) of $Fe_2(CO)_9$, and 200 ml of hexane was stirred for 24 h at room temperature. Hexane was removed from the filtered reaction mixture at ~35° (35 mm). The residue was chromatographed on a 2 × 80 cm alumina column in pentane solution. The single yellow band was eluted with pentane. Evaporation of the eluate followed by evaporative vacuum distillation at 40° (0.01 mm) gave 0.6 g (22% yield) of yellow liquid $C_6H_8Fe(CO)_3$.

Properties of $C_6H_8Fe(CO)_3$ (III).²⁰ Yellow liquid, distills 40° (0.01 mm), infrared $\nu(CO)$ in hexane 2049 (m) and 1971 (s) cm^{-1} .

Proton NMR spectrum in C_6D_6 : resonances at τ 7.14 (singlet), 8.24 (doublet, $J = 3$ Hz), and 9.56 (doublet, $J = 3$ Hz) of approximate relative intensities 4:2:2, respectively.

Carbon-13 NMR spectrum in C_6D_6 : resonances at δ 211.3 (singlet), 114.2 (singlet), 36.0 (triplet), and 32.7 (triplet).

Anal. Calcd for $C_9H_8FeO_3$: C, 49.1; H, 3.6. Found: C, 49.2; H, 3.7.

Mass spectrum (sample temperature 40°): $C_6H_8Fe(CO)_3^+$ (25), $C_6H_8Fe(CO)_2^+$ (29), $C_6H_8FeCO^+$ (13), $C_6H_8Fe^+$ (89), $C_5H_4Fe^+$ (22), $C_5H_3Fe^+$ (11), $C_3H_4Fe^+$ (100), $C_6H_8^+$ (310), $C_6H_7^+$ (670), $C_6H_5^+$ (140), $C_5H_7^+$ (71), $C_5H_5^+$ (49), Fe^+ (71), $C_4H_5^+$ (69), $C_4H_4^+$ (330), $C_4H_3^+$ (115), $C_4H_2^+$ (82), $C_3H_5^+$ (82), $C_3H_4^+$ (93), and $C_3H_3^+$ (220).

Properties of $C_{12}H_{16}Fe(CO)_2$ (IV). Yellow crystals, mp 116-

119°; infrared $\nu(\text{CO})$ in hexane 1991 (s) and 1935 (s) cm^{-1} .

Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{FeO}_2$: C, 61.8; H, 5.9; O, 11.8; mol wt 272. Found: C, 61.6; H, 5.9; O, 11.9; mol wt 259 (benzene).

Proton NMR spectrum in CDCl_3 : resonances at τ 6.63 (apparent singlet), 7.08 (broad), 7.55 (apparent singlet), 7.72 (apparent doublet, separation 17 Hz), 7.87 (apparent doublet, separation 3 Hz), 8.36 (doublet, $J = 10$ Hz), and 9.26 (doublet, $J = 10$ Hz) of approximate relative intensities 2:2:2:2:4:2, respectively.

Carbon-13 NMR spectrum in C_6D_6 : resonances at δ 215.7 (singlet), 113.8 (singlet), 104.2 (singlet), 41.5 (triplet), 32.1 (triplet), 31.9 (triplet), and 27.2 (triplet).

Mass spectrum (sample temperature 145°). The following ions of the indicated relative intensities were observed in a mass spectrum run under conditions leading to more thermal decomposition than in the previously reported¹¹ mass spectrum:

$\text{C}_{12}\text{H}_{16}\text{Fe}(\text{CO})_2^+$ (22), $\text{C}_{12}\text{H}_{16}\text{FeCO}^+$ (28), $\text{C}_{12}\text{H}_{16}\text{Fe}^+$ (100), $\text{C}_{10}\text{H}_{12}\text{Fe}^+$ (31), $\text{C}_{10}\text{H}_{10}\text{Fe}^+$ (10), $\text{C}_9\text{H}_{12}\text{Fe}^+$ (14), $\text{C}_9\text{H}_{10}\text{Fe}^+$ (16), $\text{C}_2\text{H}_{16}^+$ (190), $\text{C}_{11}\text{H}_{13}^+$ (180), $\text{C}_{10}\text{H}_{12}^+$ (185), $\text{C}_{10}\text{H}_{11}^+$ (170), C_9H_9^+ (200), C_9H_7^+ (76), C_8H_9^+ (155), C_8H_8^+ (67), C_7H_7^+ (310), C_6H_8^+ (115), C_6H_7^+ (260), C_6H_5^+ (120), C_5H_5^+ (59), C_4H_9^+ and/or FeH^+ (66), C_4H_5^+ (60), C_4H_4^+ (66), C_4H_3^+ (71), C_3H_5^+ (100), C_3H_3^+ (160), and C_2H_3^+ (81).

Other Reactions of Allene Dimer. (a) $(\text{CH}_3\text{CN})_3\text{M}(\text{CO})_3$ ($\text{M} = \text{Cr}$ and Mo). A mixture of 1.0 g (12.5 mmol) of allene dimer, the $(\text{CH}_3\text{CN})_3\text{M}(\text{CO})_3$ prepared²¹ from ~ 15 mmol of the corresponding metal hexacarbonyl, and 100 ml of heptane was boiled under reflux for 16–20 h. No evidence for the formation of any new metal carbonyl derivatives other than $\text{CH}_3\text{CNM}(\text{CO})_5$ ($\text{M} = \text{Cr}$ and Mo) was obtained either by infrared spectroscopy of the original reaction mixture or after chromatography on alumina.

(b) **Butadienetricarbonyliron.** A mixture of 1.0 g (12.5 mmol) of allene dimer, 1.0 g (5.2 mmol) of butadienetricarbonyliron,⁵ and 50 ml of benzene or octane was boiled under reflux for 16–20 h. In both cases the infrared spectrum of the reaction mixture indicated that no new metal carbonyl derivatives had formed.

(c) **1,2-Dimethylenecyclobutanetricarbonyliron (III).** A mixture of 0.5 g (6.2 mmol) of allene dimer, 1.0 g (4.5 mmol) of 1,2-dimethylenecyclobutanetricarbonyliron (III), and 50 ml of benzene was boiled under reflux for a total of 72 h. The infrared spectrum indicated that no new metal carbonyl derivatives had formed although some decomposition had occurred.

Ultraviolet irradiation of 0.3 g (1.4 mmol) of 1,2-dimethylenecyclobutanetricarbonyliron (III), 0.2 g (2.5 mmol) of allene dimer, and 150 ml of hexane for 17 h failed to give any new iron carbonyl derivatives as indicated by infrared spectroscopy.

Reaction of 3,4-Dimethylenecyclobutene with $\text{Fe}_2(\text{CO})_9$. A mixture of 2.0 g (26 mmol) of 3,4-dimethylenecyclobutene, 10.0 g (27 mmol) of $\text{Fe}_2(\text{CO})_9$, and 150 ml of tetrahydrofuran was stirred for 5 h at room temperature. The resulting mixture was filtered. The filtrate was poured into 1 l. of water. The resulting mixture was extracted with 250 ml of pentane. The pentane extracts were washed with ten 250-ml portions of water to remove traces of tetrahydrofuran. After drying over anhydrous magnesium sulfate, solvent was removed from the pentane extracts at $\sim 20^\circ$ (35 mm). The resulting liquid was chromatographed on a 2×80 cm Florisil column in pentane solution. The single yellow-orange band was eluted with pentane. Removal of pentane from the eluate at $\sim 20^\circ$ (35 mm) gave 1.9 g (31% yield) of a yellow-orange liquid, shown by its proton and carbon-13 NMR spectra to be mainly *sym*- $\text{C}_6\text{H}_6\text{Fe}(\text{CO})_4$ (VII). Evaporative vacuum distillation at $\sim 40^\circ$ (0.01 mm) resulted in extensive isomerization of this product to *unsym*- $\text{C}_6\text{H}_6\text{Fe}(\text{CO})_4$ (VIII).

A similar reaction of 3,4-dimethylenecyclobutene with $\text{Fe}_2(\text{CO})_9$ at room temperature in pentane rather than tetrahydrofuran gave a similar $\text{C}_6\text{H}_6\text{Fe}(\text{CO})_4$ product but the longer reaction times (16 vs. 5 h) resulted in more isomerization of the symmetrical isomer VII to the unsymmetrical isomer VIII even before the evaporative vacuum distillation.

Anal. Calcd for $\text{C}_{10}\text{H}_6\text{FeO}_4$: C, 48.8; H, 2.4; O, 26.0. Found: C, 49.1; H, 2.6; O, 25.9.

Infrared $\nu(\text{CO})$ in hexane: 2091 (w), 2031 (s), 2013 (s), and 2002 (vs) cm^{-1} .

Proton NMR Spectra. (a) *sym*- $\text{C}_6\text{H}_6\text{Fe}(\text{CO})_4$ in CDCl_3 : singlets at τ 2.99, 5.24, and 5.37 of approximate relative intensities 1:1:1. (b) *unsym*- $\text{C}_6\text{H}_6\text{Fe}(\text{CO})_4$ in C_6D_6 : resonances at τ 4.01 (doublet, $J = 4$ Hz), 4.29 (doublet, $J = 4$ Hz), 5.69 (singlet), 5.80

(singlet), 7.80 (doublet, $J = 5$ Hz), and 7.93 (doublet, $J = 5$ Hz) of approximate relative intensities 1:1:1:1:1:1.

Carbon-13 NMR Spectra. (a) *sym*- $\text{C}_6\text{H}_6\text{Fe}(\text{CO})_4$ in C_6D_6 : resonances at δ 210.4 (singlet), 146.2 (singlet), 97.2 (triplet), and 61.0 (doublet). (b) *unsym*- $\text{C}_6\text{H}_6\text{Fe}(\text{CO})_4$ in C_6D_6 : resonances at δ 211.9 (singlet), 155.4 (singlet), 149.8 (doublet), 135.5 (doublet), 95.8 (triplet), 81.7 (singlet), and 25.2 (triplet).

Reaction of Bicyclo[3.2.0]hepta-1,4,6-triene (IX) with $\text{Fe}_3(\text{CO})_{12}$. A mixture of 2.0 g (22 mmol) of bicyclo[3.2.0]hepta-1,4,6-triene (IX), 10.0 g (20 mmol) of $\text{Fe}_3(\text{CO})_{12}$, and 200 ml of hexane was boiled under reflux for 20 h. After cooling to room temperature, the reaction mixture was filtered and solvent removed from the filtrate at $\sim 25^\circ$ (35 mm). The liquid residue was chromatographed on a 2×80 cm alumina column in pentane solution. The single yellow band was eluted with pentane. Evaporation of the pentane eluate at $\sim 25^\circ$ (35 mm) followed by evaporative vacuum distillation at $\sim 50^\circ$ (0.01 mm) gave 2.1 g (41% yield) of yellow-orange liquid $\text{C}_7\text{H}_6\text{Fe}(\text{CO})_3$ (X).

Anal. Calcd for $\text{C}_{10}\text{H}_6\text{FeO}_3$: C, 52.2; H, 2.6. Found: C, 52.3; H, 2.6.

Infrared $\nu(\text{CO})$ in hexane: 2050 (s) and 1970 (vs) cm^{-1} .

Proton NMR spectrum in C_6D_6 : resonances at τ 4.27 (doublet triplet, $J_D = 5.0$ Hz, $J_T = 2.1$ Hz), 4.61 (doublet triplet, $J_D = 5.0$ Hz, $J_T = 2.1$ Hz), 6.50 (singlet), 6.54 (singlet), and 7.56 (triplet, $J = 2.1$ Hz) of approximate relative intensities 1:1:1:2, respectively.

Carbon-13 NMR spectrum in C_6D_6 : resonances at δ 215.4 (singlet), 138.1 (doublet), 126.3 (doublet), 97.2 (singlet), 88.6 (singlet), 55.4 (doublet), 52.9 (doublet), and 34.6 (triplet).

Mass spectrum (sample temperature 80°): $\text{C}_7\text{H}_6\text{Fe}(\text{CO})_3^+$ (24), $\text{C}_7\text{H}_6\text{Fe}(\text{CO})_2^+$ (27), $\text{C}_7\text{H}_6\text{FeCO}^+$ (10), $\text{C}_7\text{H}_6\text{Fe}^+$ (100), $\text{C}_5\text{H}_4\text{Fe}^+$ (21), $\text{C}_3\text{H}_2\text{Fe}^+$ (14), C_7H_6^+ (4), C_7H_5^+ (8), FeCO^+ (6), C_2HFe^+ (11), and Fe^+ (58). Metastable ions at m/e 177.5 m ($\text{C}_7\text{H}_6\text{Fe}(\text{CO})_3^+ \rightarrow \text{C}_7\text{H}_6\text{Fe}(\text{CO})_2^+ + \text{CO}$), m/e 122.5 m ($\text{C}_7\text{H}_6\text{FeCO}^+ \rightarrow \text{C}_7\text{H}_6\text{Fe}^+ + \text{CO}$), m/e 98.5 w ($\text{C}_7\text{H}_6\text{Fe}^+ \rightarrow \text{C}_5\text{H}_4\text{Fe}^+ + \text{C}_2\text{H}_2$), and m/e 21.5 s ($\text{C}_7\text{H}_6\text{Fe}^+ \rightarrow \text{Fe}^+ + \text{C}_7\text{H}_6$).

Results

The reaction between allene dimer and $\text{Fe}_3(\text{CO})_{12}$ gave two products. Each product was formed in $\sim 20\%$ yield based on allene dimer indicating that each product originates from the 1,2-dimethylenecyclobutane (I) composing $\sim 85\%$ of the allene dimer rather than from the 1,3-dimethylenecyclobutane (II) composing the remaining $\sim 15\%$ of the allene dimer.

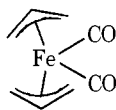
The less strongly adsorbed product from 1,2-dimethylenecyclobutane and $\text{Fe}_3(\text{CO})_{12}$ is a yellow-orange liquid of stoichiometry $\text{C}_6\text{H}_8\text{Fe}(\text{CO})_3$ formulated as the diene complex III. The infrared spectrum of this complex exhibits $\nu(\text{CO})$ frequencies at 2049 and 1971 cm^{-1} similar to the reported⁵ $\nu(\text{CO})$ frequencies at 2051 and 1978 cm^{-1} in butadienetricarbonyliron. The proton NMR spectrum of $\text{C}_6\text{H}_8\text{Fe}(\text{CO})_3$ (III) exhibits a pair of doublets at τ 8.24 and 9.56 assigned to the two nonequivalent protons of the exocyclic methylene groups similar to the reported²² resonances at τ 8.32 and 9.78 in butadienetricarbonyliron. The carbon-13 NMR resonances in $\text{C}_6\text{H}_8\text{Fe}(\text{CO})_3$ (III) at δ 211.3, 114.2, 36.0, and 32.7 can be assigned to the three carbonyl groups, the olefinic ring carbons bearing no hydrogen atoms, and the two types of CH_2 carbons, respectively, on the basis of their chemical shifts and off-resonance decoupling experiments. The mass spectrum of $\text{C}_6\text{H}_8\text{Fe}(\text{CO})_3$ (III) exhibited the expected molecular ion and the ions formed by successive carbonyl losses from the molecular ion.

The more strongly adsorbed product from 1,2-dimethylenecyclobutane and $\text{Fe}_3(\text{CO})_{12}$ is a yellow crystalline solid of stoichiometry $\text{C}_{12}\text{H}_{16}\text{Fe}(\text{CO})_2$. The mass spectrum of this complex when run under conditions leading to appreciable thermal decomposition in the mass spectrometer exhibited intense hydrocarbon ions up to $\text{C}_{12}\text{H}_{16}^+$ suggesting that two 1,2-dimethylenecyclobutane units are coupled

through carbon-carbon bond formation to give the $C_{12}H_{16}$ unit in $C_{12}H_{16}Fe(CO)_2$. Attempts to isolate the $C_{12}H_{16}$ ligand from this complex by oxidative degradation with ceric ammonium nitrate in ethanol solution gave a yellow oil with a sweet odor. This oil was too unstable for purification by evaporative vacuum distillation. The three highest m/e ions of significant relative intensity in the mass spectrum of this yellow oil corresponded to $C_{13}H_{16}O^+$ (i.e., $C_{12}H_{16} + CO$), $C_{12}H_{16}O^+$, and $C_{12}H_{16}^+$.

The carbon-13 NMR spectrum of the $C_{12}H_{16}$ ligand in $C_{12}H_{16}Fe(CO)_2$ exhibited two resonances corresponding to hydrogen-free carbons at δ 113.8 and 104.2 and four resonances corresponding to CH_2 carbons at δ 41.5, 32.1, 31.9, and 27.2. This indicates that the $C_{12}H_{16}$ ligand contains a plane of symmetry leading to six nonequivalent pairs of carbon atoms rather than 12 individually different carbon atoms. The carbon-13 NMR spectrum of the $C_{12}H_{16}$ ligand in $C_{12}H_{16}Fe(CO)_2$ also indicates the absence of hydrogen migration in the formation of this $C_{12}H_{16}$ ligand from two 1,2-dimethylenecyclobutane units.

This analysis of the carbon-13 NMR spectrum of $C_{12}H_{16}Fe(CO)_2$ suggests structure IV for this complex. The $C_{12}H_{16}$ unit in this structure functions as a chelating bis(η^3 -allyl) ligand and contains the required plane of symmetry. The coordination around the iron atom in $C_{12}H_{16}Fe(CO)_2$ (IV) is thus completely analogous to that in the unsubstituted $(C_3H_5)_2Fe(CO)_2$ (XIII).²³



XIII

The formation of the unusual complex $C_{12}H_{16}Fe(CO)_2$ (IV) from the 1,3-diene I and iron carbonyls raised the question as to whether similar complexes could be formed from the other types of 1,3-diene reactions. Attempts to prepare a related complex by reaction of butadienetricarbonyliron with 1,2-dimethylenecyclobutane were unsuccessful. Furthermore, reaction of the 1,2-dimethylenecyclobutane complex $C_6H_8Fe(CO)_3$ (III) with excess 1,2-dimethylenecyclobutane in boiling benzene similar to the conditions used to prepare $C_{12}H_{16}Fe(CO)_2$ from $Fe_3(CO)_{12}$ and 1,2-dimethylenecyclobutane did not give any $C_{12}H_{16}Fe(CO)_2$ (IV) thereby suggesting that $C_6H_8Fe(CO)_3$ (III) is not an intermediate in the formation of $C_{12}H_{16}Fe(CO)_2$ (IV). In addition, attempts to prepare related complexes $C_{12}H_{16}M(CO)_3$ ($M = Cr$ and Mo) from reactions of 1,2-dimethylenecyclobutane with the very reactive acetonitrile complexes²¹ *fac*-(CH_3CN)₃ $M(CO)_3$ ($M = Cr$ and Mo) were unsuccessful.

The reactions of iron carbonyls with 1,2-dimethylenecyclobutane derivatives containing a third carbon-carbon double bond located in the cyclobutane ring such as the hydrocarbons VI and IX proceeded entirely differently from the reaction of iron carbonyls with 1,2-dimethylenecyclobutane discussed above. The hydrocarbon 3,4-dimethylenecyclobutene (VI), an isomer of benzene, is so unstable with respect to polymerization that very mild reaction conditions were necessary to form iron carbonyl complexes. The best results were obtained by using $Fe_2(CO)_9$ in tetrahydrofuran, a system recently shown by Cotton and Troup²⁴ to be effective for preparing iron tetracarbonyl complexes under extremely mild conditions.

The reaction of 3,4-dimethylenecyclobutene with $Fe_2(CO)_9$ in tetrahydrofuran at room temperature gave a very unstable yellow liquid product shown to be $C_6H_6Fe(CO)_4$ by its elemental analyses and $\nu(CO)$ frequencies at 2091, 2031, 2013, and 2002 cm^{-1} similar to the $\nu(CO)$

frequencies at 2105, 2042, 2029, and 2008 found for the acrylonitrile complex²⁵ $CH_2=CHCNFe(CO)_4$ after making some allowance for the electron-withdrawing effects of the cyano group in the latter complex. The proton and carbon-13 NMR spectra of a sample of $C_6H_6Fe(CO)_4$ which had not been heated above room temperature at any point during its preparation indicated formulation as the symmetrical isomer VII on the basis of only three resonances of the appropriate multiplicities for the six C_6H_6 ring carbons on the carbon-13 NMR spectrum. However, mild warming of this $C_6H_6Fe(CO)_4$ derivative, even to the extent required for evaporative vacuum distillation, resulted in its isomerization to the unsymmetrical isomer VIII as indicated by the disappearance of the NMR patterns from the symmetrical isomer VII and the appearance of new NMR patterns with six carbon-13 resonances for the six C_6H_6 ring carbons.

The positions of the carbon-13 NMR resonances in the two isomers of $C_6H_6Fe(CO)_4$ also support the proposed structures VII and VIII. The carbon-13 NMR spectrum of the free ligand 3,4-dimethylenecyclobutene (VI) exhibits resonances at δ 150.0, 146.0, and 94.4 shown by off-resonance decoupling to correspond to the hydrogen-free carbon, the CH carbon, and the CH_2 carbon, respectively. In the carbon-13 NMR spectrum of *sym*- $C_6H_6Fe(CO)_4$ the CH carbon resonance is shifted far upfield to δ 61.0 whereas the other two C_6H_6 carbon resonances remain within 5 ppm of their positions in the free ligand. In the carbon-13 NMR spectrum of *unsym*- $C_6H_6Fe(CO)_4$ both hydrogen-free carbon and CH_2 carbon resonances are shifted far upfield to δ 81.7 and 25.2, respectively, whereas the other four C_6H_6 carbon resonances remain within 11 ppm of their positions in the free ligand.

The hydrocarbon bicyclo[3.2.0]hepta-1,4,6-triene (IX), although still extremely sensitive to polymerization and oxidation,¹⁵ nevertheless was sufficiently more stable than 3,4-dimethylenecyclobutene (VI) that it reacted with $Fe_3(CO)_{12}$ in boiling benzene without excessive polymerization to give a liquid $C_7H_6Fe(CO)_3$ derivative in ~40% yield. The proton and carbon-13 NMR spectra of $C_7H_6Fe(CO)_3$ indicated rearrangement of the C_7H_6 ligand with hydrogen migration but without carbon-carbon bond cleavage to give a product of structure X. In the proton NMR spectrum of $C_7H_6Fe(CO)_3$ (X) the two double triplets at τ 4.27 and 4.61 can be assigned to the two nonequivalent uncomplexed olefinic protons in the five-membered ring, the two closely spaced singlets at τ 6.50 and 6.54 can be assigned to the two slightly nonequivalent cyclobutadiene protons, and the triplet at τ 7.56 can be assigned to the CH_2 protons of the five-membered ring. In the carbon-13 NMR spectrum of $C_7H_6Fe(CO)_3$ (X) the four carbons of the complexed cyclobutadiene ring appear at δ 97.2, 88.6, 55.4, and 52.9, the CH_2 (aliphatic) carbon of the five-membered ring appears at δ 34.6, and the two uncomplexed olefinic carbons of the five-membered ring appear at δ 138.1 and 126.3, respectively.

One interesting feature of this work is the discovery of conditions where hydrocarbons unstable in the pure state at room temperature such as VI and IX can be successfully converted to iron carbonyl complexes without total loss of the unstable hydrocarbon through oligomerization, polymerization, or other side reactions. However, as expected there appears to be a lower limit to the stability of hydrocarbons which can be used for syntheses of this type. For example, none of our attempts to prepare iron carbonyl complexes of the extremely sensitive hydrocarbon 1,2,3,4-tetramethylenecyclobutane (XIV)²⁶ using either $Fe_2(CO)_9$ in pentane at room temperature or $Fe_3(CO)_{12}$ in boiling hexane gave any new iron carbonyl complexes apparently

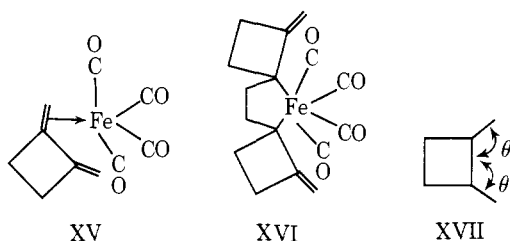


XIV

because the hydrocarbon XIV polymerized rather than reacted with the iron carbonyl despite the presence of several 1,3-diene functionalities in XIV suitable for forming iron carbonyl complexes.

Discussion

The most unusual feature of this work is the discovery of a new type of complex, $C_{12}H_{16}Fe(CO)_2$, formed by a reaction of a 1,3-diene with iron carbonyls. Formation of $C_{12}H_{16}Fe(CO)_2$ (IV) from 1,2-dimethylenecyclobutene and iron carbonyls can involve the intermediate olefin-iron tetracarbonyl complex XV analogous to VIII obtained from 3,4-dimethylenecyclobutene (VI) and $Fe_2(CO)_9$. Such an olefin-iron tetracarbonyl complex XV can couple with a second 1,2-dimethylenecyclobutane to form a diolefinic metallocyclic intermediate such as XVI. Displacement of two carbonyl groups in XVI by the two uncomplexed carbon-carbon bonds can then lead to the observed product IV. The interesting question arising from this work is why 1,2-dimethylenecyclobutane appears to be unique among 1,3-dienes in its reaction with $Fe_3(CO)_{12}$ to form IV as well as the usual III.



A survey of metal complexes of planar unsaturated carbon systems in 1969²⁷ indicated that only networks of sp^2 carbon atoms with a diameter (maximum carbon-carbon distance) of no more than 2.1 carbon-carbon bond lengths could form complexes in which all carbon atoms of the network are bonded to a single metal atom. If the exocyclic methylene groups in 1,2-dimethylenecyclobutane bisect the exterior angles of the cyclobutane square as would be expected for minimization of the total angular strain (i.e., the angle θ in structure XVII is 135°), then the diameter of the network of the four sp^2 carbon atoms of the 1,2-dimethylenecyclobutane system is 2.414 which is greater than the 2.1 limiting value. In order for the diameter of the 1,2-dimethylenecyclobutane system to decrease to the 2.1 limiting value the exocyclic methylene groups must approach each other until the angle θ is 123.3° (i.e., $90^\circ + \arcsin((2.1 - 1)/2)$) thereby increasing the total angular strain. That this distortion of the exocyclic methylene groups is possible is suggested by the ability to isolate the (diene) $Fe(CO)_3$ complex III from the reaction between 1,2-dimethylenecyclobutane and $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$. However, this necessary distortion of the exocyclic methylene groups in converting the olefin-iron tetracarbonyl XV to the diene-iron tricarbonyl III creates an energy barrier for bonding the second carbon-carbon double bond of 1,2-dimethylenecyclobutane to the same metal atom as the first double bond. This energy barrier means that other reaction pathways of the olefin-iron tetracarbonyl XV such as the successive formation of XVI and finally IV can compete effectively with the more normal collapse of XV to give III. In all of the 1,3-dienes which have been treated with iron carbonyls up to the present time⁷ there are no structural reasons for a similar

energy barrier for bonding the second carbon-carbon double bond of the 1,3-diene to the metal atom after the first carbon-carbon double bond of this 1,3-diene has already been bonded to the same metal atom. In this way simple angular strain and maximum diameter considerations can account for the unique behavior of 1,2-dimethylenecyclobutane in its reactions with iron carbonyls.

The interesting feature of the reaction of 3,4-dimethylenecyclobutene (VI) with $Fe_2(CO)_9$ is the formation of the two isomers of $C_6H_6Fe(CO)_4$ (VII and VIII). The thermal conversion of the symmetrical isomer VII to the unsymmetrical isomer VIII is similar to some reported²⁸ interconversions of shift isomeric tetrahapto iron tricarbonyl complexes of 1,6-disubstituted hexatrienes and 1,8-trisubstituted octatetraenes where a metal atom which only bonds to a portion of a network of sp^2 carbon atoms can move throughout the network to form stable isomeric products where the number of carbon atoms from the network bonding to a metal atom is constant. The failure to obtain an iron tricarbonyl complex from 3,4-dimethylenecyclobutene (VI) and iron carbonyls can be attributed to the instability of this hydrocarbon under conditions required for the decarbonylations.

The formation of the cyclobutadiene complex $C_7H_6Fe(CO)_3$ (X) from IX and $Fe_3(CO)_{12}$ appears to be the first reported example of the formation of a cyclobutadiene-metal complex by a hydrogen migration reaction. The ability for iron carbonyls to cause similar diolefin isomerizations involving hydrogen migration is exemplified by reactions of iron carbonyls with nonconjugated dienes such as 1,4-pentadiene^{6,7} and 1,4-cyclohexadiene^{6,7} to form iron tricarbonyl complexes of the corresponding conjugated dienes. The bicyclic C_7H_6 cyclobutadiene ligand in $C_7H_6Fe(CO)_3$ (X) is closely related structurally to the C_8H_7 dihydropentalenyl ligand in $C_8H_7Mn(CO)_3$ (XI)¹⁶ and the C_9H_8 indene ligand in $C_9H_8Cr(CO)_3$ (XII).¹⁷

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Axial Ligation Modes in Iron(III) Porphyrins. Models for the Oxidized Reaction States of Cytochrome P-450 Enzymes and the Molecular Structure of Iron(III) Protoporphyrin IX Dimethyl Ester *p*-Nitrobenzenethiolate

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Abstract: Cytochrome P-450 monooxygenase enzymes contain a protoporphyrin IX prosthetic group and exhibit five reaction states, in each of which the nature of axial ligation to Fe(II, III) is uncertain. The occurrence of sulfur coordination has been a matter of active speculation. The two oxidized states, ox-P-450 (resting, low spin) and ox-P-450·S (substrate bound, high spin), contain Fe(III) with apparent six and five coordination, respectively. In an attempt to develop experimental criteria for identifying axial ligands in iron(III) porphyrins, the series of complexes Fe(P)L (high spin) and Fe(P)LL' (low spin), P = octaethylporphyrin, protoporphyrin IX dimethyl ester (PPIXDME) dianions, have been isolated and generated in situ, respectively, and subjected to detailed physical studies. Axial ligands L and L' include a variety of oxygen, sulfur, and nitrogen donors intended to model possible protein side chain coordination. Isolable Fe(P)SR complexes were obtained with R = aryl. The crystal structure of Fe(PPIXDME)(SC₆H₄-*p*-NO₂) has been determined by x-ray diffraction techniques utilizing 6320 observations collected by counter methods. The compound crystallizes in space group *C*₁¹-*P*¹ with two molecules in a cell of dimensions *a* = 13.585 (6), *b* = 14.016 (2), *c* = 13.297 (2) Å, α = 110.83 (2), β = 119.74 (2), and γ = 62.60 (2)°. The observed density of 1.35 (2) g cm⁻³ compares favorably with the calculated density of 1.378 g cm⁻³. Refinement of an anisotropic model (497 variables) by full-matrix least-squares methods leads to a conventional *R* index (on *F*²) of 0.126 for the 6320 observations and to a conventional *R* index (on *F*) of 0.071 for the 3225 observations having *F*_o > 3σ(*F*_o). The molecule exhibits near square pyramidal geometry with an Fe-S distance of 2.324 (2) Å and Fe-N distances ranging from 2.042 (5) to 2.081 (5) and averaging to 2.064 Å. The iron atom is 0.448 Å above the mean plane of the porphyrin core, which is nearly planar (mean deviation from the mean plane is 0.038 Å) but exhibits a slight ruffling that corresponds roughly to an S₄ distortion. Although the mean dimensions within the porphyrin agree well with previously reported values, there is a perceptible alternation in the lengths of the C_b-C_a bonds around the periphery of the porphyrin as well as an alternation of the C_a-C_m bonds such that there occurs a long-short-long-short . . . sequence of C_b-C_a, C_a-C_m, C_m-C_a, C_a-C_b bonds. The phenyl ring makes a dihedral angle of 11.1° with the porphyrin plane, and is situated away from the bulky propionic ester substituents. Extensive compilations of results are presented and include (i) electronic spectral data, (ii) principal *g* values evaluated from EPR spectra, (iii) Mössbauer parameters, (iv) effective magnetic moment values and crystal field parameters obtained from field dependent (≤60 kOe) magnetization data. Of the species Fe(P)L (L = ArS⁻, ArO⁻, OAc⁻) and acid-metmyoglobin or hemoglobin, Fe(PPIXDME)(SAr) complexes provide the closest approach to the optical, EPR, and Mössbauer properties of ox-P-450·S. Of interest are the values of the saturation magnetic hyperfine field at the Fe nucleus, obtained from high-field (≤80 kOe) Mössbauer and magnetization measurements at 4.2 K. For L = O- and N-donor ligands *H*_{hf}⁰ ≥ -500 kOe whereas *H*_{hf}⁰ = -476 ± 10 and -448 ± 10 kOe for Fe(PPIXDME)(SC₆H₄-*p*-NO₂) and ox-P-450_{cam}·S, respectively. Low-temperature optical and EPR spectra of Fe(P)LL' complexes (L = N-, O-, S-donor ligands) together with data for cytochromes *b* and *c*, when compared with corresponding enzyme properties, indicate thiolate sulfur coordination in ox-P-450. With the provisos that not all possible axial ligation modes of the enzyme, simulated by L or L/L' combinations, could be experimentally tested and that synthetic porphyrins may have limitations as models of biological heme coordination the following conclusions are drawn: (i) the most probable axial ligation mode in the ox-P-450·S state is Cys-S-Fe; (ii) the most probable modes in the ox-P-450 state are Cys-S-Fe-L', with L' = His, Lys(Arg), Cys-SH, Met, and Asn(Gln). No further conclusions regarding L' could be drawn from the experimental data obtained here.

The cytochrome P-450 enzymes are prominent members of the monooxygenase (mixed-function oxidase) class of enzymes which catalyze the incorporation of one atom of dioxygen into a substrate while the other is reduced to water. The P-450 enzymes, also designated as cytochromes *m* in a recent nomenclature proposal,² are found in mammalian microsomes and mitochondria, and in bacteria. They have been implicated in the mammalian metabolism

of lipids and steroids, amino acid biosynthesis, oxidative degradation of numerous xenobiotics, and facilitate yeast and bacterial growth on nonphysiological carbon sources. The biological and physical properties of these enzymes have been summarized or reviewed elsewhere.³⁻⁹

A significant advance in clarifying the nature of P-450-dependent oxygenase reactions has been the isolation, purification, and crystallization of the cytochrome P-450 en-