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Organometallic Chemistry of the Transition Metals. IX. Reactions between Metal Carbonyls and Dimethylaminofulvenes[1]

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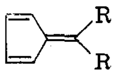
Received December 16, 1963

The hexacarbonyls of chromium and molybdenum react with 6-dimethylaminofulvene and 6,6-bis(dimethylamino)fulvene to form dark red to yellow complexes of the general formula (fulvene)M(CO)$_3$ (M = Cr or Mo). Iron pentacarbonyl reacts with 6-dimethylaminofulvene to give mainly a red compound, $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$, m.p. 175–177°. A minor by-product in this reaction is a red isomer, m.p. 238–241°. The conversion of the $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$, m.p. 175–177°, to the orange methyl derivative $[C_5H_4CHN(CH_3)_2Fe(CO)_2CH_3]_2$ is described.

Introduction

Several years ago the reactions between various 6,6-dialkylfulvenes (I) and the hexacarbonyls M(CO)$_6$ (M = Mo or W) were described.[2] In each case uptake of hydrogen from the solvent or excess fulvene was noted and substituted cyclopentadienylmetal tricarbonyl dimers (II) were obtained.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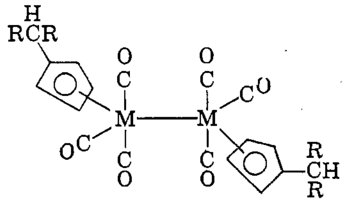
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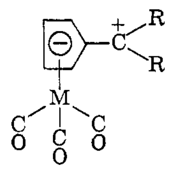
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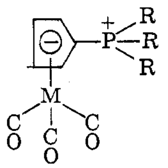
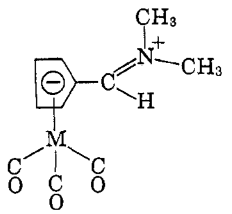
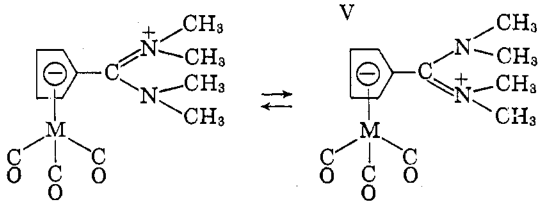

IV

A possible intermediate in the formation of II from I and M(CO)$_6$ is the zwitterionic monomeric derivative III, analogous to triphenylphosphoniumcyclopentadienylidemolybdenum tricarbonyl (IV)[3] but with a positively charged carbon atom instead of the positively charged phosphorus atom in IV. In contrast to the relatively stable tetracovalent positively charged phosphorus atom in IV, the tricovalent electrophilic positively charged carbon atom in III would be expected to be very reactive, tending to acquire a fourth group to attain the favored covalency of four. Thus, it is reasonable to expect III to abstract hydrogen and dimerize to form II.

It appeared possible to stabilize derivatives similar to III if the R groups attached to the positively charged carbon atom were of a type which would delocalize this positive charge. An obvious R group to accomplish this purpose is a dialkylamino group which would form derivatives (V) where the nitrogen atom would receive most of the positive charge.

Such considerations prompted us to investigate the reactions between 6-dimethylaminofulvene[4,5] and 6,6-bis(dimethylamino)fulvene[4,6] and the hexacarbonyls of chromium, molybdenum, and tungsten hoping to obtain compounds related to V. In this paper we describe the preparation and properties of the chromium and molybdenum derivatives of general structures V and VI (R = methyl). Due to the relative inertness of tungsten hexacarbonyl[7] conditions suitable for preparing the chromium and molybdenum derivatives were not suitable for preparing the analogous tungsten derivatives.


V


VIa VIb

Several iron complexes from reactions between iron carbonyls (mainly Fe$_2$(CO)$_9$) and various fulvenes, generally under rather mild conditions, have also been described.[8] In our work with dimethylaminofulvene, iron pentacarbonyl under relatively vigorous conditions (~135° for several hours) was found to give relatively good yields of $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$ and much smaller quantities of a closely related iso-

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[1] For part VIII of this series see R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 796 (1964).

[2] E. W. Abel, A. Singh, and G. Wilkinson, *J. Chem. Soc.*, 1321 (1960).

[3] E. W. Abel, A. Singh, and G. Wilkinson, *Chem. Ind.* (London), 1067 (1959).

[4] Subsequently in this paper the designations "dimethylaminofulvene" and "bis(dimethylamino)fulvene" will refer to 6-dimethylaminofulvene and 6,6-bis(dimethylamino)fulvene, respectively.

[5] (a) H. Meerwein, W. Florian, N. Schön, and G. Stopp, *Ann.*, **641**, 1 (1961); (b) K. Hafner, K. H. Vöpel, G. Ploss, and C. König, *ibid.*, **661**, 52 (1963).

[6] K. Hafner, private communication.

[7] R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3590 (1961); R. B. King, Ph.D. Thesis, Harvard University, 1961.

[8] E. Weiss and W. Hübel, *Ber.*, **95**, 1186 (1962).

Table I

Dimethylaminofulvene–Metal Tricarbonyl Complexes

Compound	Color	M.p.	Yield (unrecrystallized), %		Analyses C	H	N	O	Metal
(1) $C_5H_4CHN(CH_3)_2Cr(CO)_3$	Red-violet	218–222° dec.	69	Calcd.	51.3	4.3	5.4	18.7	20.2
				Found	50.1	4.4	5.1	19.6	19.6
(2) $C_5H_4CHN(CH_3)_2Mo(CO)_3$	Red	Dec. 230–240° without melting	90	Calcd.	43.8	3.7	4.7	16.0	31.9
				Found	43.3	4.0	4.7	16.2	31.6
(3) $C_5H_4C[N(CH_3)_2]_2Cr(CO)_3$	Red	241–243° dec.	9[a]	Calcd.	45.4	4.6	8.2	14.0	27.9
				Found	44.3	5.2	7.9	14.4	28.0
(4) $C_5H_4C[N(CH_3)_2]_2Mo(CO)_3$	Yellow	281–284° dec.	93	Calcd.	52.0	5.3	9.3	16.0	17.3
				Found	51.9	5.5	9.1	15.9	17.0

[a] Much unchanged $Cr(CO)_6$ and bis(dimethylamino)fulvene were recovered.

meric material. This paper also describes the preparation, properties, and some reactions of these iron carbonyl complexes.

Experimental

Infrared spectra were generally taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 21 spectrometer. In addition, the metal carbonyl and carbon–nitrogen double bond regions of the infrared spectra of selected compounds were investigated in greater detail in halocarbon oil mulls on a Beckman IR-9 spectrometer. Ultraviolet spectra were taken in dioxane solution and recorded on a Cary Model 14 spectrometer. Proton n.m.r. spectra were taken in chloroform and hexadeuterioacetone (Merck Sharp and Dohme of Canada) solutions and recorded on a Varian A-60 spectrometer. Microanalyses and molecular weight determinations (Mechrolab vapor pressure osmometer in benzene solution for the iron complexes) were carried out by Pascher Mikroanalytisches Laboratorium, Bonn, Germany, and Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Reagents.—Tetrahydrofuran was freshly distilled over lithium aluminum hydride immediately before use. The sources of the various metal carbonyls have been indicated in previous papers of this series.

Dimethylaminofulvene.[5]—This fulvene was obtained essentially by the procedure of Hafner, *et al.*,[5b] from the adduct of dimethylformamide and triethyloxonium tetrafluoroborate and sodium cyclopentadienide in tetrahydrofuran. The product was isolated as pale yellow crystals, m.p. 66.5–67° (lit. 67°,[5a] 68°[5b]) in 53% yield by pentane extraction, crystallization, and vacuum sublimation similar to the isolation of bis(dimethylamino)fulvene described below.

Proton N.m.r. Spectrum.—Resonance (CS_2 solution) at τ 3.23 (singlet), 3.73 (triplet, J = 2 c.p.s.), 3.94 (triplet, J = 2 c.p.s.), and 6.98 (singlet) of relative intensities 1:2:2:6.

Bis(dimethylamino)fulvene.—Hafner[8] has indicated the preparation of this fulvene by treatment of the diethyl acetal of tetramethylurea with cyclopentadiene. We prepared bis(dimethylamino)fulvene by an adaptation of the reaction used above for the preparation of dimethylaminofulvene.

A mixture of 80 g. (420 mmoles) of triethyloxonium tetrafluoroborate[9] and 46.4 g. (400 mmoles) of tetramethylurea was heated gently with stirring such that the diethyl ether formed in the reaction refluxed at a steady rate. After ~1 hr. this oily mixture was added at 0° to a solution of sodium cyclopentadienide prepared from 46.0 g. (1000 mg.-atoms of sodium) of a 50% sodium dispersion in mineral oil and 125 ml. (~1500 mmoles) of freshly cracked cyclopentadiene in 450 ml. of tetrahydrofuran.

After stirring the straw-colored reaction mixture for several hours at room temperature, tetrahydrofuran was removed at ~30 mm. The residue was dried at 25° (1 mm.) until it could be readily removed from the flask. It was then transferred to the thimble of a Soxhlet extraction apparatus and extracted continuously with ~500 ml. of boiling pentane heated with an oil bath. The use of a nitrogen atmosphere was avoided since the pentane vapors protected the fulvene sufficiently from oxidation.

During the extraction process much of the bis(dimethylamino)fulvene precipitated from the pentane solution. To ensure complete separation of the product the extract was cooled to −78°. The crystals of bis(dimethylamino)fulvene were filtered and purified finally by sublimation at 78° (0.5 mm.). The yield of pale yellow crystalline bis(dimethylamino)fulvene, m.p. 82–84°, was 15.0 g. (23%). When spilled on the skin, bis(dimethylamino)fulvene left red stains.

Anal. Calcd. for $C_9H_{16}N_2$: C, 73.2; H, 9.8; N, 17.1. Found: C, 72.9; H, 9.8; N, 17.4.

Infrared Spectrum.—C–H bands at 3030 (w), 2970 (vw), 2900 (m), and 2860 (sh) cm.$^{-1}$; other bands at 1540 (s), 1525 (s), 1480 (m), 1470 (m), 1455 (sh), 1440 (m), 1420 (m), 1400 (m), 1380 (s), 1355 (s), 1340 (s), 1325 (m), 1230 (w), 1198 (w), 1137 (sh), 1130 (s), 1095 (s), 1064 (m), 1055 (m), 1050 (m), 1018 (m), 933 (s), 890 (m), 728 (s), and 712 (m) cm.$^{-1}$.

Proton N.m.r. Spectrum.—Resonances at τ 3.75 (complex multiplet) and 6.95 (singlet) of relative intensity 4:12.

Reactions of Chromium and Molybdenum Hexacarbonyls with the Dimethylaminofulvenes.—A mixture of 10 mmoles of chromium or molybdenum hexacarbonyl and 10 mmoles of dimethylaminofulvene or bis(dimethylamino)fulvene in 40–50 ml. of an alkylcyclohexane was refluxed ~20 hr. under nitrogen with magnetic stirring. The molybdenum hexacarbonyl reactions were conducted in methylcyclohexane and the chromium hexacarbonyl reactions in ethylcyclohexane. The reaction mixture gradually turned to the yellow or dark red color of the product.

After cooling to room temperature, the insoluble product was removed by filtration. Washing with several portions of pentane ensured removal of any impurities (such as unreacted fulvene) soluble in hydrocarbons. Heating the crude product at 50–70° (0.1 mm.) for several hours ensured removal of any unchanged chromium or molybdenum hexacarbonyl.

The products were purified finally by recrystallization either from dichloromethane–hexane or preferably from acetone–benzene mixtures. The rather low solubilities, especially of the bis(dimethylamino)fulvene complexes, made such recrystallizations difficult and molecular weight determinations (osmometer) unreliable.

The general properties and analyses of the four dialkylaminofulvene–metal tricarbonyl complexes are listed in Table I; spectroscopic properties (infrared, ultraviolet, visible, and proton n.m.r.) are listed in Table II. The bis(dimethylamino)fulvene complexes were insufficiently soluble for satisfactory proton n.m.r. spectra. Even in hexadeuterioacetone the resonances due to the twelve methyl protons were very weak. The molybdenum complex $C_5H_4C[N(CH_3)_2]_2Mo(CO)_3$ appeared to be too sparingly soluble and unstable in dioxane to obtain a reliable ultraviolet spectrum. Conductivity measurements in acetone on all four compounds clearly indicated them to be nonconductors.

Reaction between Dimethylaminofulvene and Iron Pentacarbonyl.—A mixture of 10 ml. (14.6 g., 74.5 mmoles) of iron

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(9) H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, and G. Willfang, *J. prakt. Chem.*, **154**, 83 (1939).

TABLE II

SPECTROSCOPIC PROPERTIES OF DIMETHYLAMINOFULVENE–METAL TRICARBONYL COMPLEXES

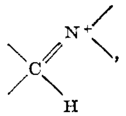
(A) Infrared spectra, cm.$^{-1}$

Compound	Metal carbonyl bands[a]	C=N bands[a]	Other bands[b,c]
(1) $C_5H_4CHN(CH_3)_2Cr(CO)_3$	1909 (s), 1820 (sh), 1788 (s)	1623 (s)	1455 (vw), 1420 (sh), 1413 (m), 1405 (w), 1375 (m), 1285 (w), 1130 (w), 1050 (vw), 933 (w), 815 (w), 687 (w)
(2) $C_5H_4CHN(CH_3)_2Mo(CO)_3$	1908 (s), 1815 (sh), 1785 (s)	1617 (s)	1445 (vw), 1417 (w), 1410 (w), 1400 (w), 1362 (m), 1280 (vw), 1126 (w), 1050 (vw), 934 (vw), 920 (vw), 798 (w)
(3) $C_5H_4C[N(CH_3)_2]_2Cr(CO)_3$	1914 (s), 1799 (s), 1777 (s)	1572 (m), 1525 (m)	1470 (m), 1460 (m), 1428 (w), 1415 (m), 1400 (m), 1386 (vw), 1370 (w), 1300 (w), 1230 (vw), 1200 (vw), 1160 (w), 1145 (vw), 1135 (vw), 1104 (m), 1068 (w), 1060 (w), 1056 (w), 1042 (vw), 942 (w), 890 (sh), 885 (w), 847 (vw), 812 (w), 726 (vw), 686 (w)
(4) $C_5H_4C[N(CH_3)_2]_2Mo(CO)_3$	1914 (s), 1803 (s), 1783 (s)	1571 (m), 1525 (m)	1470 (s), 1455 (s), 1420 (sh), 1410 (s), 1400 (s), 1360 (s), 1245 (m), 1226 (vw), 1195 (vw), 1157 (w), 1142 (w), 1132 (w), 1096 (s), 1060 (s), 1055 (m), 1036 (w), 940 (m), 887 (w), 885 (sh), 843 (vw), 835 (vw), 796 (m), 720 (w)

(B) Ultraviolet and visible spectra in dioxane solution, mμ

Compound	Maxima[d]
(1) $C_5H_4CHN(CH_3)_2Cr(CO)_3$	222 (28,100), 264 (19,100), 324 (5980), 471 (5560)
(2) $C_5H_4CHN(CH_3)_2Mo(CO)_3$	222 (12,700), 253 (11,500), 319 (8140), 442 (2910)
(3) $C_5H_4C[N(CH_3)_2]_2Cr(CO)_3$	220 (19,500), 269 (12,200), 343 (3660), 512 (2450)
(4) $[C_5H_5Mo(CO)_3]_2$	222 (32,350), 388 (18,600), 509 (1370)

(C) Proton n.m.r. spectra in hexadeuterioacetone solution

Compound	 τ	Five-membered ring protons, τ	Methyl protons, τ
(1) $C_5H_4CHN(CH_3)_2Cr(CO)_3$	2.18	4.91	6.54, 6.70
(2) $C_5H_4CHN(CH_3)_2Mo(CO)_3$	1.99	4.34,[e] 4.49[e]	6.59, 6.70
(3) $C_5H_4C[N(CH_3)_2]_2Cr(CO)_3$[f]	...	Not observed[f]	6.66
(4) $C_5H_4C[N(CH_3)_2]_2Mo(CO)_3$[f]	...	Not observed[f]	6.68

[a] Beckman IR-9 spectrometer, halocarbon oil mulls. [b] Perkin-Elmer Model 21 spectrometer, KBr pellets. [c] The C–H bands in these compounds (at ~3000 cm.$^{-1}$) when observable at all were very weak. Since they were not consistently observed in all four compounds, they are not given in this table. [d] Extinction coefficients given in parentheses. [e] Triplets, $J = \sim 2$ c.p.s. [f] Saturated solutions of these compounds in hexadeuterioacetone were too weak for satisfactory n.m.r. spectra to be obtained. Only the methyl resonances could be unequivocally observed.

pentacarbonyl, 6.0 g. (50 mmoles) of dimethylaminofulvene, and 250 ml. of ethylcyclohexane was refluxed 21 hr. under nitrogen with magnetic stirring. The reaction mixture was allowed to cool to room temperature and then filtered by gravity. Solvent was removed from the dark red filtrate at ~0.5 mm. The red crystals remaining were extracted with 150 ml. of benzene in several portions and the filtered extracts chromatographed on a 5 × 45 cm. alumina column. The chromatogram was developed with benzene. A large dark red band followed by a smaller red band appeared. A brown band remained at the top of the column and the second red band was immediately preceded by a very small green band. The brown and green bands appeared to contain only very small amounts of rather intractable oils and were not further investigated. The first red band was eluted with benzene and the second red band with dichloromethane. Both eluates were filtered and solvent was removed from the filtrate at ~30 mm., leaving behind red crystalline solids which were washed with pentane and dried.

The benzene eluate from the first red band gave 5.4 g. (46.3% yield) of $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$ (isomer A), m.p. 175–177°, after one recrystallization from dichloromethane–hexane. The dichloromethane eluate from the second red band gave 0.4 g. (3.4% yield) of $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$ (isomer B), m.p. 237–240°, which was not recrystallized.

Anal. Calcd. for $C_{20}H_{22}N_2O_4Fe_2$: C, 51.4; H, 4.7; N, 6.0 Fe, 23.9; O, 13.7; mol. wt., 466. Found (isomer A): C, 50.7 51.9; H, 4.7, 4.8; N, 6.0, 6.0; Fe, 24.4, 23.6; O, 14.4, 13.6 mol. wt., 523. Found (isomer B): C, 51.6, 51.6; H, 4.9, 4.7 N, 6.0, 6.1; Fe, 23.7, 23.3; O, 13.6, 15.3; mol. wt., 471.

Infrared Spectra.—Isomer A: C–H bands at 3040 (vw), 2890 (m), 2810 (sh), and 2750 (m) cm.$^{-1}$; see Table III for terminal and bridging metal carbonyl bands; other bands at 1450 (m), 1402 (w), 1378 (w), 1363 (vw), 1348 (w), 1333 (sh), 1290 (vw), 1276 (vw), 1243 (w), 1203 (vw), 1188 (w), 1152 (vw), 1140 (vw), 1075 (w), 1057 (w), 1034 (m), 1010 (m), 967 (w), 925 (vw), 915 (w), 870 (w), 861 (w), 851 (w), 846 (w), 830 (w), 825 (sh), and 740 (w) cm.$^{-1}$. Isomer B: C–H bands at 3075 (w), 2900 (m), 2830 (w), 2800 (m), and 2750 (m) cm.$^{-1}$; see Table III for terminal and bridging metal carbonyl bands; other bands at 1470 (w), 1455 (m), 1438 (w), 1415 (vw), 1257 (w), 1183 (vw), 1169 (w), 1165 (m), 1146 (w), 1095 (w), 1087 (w), 1080 (w), 1042 (m), 1032 (m), 1020 (m), 998 (m), 860 (m), 845 (m), 826 (w), 764 (w), and 756 (m) cm.$^{-1}$.

Ultraviolet Spectra.—Isomer A: maximum at 342 mμ (ϵ 11,800); end absorption at 210 mμ (ϵ 40,700). Isomer B: maximum at 339 mμ (ϵ 11,800); end absorption at 210 mμ (ϵ 27,900). $[C_5H_5Fe(CO)_2]_2$: maxima at 217 mμ (ϵ 35,400) and 343 mμ (ϵ 12,000).

TABLE III

METAL CARBONYL BANDS IN SOME DIMETHYLAMINOFULVENE COMPLEXES OF IRON CARBONYL (CM.$^{-1}$)[a]

Compound	Terminal carbonyl bands	Bridging carbonyl bands
$[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$		
Isomer A	2000 (s), 1984 (s), 1937 (s)	1778 (s), 1768 (s)
Isomer B	1989 (s), 1947 (m)	1756 (s)
$[C_5H_4CHN(CH_3)_2Fe(CO)_2CH_3]_2$	1995 (s), 1940 (s)	None
$\{[C_5H_4CHNH(CH_3)_2Fe(CO)_2Cl]_2\}^{+2}$	2057 (s), 2006 (s), 1992 (s), 1983 (s)	1768 (s)

[a] Beckman IR-9 spectrometer, halocarbon oil mulls.

Visible Spectra.—Both isomers A and B showed a gradual decrease in absorption from 400 to 600 mμ with no maxima.

Proton N.m.r. Spectra.—Isomer A: resonances at τ ~4.9 (complex apparent unsymmetrical triplet[10]), 6.93 (singlet), and 7.78 (singlet) of relative intensities 8:2:12. Isomer B: resonances at τ 4.73 (broad), 5.23 (broad), 7.05 (singlet), and 8.00 (singlet) of relative intensities 4:4:2:12.

Preparation of $[C_5H_4CHN(CH_3)_2Fe(CO)_2CH_3]_2$.—A solution of 1.18 g. (2.5 mmoles) of $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$ (isomer A) in 60 ml. of tetrahydrofuran was stirred 1.5 hr. with a sodium amalgam prepared from 0.3 g. (13 mg.-atoms) of sodium metal and 4 ml. (~54 g.) of mercury. The dark red color of the $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$ soon became yellow-gray. After the reaction period was over, excess amalgam was removed and 1.0 ml. (2.28 g., 16 mmoles) of methyl iodide added. After stirring ~16 hr. at room temperature, solvent was removed from the reaction mixture at ~30 mm. Nitrogen was admitted and the residue extracted with three 50-ml. portions of dichloromethane. Solvent was removed from the filtered extracts at ~30 mm., leaving behind light orange-brown crystals which were washed with three 15-ml. portions of pentane and dried. After one recrystallization from dichloromethane–hexane, 0.5 g. (40% yield) of orange-brown crystalline $[C_5H_4CHN(CH_3)_2Fe(CO)_2CH_3]_2$, m.p. 170–171° dec., was obtained.

Anal. Calcd. for $C_{22}H_{28}N_2O_4Fe_2$: C, 53.2; H, 5.6; N, 5.5; mol. wt., 496. Found: C, 53.0; H, 5.5; N, 5.5; mol. wt., 454.

Infrared Spectrum.—C–H bands at 3080 (vw), 2940 (sh), 2925 (m), 2875 (m), 2850 (m), 2820 (m), and 2775 (m) cm.$^{-1}$; see Table III for terminal metal carbonyl bands; other bands at 1475 (m), 1445 (m), 1410 (br, sh), 1395 (w), 1375 (vw), 1355 (w), 1335 (w), 1262 (w), 1255 (w), 1215 (w), 1160 (s), 1094 (w), 1048 (m), 1030 (m), 1017 (s), 922 (w), 898 (m), 857 (m), 824 (s), 820 (s), 798 (w, br), and 730 (m) cm.$^{-1}$.

Ultraviolet Spectrum.—Shallow maximum at 352 mμ (ϵ 2760).

Visible Spectrum.—Gradual decrease in absorption from 400 to 600 mμ without any maxima.

Proton N.m.r. Spectrum.—Resonances at τ ~5.3 (complex multiplet[11]), 6.54 (singlet), 7.88 (singlet), and 9.92 (singlet) of relative intensities 8:2:12:6.

Other Reactions of $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$ (Isomer A). Iodine.—A mixture of 0.47 g. (1.0 mmole) of $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$ (isomer A), 0.38 g. (1.5 mmoles) of iodine, and 25 ml. of chloroform was refluxed 1 hr. under nitrogen. After removing excess iodine from the reaction mixture with excess aqueous sodium thiosulfate, 0.33 g. of a brown crystalline solid, m.p. 107° dec., was isolated on evaporation at ~30 mm. and purified by washing with pentane. Analysis indicated the product to be a mixture, partial loss of dimethylamino groups having occurred. The infrared spectrum exhibited terminal carbonyl bands at 2030 (vs), 2020 (vs), 1975 (vs), and 1965 (vs) cm.$^{-1}$ and a bridging carbonyl band at 1690 (s) cm.$^{-1}$. The ultraviolet spectrum of this product was almost identical with that of $C_5H_5Fe(CO)_2I$.

Hydrochloric Acid and Air.—Air was bubbled through a mixture of 0.47 g. (1 mmole) of $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$ (isomer A), 1.5 ml. of ~35% aqueous hydrochloric acid, 10 ml. of chloroform, and 10 ml. of 95% ethanol for 24 hr. Chloroform and ethanol lost by evaporation were replaced for the first 7 hr. but after this period the solvent was allowed to evaporate completely. At the end of the reaction period a dark red solid remained. This was washed with 25 ml. of dichloromethane followed by five 20-ml. portions of tetrahydrofuran and finally dried 20 hr. at 25° (0.2 mm.) to give 0.38 g. (62% yield) of hygroscopic dark red solid $\{[C_5H_4CHNH(CH_3)_2Fe(CO)_2Cl]_2\}Cl_2$.

This red solid was insoluble in pentane, dichloromethane, and tetrahydrofuran; sparingly soluble in acetone; and very soluble in water. The bright red aqueous solution (pH ~5) gave a tan precipitate with sodium tetraphenylborate. Its low solubility in the usual organic solvents and its hygroscopicity discouraged attempts at further purification.

Anal. Calcd. for $C_{20}H_{22}Cl_4NO_4Fe_2$: C, 39.3; H, 3.9; N, 4.6; Cl, 23.3; O, 10.5; Fe, 18.3. Found: C, 39.8; H, 4.2; N, 5.0; Cl, 21.5; O, 13.5; Fe, 16.3.

Infrared Spectrum.—N–H band at 3370 (m) cm.$^{-1}$; C–H bands at 3080 (vw, sh), 3040 (w), and 2925 (w) cm.$^{-1}$, see Table III for terminal and bridging metal carbonyl bands, other bands at 2680 (w), 1620 (w), 1473 (m), 1415 (w), 1282 (vw), 1246 (vw), 1160–1135 (vw, br), 1050 (w), 1032 (w), 990 (vw), 984 (vw), 930 (w), 864 (w), and 835 (vw) cm.$^{-1}$.

Conductivity.—A molar conductance of 775 ± 15 ohm^{-1} cm.^{2} mole^{-1} was found in aqueous solutions of four concentrations in the range 7.2×10^{-4} to 3.2×10^{-3} *M*.

Discussion

(A) Chromium and Molybdenum Complexes.—The dimethylaminofulvene–metal tricarbonyl complexes of chromium and molybdenum are red to yellow fairly air-stable high-melting solids. The molybdenum complexes are lighter in color than the corresponding chromium complexes and the bis(dimethylamino)fulvene complexes lighter in color than the corresponding dimethylaminofulvene complexes (Table I). All complexes, especially those of bis(dimethylamino)fulvene, are sparingly soluble in organic solvents, especially nonpolar ones. This low solubility made molecular weight determinations unreliable. Moreover, satisfactory proton n.m.r. spectra even in hexadeuterioacetone could not be obtained for the two bis(dimethylamino)fulvene complexes due to insufficient solubility.

The spectroscopic properties clearly indicate these complexes to have structures V and VI. The ultraviolet and visible spectra of three of the four complexes[12] exhibited a total of four maxima in analogous positions. On the other hand, the ultraviolet spectrum of $[C_5H_5Mo(CO)_3]_2$ lacks the maximum in the region 253–269 mμ present in all four dimethylaminofulvene–metal tricarbonyl complexes. In addition, the red colors of the dimethylaminofulvene–chromium tri-

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[10] Individual peaks at τ 4.74, 4.87, and 5.06.

[11] Discernible peaks at τ 5.22, 5.32, and 5.44.

[12] The complex $C_5H_4C[N(CH_3)_2]_2Mo(CO)_3$ was too insoluble and unstable in dioxane solutions for reliable ultraviolet and visible spectra to be obtained.

carbonyl complexes contrast with the green color of $[C_5H_5Cr(CO)_3]_2$[13] and the yellow to red colors of the dimethylaminofulvene–molybdenum tricarbonyl complexes differ distinctly from the red-purple color of $[C_5H_5Mo(CO)_3]_2$. Thus, the ultraviolet and visible spectra of the dimethylaminofulvene–metal tricarbonyl complexes appear to rule out dimeric structures with metal–metal bonds analogous to the cyclopentadienylmetal tricarbonyl dimers.

The infrared spectra of the dimethylaminofulvene–metal tricarbonyl complexes provide excellent evidence for structures V and VI. Thus, the infrared spectra of the complexes $C_5H_4CHN(CH_3)_2M(CO)_3$ besides exhibiting the usual strong metal carbonyl bands exhibit a single strong band at 1623 cm.$^{-1}$ (chromium complex) or at 1617 cm.$^{-1}$ (molybdenum complex) which may be assigned to the carbon–nitrogen double bond in structure V. The infrared spectra of the complexes $C_5H_4C[N(CH_3)_2]_2M(CO)_3$ exhibit two bands of medium intensity at 1572 and 1525 cm.$^{-1}$ (chromium complex) or at 1571 and 1525 cm.$^{-1}$ (molybdenum complex) which may be assigned to the carbon–nitrogen multiple bonds in structure VI. The lower frequencies of the carbon–nitrogen bonds in the bis-(dimethylamino)fulvene complexes (VI) as compared with the dimethylaminofulvene complexes (V) are scarcely surprising as the average carbon–nitrogen bond order in the former complexes cannot exceed 1.5 due to equal contributions of the resonance structures VIa and VIb.

The proton n.m.r. spectra (Table II) of the dimethylaminofulvene–metal tricarbonyl complexes also support structure V for these complexes. A resonance is observed at τ 2.18 (chromium complex) or τ 1.99 (molybdenum complex) which on the basis of its relative intensity may be assigned to the single proton bonded to the side-chain carbon atom of the fulvene also double bonded to the nitrogen. The low-field position of this resonance comparable to that of protons bonded to sp^2-hybridized ethylenic and aromatic carbon atoms rather than to protons bonded to sp^3-hybridized saturated aliphatic carbon atoms indicates that this proton is bonded to a carbon atom with sp^2-hybridization as required for the carbon–nitrogen double bond in structure V. The proton n.m.r. spectrum of the chromium complex $C_5H_4CHN(CH_3)_2Cr(CO)_3$ also exhibits a single resonance at τ 4.91 which may be assigned to the four protons of the five-membered ring π-bonded to the chromium atom. Chemical shifts of cyclopentadienyl protons π-bonded to a transition metal occur in this region as observed in numerous such compounds measured in this laboratory. The corresponding four protons of the molybdenum complex $C_5H_4CHN(CH_3)_2Mo(CO)_3$ exhibit two coupled triplets (J = 2 c.p.s.) at τ 4.34 and 4.49 in the proton n.m.r. spectrum indicating appreciable chemical shift differences between the two protons bonded to the two carbon atoms in α-positions and the two protons bonded to the two carbon atoms in β-positions relative to the carbon atom bearing the side chain. Finally both derivatives $C_5H_4CHN(CH_3)_2M(CO)_3$ exhibit *two* singlet methyl resonances of equal intensities at τ 6.54 and 6.70 (chromium complex) or τ 6.59 and 6.70 (molybdenum complex) indicating nonequivalence of the two methyl groups. In structure V the two methyl groups are nonequivalent due to restricted rotation around the carbon–nitrogen double bond. One of the methyl groups is located in a *cis* position relative to the five-membered ring π-bonded to the metal atom and in a *trans* position relative to the hydrogen atom; the other methyl group is in a *trans* position relative to the five-membered ring and in a *cis* position relative to the hydrogen atom. Thus the nonequivalence of the two methyl groups observed in the n.m.r. spectra of the $C_5H_4CHN(CH_3)_2M(CO)_3$ complexes as well as the strong band at 1623 or 1617 cm.$^{-1}$ in their infrared spectra clearly demonstrates the presence of the carbon–nitrogen double bond.

Although the preparation of the complexes $C_5H_4CHN(CH_3)_2M(CO)_3$ (M = Cr or Mo) is readily accomplished in good yield using the procedures described in the Experimental section, the attempted preparation of the tungsten analog $C_5H_4CHN(CH_3)_2W(CO)_3$ by heating tungsten hexacarbonyl with dimethylaminofulvene in refluxing ethylcyclohexane or cyclooctane did not give satisfactory results, unchanged starting materials being recovered or only black decomposition products being obtained.

(B) **Iron Complexes.**—The preparation of the chromium and molybdenum complexes described above made of interest an investigation of reactions of other types of metal carbonyls with the dimethylaminofulvenes. Previous results with dialkylfulvenes and iron carbonyls[8] suggested reactions between dimethylaminofulvenes and iron carbonyls. Heating iron pentacarbonyl with dimethylaminofulvene in boiling ethylcyclohexane gave two red crystalline products readily separable by chromatography. Complete analyses of both products indicated the compositions $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$.

The predominant reaction product of this composition, dark red crystals, m.p. 175–177° (isomer A), was more readily soluble in organic solvents than the chromium and molybdenum derivatives discussed above. The molecular weight determination and the absence of a carbon–nitrogen double bond frequency at ~1600 cm.$^{-1}$ in the infrared spectrum clearly eliminate structure VII analogous to structure V postulated for the chromium and molybdenum tricarbonyl complexes of dimethylaminofulvene. Similarities in the ultraviolet spectra of $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$ (isomer A) and of $[C_5H_5Fe(CO)_2]_2$ and the presence of bridging carbonyl bands at 1778 and 1768 cm.$^{-1}$ in the infrared spectrum of $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$ (isomer A) indicate a structure analogous to the well-established structure for $[C_5H_5Fe(CO)_2]_2$ (VIII).[14]

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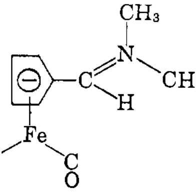
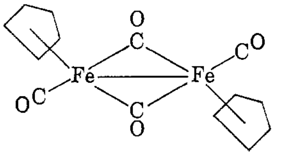
[13] E. O. Fischer, W. Hafner, and H. O. Stahl, *Z. anorg. allgem. Chem.*, **282**, 47 (1955).

[14] O. S. Mills, *Acta Cryst.*, **11**, 620 (1958).

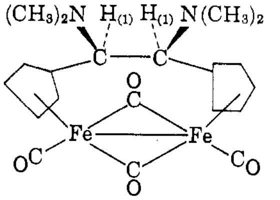
The proton n.m.r. spectrum of $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$ suggests structure IX for this complex.[15] The complex resonance at $\tau \sim 4.9$ may be assigned to the eight protons of the two five-membered rings π-bonded to the iron atoms. The complexity of this resonance may be attributed to slight differences in the chemical shifts of the protons bonded to the carbon atoms in α-positions and to the carbon atoms in β-positions relative to the carbon atoms of the five-membered ring bearing the side chain. In addition the singlet resonance at τ 6.93 may be assigned to the two protons $H_{(1)}$. The relative intensity of this resonance clearly indicates its origin from two rather than four protons. Moreover, in contrast to the corresponding protons in the complexes $C_5H_4CHN(CH_3)_2M(CO)_3$ (M = Cr or Mo), this resonance appears in a position more characteristic of protons bonded to sp^3-hybridized carbon atoms rather than to sp^2-hybridized carbon atoms. The final feature of the proton n.m.r. spectrum is the single methyl resonance at τ 7.78 indicating equivalence of all of the methyl groups. This contrasts with the corresponding feature of the spectrum of the $C_5H_4CHN(CH_3)_2M(CO)_3$ compounds (V) where the two methyl groups are seen to be nonequivalent.



VII

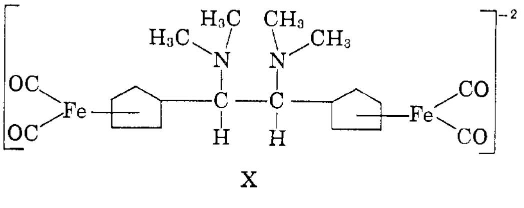


VIII

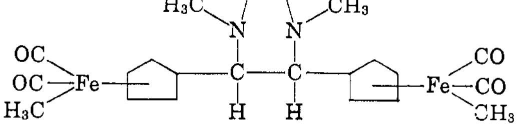


IX

In structure IX for $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$ the two "halves" of the molecule are not only held together by an iron–iron bond and bridging carbonyl groups as in $[C_5H_5Fe(CO)_2]_2$ but also by a *carbon–carbon* single bond. A characteristic reaction of $[C_5H_5Fe(CO)_2]_2$ is its cleavage with dilute sodium amalgam in methanol[16] or tetrahydrofuran[17] solution to produce the *monomeric* anion $[C_5H_5Fe(CO)_2]^-$, readily identified by its reaction with methyl iodide to form the likewise monomeric methyl derivative $C_5H_5Fe(CO)_2CH_3$ in good yield.[17] Dilute sodium amalgam is thus a suitable reagent for cleaving metal–metal bonds concurrently converting any bridging carbonyl groups to terminal carbonyl groups. Carbon–carbon bonds such as the bond also holding the "halves" of $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$ together are stable to most reagents including sodium amalgam. Thus cleavage of $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$ (isomer A) (IX) with dilute sodium amalgam should give a *dimeric* anion $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2^{-2}$ (X) if structure IX, as indicated by the n.m.r. spectrum discussed above, is indeed correct. The methyl derivative $[C_5H_4CHN(CH_3)_2Fe(CO)_2CH_3]_2$ (XI) formed by reaction of the anion X with methyl iodide would also be dimeric.



X



XI

In agreement with these predictions, the dark red tetrahydrofuran solution of $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$ soon became yellow-gray upon stirring with excess dilute sodium amalgam at room temperature. After treatment of this solution with excess methyl iodide, an orange crystalline methyl derivative could be isolated from the reaction mixture. Analyses and molecular weight determinations indicated this methyl derivative to be the expected *dimeric* derivative $[C_5H_4CHN(CH_3)_2Fe(CO)_2CH_3]_2$ (XI).

The proton n.m.r. spectrum is in accord with structure XI for $[C_5H_4CHN(CH_3)_2Fe(CO)_2CH_3]_2$. Besides exhibiting resonances at $\tau \sim 5.3$, 6.54, and 7.88 corresponding to the resonances at $\tau \sim 4.9$, 6.93, and 7.78 in $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$, a new singlet resonance is observed at τ 9.92 which on the basis of its relative intensity and similarity in chemical shift to the methyl resonance at τ 9.85 in $CH_3Fe(CO)_2C_5H_5$ may be assigned to the protons of the two methyl groups directly bonded to the two iron atoms. The infrared spectrum of $[C_5H_4CHN(CH_3)_2Fe(CO)_2CH_3]_2$ clearly demonstrates the absence of bridging carbonyl groups. The ultraviolet and visible spectra of $[C_5H_4CHN(CH_3)_2Fe(CO)_2CH_3]_2$ resemble those of certain $RFe(CO)_2C_5H_5$ compounds recently measured in this laboratory to be described in other papers.

Cleavage of $[C_5H_5Fe(CO)_2]_2$ may also be carried out with iodine to give $C_5H_5Fe(CO)_2I$[18] or with hydrochloric acid and air to give $C_5H_5Fe(CO)_2Cl$.[19] Iodine reacted with $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$ (isomer A) in refluxing chloroform solution to give a brown crystalline material. The similarity between the ultraviolet spectrum of this material and that of $C_5H_5Fe(CO)_2I$ indicated this product to be a substituted $C_5H_5Fe(CO)_2I$. Low nitrogen analyses indicated the loss of some of the dimethylamino groups in this reaction.

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(15) An analogous structure has been suggested for a product apparently of composition $(C_8H_{10})_2Fe_2(CO)_4$ obtained in 3.6% yield and in an impure condition from 6,6-dimethylfulvene and iron pentacarbonyl at 150° (ref. 8).

(16) E. O. Fischer and R. Böttcher, *Z. Naturforsch.*, **10b**, 600 (1955).

(17) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

(18) T. S. Piper and G. Wilkinson, *ibid.*, **2**, 38 (1956).

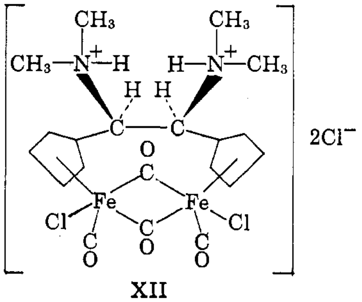
(19) T. S. Piper, F. A. Cotton, and G. Wilkinson, *ibid.*, **1**, 165 (1955).

This reaction product appears to be a mixture, however, since the analytical data do not agree with a reasonable formula. Interestingly enough, this product exhibited a band in the infrared spectrum at 1690 cm.$^{-1}$ which may be due to a bridging carbonyl group.

Reaction of $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$ (isomer A) with hydrochloric acid and air in a chloroform–ethanol solution analogous to the preparation of $C_5H_5Fe(CO)_2Cl$[19] gave a dark red solid, sparingly soluble in organic solvents, even tetrahydrofuran, but hygroscopic and very soluble in water. Analytical data and the high conductivity of aqueous solutions suggested the formulation of this solid as the ionic derivative $\{[C_5H_4CHNH(CH_3)_2Fe(CO)_2Cl]_2\}Cl_2$. In view of the strong infrared band at 1768 cm.$^{-1}$ indicating the probable presence of bridging carbonyl groups, structure XII is suggested for $\{[C_5H_4CHNH(CH_3)_2Fe(CO)_2Cl]_2\}Cl_2$. This structure, if correct, would represent a rare example of bridging carbonyl groups without metal–metal bonds. However, the two "halves" of XII are not held together only by the apparently labile[20] bridging carbonyl groups but also by a very stable carbon–carbon bond. The formation of XII would be expected to occur readily by protonation by excess hydrochloric acid of the $[C_5H_4CHN(CH_3)_2Fe(CO)_2Cl]_2$ initially formed by cleavage of the iron–iron bond.

The final dimethylaminofulvene–iron carbonyl derivative requiring explanation is the second, much rarer, isomer $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$ (isomer B), m.p. 237–240°, obtained in low yield in the original reaction between iron pentacarbonyl and dimethylaminofulvene. The ultraviolet and visible spectra are very similar to those of the isomeric $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$ (isomer A) discussed above. The infrared spectrum of isomer B exhibits a single band due to the bridging carbonyl groups. The proton n.m.r. spectrum of $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$ (isomer B) exhibits rather broad resonances at τ 4.73 and 5.23 corresponding to two different kinds of five-membered ring protons as well as singlet resonances at τ 7.05 and 8.00 corresponding entirely to the resonances at τ 6.93 and 7.78 of $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$ (isomer A). Except for the greater separation between two different kinds of protons on the five-membered rings, the proton n.m.r. spectra of isomers A and B are very similar.

Unfortunately, the low yield of $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$ (isomer B) has prevented further study of this material. The similarities in the spectroscopic properties of the two isomers suggest very similar structures. It will be noted in structure IX that the rigidity of the ring system including the two iron atoms, the two π-bonded five-membered rings, and the carbon atoms linking the two five-membered rings permits the existence of two stereoisomers depending on whether both hydrogen atoms $H_{(1)}$ are on the same side (*cis* or *meso* isomer as illustrated in IX) or on the opposite side (*trans* or *racemic* isomer) of this large ring.[21] The data presently available do not permit an unequivocal decision as to which stereoisomer corresponds to isomer A and which to isomer B. Further studies are required to resolve this question.



XII

Acknowledgment.—The authors are indebted to Prof. K. Hafner, University of Munich, Germany, for communicating some results prior to publication.

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(20) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 791 (1964).

(21) The authors are indebted to a referee for suggestions concerning this isomerism.