that back bonding to the carbonyls occurs largely through d_{xy} and $d_{x^2-y^2}$.

In Table II we give a representative selection of those M–C–O bond angles which have been reported —there is too much data available to be comprehensive. It is seen that these bonds are almost invariably bent, the average deviation from linearity being *ca.* 5°.

TABLE II

REPRESENTATIVE MCO BOND ANGLES[a]

Compound	M–C–O angles, deg.	Ref.
$[C_2H_5SFe(CO)_3]_2$	168, 175, 175, 169, 169, 178 (±4°)	*b*
π-$(C_5H_5)Mn(CO)_3$	178, 180, 176	*c*
$Co_2(CO)_8$	176, 175, 177	*d*
$Fe_5(CO)_{15}C$	172, 168, 176, 175, 175, 180, 176, 170, 174, 179, 173, 174, 169, 177, 172 (±4°)	*e*
$(C_6H_5)_2C_2Co_2(CO)_6$	178, 176, 178, 179, 176, 174	*f*
$C_4H_6Fe(CO)_3$	179, 178, 178	*g*
$C_8H_8Fe(CO)_3$	173, 178, 178 (±1°)	*h*
$C_8H_8Fe_2(CO)_6$	173, 177, 176, 178, 177, 176 (±3°)	*h*

[a] Average errors are quoted where these data are available. [b] L. F. Dahl and C. H. Wei, *Inorg. Chem.*, **2**, 328 (1963). [c] A. F. Berndt and R. E. March, *Acta Cryst.*, **16**, 119 (1963). [d] G. G. Sumner, H. P. Klug, and L. E. Alexander, *ibid.*, **17**, 732 (1964). [e] E. H. Braye, L. F. Dahl, W. Hübel, and D. L. Wampler, *J. Am. Chem. Soc.*, **84**, 4633 (1962). [f] W. G. Sly, *ibid.*, **81**, 18 (1959). [g] O. S. Mills and G. Robinson, *Acta Cryst.*, **16**, 758 (1963). [h] B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2084 (1962).

In conclusion, it should be noted that the discussion in this paper is also applicable to other MR_3 groups, of which $M(CN)_3$ and $M(NO)_3$ are perhaps the most important.

CONTRIBUTION FROM THE MELLON INSTITUTE,
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Organosulfur Derivatives of the Metal Carbonyls. VIII. New Aspects of the Chemistry of Methylthio Derivatives of Iron Carbonyl[1]

BY R. B. KING AND M. B. BISNETTE

Received May 14, 1965

The reactions between dodecacarbonyltriiron and various sulfides, mercaptans, and disulfides to give the stable red $[RSFe(CO)_3]_2$ compounds were first discovered by Hieber and Spacu[2] in 1937 and subsequently studied further by various research groups.[3-7] Even the earliest workers with these compounds noted that the more reactive dodecacarbonyltriiron was necessary for the formation of reasonable quantities of $[RSFe(CO)_3]_2$ compounds in thermal reactions with organic sulfur compounds; the more readily available but less reactive pentacarbonyliron gave little or no $[RSFe(CO)_3]_2$ compounds when allowed to react with similar organic sulfur compounds. Only in 1963 were discovered certain fairly unusual chelate-type organosulfur compounds, notably bis(trifluoromethyl)dithietene[7] and 3,4-toluenedithiol,[7] which gave appreciable quantities of $[RSFe(CO)_3]_2$ compounds on treatment with pentacarbonyliron at atmospheric pressure. However, aliphatic disulfides and mercaptans, even chelating ones such as 1,2-ethanedithiol, gave very low yields of $[RSFe(CO)_3]_2$ compounds on treatment with pentacarbonyliron at atmospheric pressure.

We have now found that $[CH_3SFe(CO)_3]_2$ can be synthesized very easily and efficiently in 60% yield by heating pentacarbonyliron with dimethyl disulfide in an autoclave in the presence of carbon monoxide under pressure. The proton n.m.r. spectrum of the product obtained from this reaction indicated it to contain 70 to 80% of *anti*-$[CH_3SFe(CO)_3]_2$ (previously[6] designated as "isomer A") and 20 to 30% of *syn*-$[CH_3SFe(CO)_3]_2$ (previously[6] designated as "isomer B").[8]

In a further study of this reaction pentacarbonyliron and dimethyl disulfide were heated in a sealed autoclave in the *absence* of any additional carbon monoxide. Some $[CH_3SFe(CO)_3]_2$ was also formed in this reaction; however the major product was a red solid completely insoluble in all organic solvents tried including even acetone and dichloromethane, which dissolve most metal carbonyl derivatives. Analyses indicated this red material to be $[(CH_3S)_2Fe(CO)_2]_n$. The insolubility of this compound suggests it to be a polymer analogous to the closely related polymeric carbonyl halides $[M(CO)_2I_2]_n$ (M = Fe[9] or Ru[10]) and to the recently reported[11] nitrosyl halides $[M(NO)_2Cl_2]_n$ (M = Mo or W). In the case of $[(CH_3S)_2Fe(CO)_2]_n$ the iron atoms in the polymer would be linked by sulfur bridges as depicted in I. Each iron atom is bonded to four sulfur atoms and two carbonyl groups and is thus hexacoordinate. The presence of two strong infrared carbonyl stretching frequencies at 2010 and 1956 cm.$^{-1}$ indicates that the two carbonyl groups occupy *cis* positions as indicated in I. This region of the infrared spectrum resembles entirely that of the related carbonyl and nitrosyl halides cited above. An attempt to obtain $[(CH_3S)_2Fe(CO)_2]_n$ from $[CH_3SFe(CO)_3]_2$ and excess dimethyl disulfide in boiling toluene resulted instead in a brown insoluble pyrophoric solid with complete destruction of the red $[CH_3SFe(CO)_3]_2$. This ability of $[CH_3SFe(CO)_3]_2$ to react further with excess dimethyl disulfide in an open system suggests a reason for the failure to obtain appreciable quantities of $[CH_3$-

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[1] For part VII of this series see R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4**, 486 (1965).

[2] W. Hieber and P. Spacu, *Z. anorg. allgem. Chem.*, **233**, 353 (1937).

[3] W. Hieber and C. Scharfenberg, *Ber.*, **73**, 1012 (1940).

[4] W. Hieber and W. Beck, *Z. anorg. allgem. Chem.*, **305**, 265 (1960).

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[6] R. B. King, *J. Am. Chem. Soc.*, **84**, 2460 (1962).

[7] R. B. King, *ibid.*, **85**, 1584 (1963).

[8] For X-ray crystallographic evidence for assignment of the *anti*- and *syn*- configurations to isomers A and B, respectively, see L. F. Dahl and C. W. Wei, *Inorg. Chem.*, **2**, 328 (1963).

[9] W. Hieber and H. Lagally, *Z. anorg. allgem. Chem.*, **245**, 295 (1932).

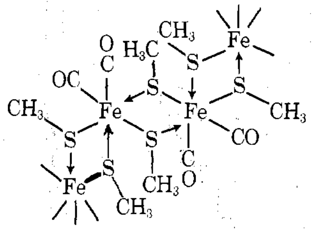
[10] R. J. Irving, *J. Chem. Soc.*, 2879 (1956).

[11] F. A. Cotton and B. F. G. Johnson, *Inorg. Chem.*, **3**, 1609 (1964).

$SFe(CO)_3]_2$ from dimethyl disulfide and pentacarbonyliron at atmospheric pressure.

Hieber and Zeidler[12] have found $[RSFe(CO)_3]_2$ compounds to react with certain tertiary phosphines, phosphites, and arsines to give compounds of the types $(RS)_2Fe_2(CO)_5L$ or $(RS)_2Fe_2(CO)_4L_2$. We have now found $[CH_3SFe(CO)_3]_2$ to react slowly with bicyclo[2.2.1]heptadiene-2,5[13] in boiling benzene to give dark brown crystalline $(CH_3S)_2Fe_2(CO)_4C_7H_8$. The expected structure (II)[14] for this compound was confirmed by its proton n.m.r. spectrum.[15] This spectrum was investigated in both benzene and hexafluorobenzene solutions in order to separate the fortuitously identical chemical shifts in carbon disulfide solution of the three methyl protons of one CH_3S group and the two bridge methylene protons of the bicycloheptadiene ligand. Benzene and hexafluorobenzene exhibited opposite solvent effects in this case.

Analogous treatment of $[CH_3SFe(CO)_3]_2$ with 1,5-cyclooctadiene, 1,3,5-cyclooctatriene, cyclooctatetraene, cycloheptatriene, or butadiene did not give analogous $(CH_3S)_2Fe_2(CO)_4$ (diolefin) complexes. In the case of cyclooctatetraene small amounts of impure $C_8H_8Fe(CO)_3$[17] were obtained and identified by its characteristic sharp n.m.r. resonance at τ 4.83 (authentic $C_8H_8Fe(CO)_3$; $\tau(C_8H_8)$ 4.82).[18] Otherwise no products besides the two isomers of $[CH_3SFe(CO)_3]_2$ were observed upon chromatography of the reaction mixtures. The inability to obtain olefin complexes from these other olefins is not particularly surprising since previous results suggest bicycloheptadiene to be one of the most reactive olefins with regard to π-complex formation.[19,20]



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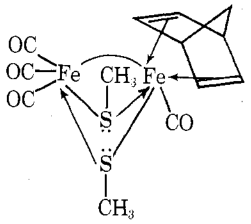

II

Hayter[21] found the compounds $[(CH_3)_2EFe(CO)_3]_2$ (E = P or As) to react with halogens to form the halides $[(CH_3)_2EFe(CO)_3X]_2$. However, treatment of $[CH_3SFe(CO)_3]_2$ with bromine or iodine in dichloromethane solutions gave orange or brown products, respectively, which appeared to be complex mixtures containing some material with halogen bridges replacing the CH_3S bridges.

Ultraviolet spectra of $[RSFe(CO)_3]_2$ compounds have not been previously reported. We have now measured several such spectra in cyclohexane solution using a Cary Model 14 spectrometer. The positions of maxima and the extinction coefficients (ϵ) are as follows: *anti*-$[CH_3SFe(CO)_3]_2$, 331 mμ (12,600); *syn*-$[CH_3SFe(CO)_3]_2$, 332 mμ (11,230); $[C_2H_5SFe(CO)_3]_2$, 331 mμ (10,800); $C_2H_4S_2Fe_2(CO)_6$, 323 mμ (16,000); $C_2F_4S_2Fe_2(CO)_6$, 328 mμ (20,600); $C_4F_6S_2Fe_2(CO)_6$, 305 mμ (9200) and 341 mμ (12,500); $C_7H_6S_2Fe_2(CO)_6$, 334 mμ (17,400); and $(CH_3S)_2Fe_2(CO)_4C_7H_8$, 355 m$\mu$ (9760).

Experimental

Proton n.m.r. spectra were taken on a Varian Associates Model A-60 spectrometer in the indicated solvents using hexamethyldisiloxane (τ 9.95) as an internal standard. Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Duplicate values reported here are on samples from two independent preparations. Molecular weight determinations were performed in benzene solution by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., using a Mechrolab vapor pressure osmometer. Melting points were taken in capillaries and are uncorrected.

Pentacarbonyliron, dimethyl disulfide, and bicycloheptadiene were all commercial samples used without further purification. Reactions under pressure were carried out in rocking autoclaves.

Large Scale Preparation of $[CH_3SFe(CO)_3]_2$.—An autoclave of 1.4 l. internal capacity was charged with a mixture of 270 ml. (394 g., 2.05 moles) of pentacarbonyliron and 100 ml. (106 g., 1.13 moles) of dimethyl disulfide. After pressurizing with 65 atm. of carbon monoxide the autoclave was heated ~20 hr. at 120–130°. After the reaction period was over, the autoclave was allowed to cool to room temperature, vented, and opened. The solid red cake of product was washed out of the autoclave with diethyl ether. After removal of this diethyl ether at ~25° (25 mm.) the red solid was extracted continuously with boiling pentane in a Soxhlet apparatus until the fresh extracts were no longer red. The resulting pentane extract was cooled to −78° to complete separation of the product. The resulting red crystals were filtered and dried to give 220 g. (57.5% yield) of red crystalline $[CH_3SFe(CO)_3]_2$, m.p. 65–68°.[22]

By integration of its proton n.m.r. spectrum the product from one of these preparations analyzed for 80% of *anti*-$[CH_3SFe(CO)_3]_2$ and 20% of the *syn* isomer; the product from another such preparation analyzed for 70% of the *anti* isomer and 30% of the *syn* isomer.

Preparation of the Polymer $[(CH_3S)_2Fe(CO)_2]_n$.—A mixture of 100 ml. (146 g., 0.745 mole) of pentacarbonyliron and 250 ml. (262 g., 2.77 moles) of dimethyl disulfide was heated in the autoclave of 1.4 l. internal capacity at 100–140° for 24 hr. under autogenous pressure. The autoclave was then cooled to room temperature and the carbon monoxide pressure (~35 atm. at room temperature) vented. The contents of the bomb were filtered by suction. The red insoluble polymer $[(CH_3S)_2Fe(CO)_2]_n$ was washed free from $[CH_3SFe(CO)_3]_2$ and other soluble impurities with several portions of acetone until the acetone washings were no longer red. After drying, the red insoluble powder weighed 110 g. (71.6% yield based on iron pentacarbonyl). Fur-

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[12] W. Hieber and A. Zeidler, *Z. anorg. allgem. Chem.*, **329**, 92 (1964).

[13] Designated in the following text simply as "bicycloheptadiene."

[14] A sterically unlikely symmetrical structure for $(CH_3S)_2Fe_2(CO)_4C_7H_8$ with two carbonyl groups bonded to each iron atom and with the bicycloheptadiene ligand acting as a bridging group cannot be conclusively excluded on the basis of the available data. However, it is probable that such a symmetrical structure would give rise to only two strong carbonyl absorptions in the infrared spectrum, whereas three strong infrared bands and two medium intensity infrared bands are observed in this general region.

[15] The detailed interpretation of this n.m.r. spectrum is entirely analogous to that of $C_7H_8M(CO)_4$ (M = Cr or Mo) and $C_5H_5CoC_7H_8$.[16] Space limitations prevent its discussion here.

[16] M. A. Bennett, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 2037 (1961); R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3590 (1961); R. B. King, P. M. Treichel, and F. G. A. Stone, *ibid.*, **83**, 3593 (1961).

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[18] These spectra were both taken in carbon disulfide solution.

[19] G. Winkhaus and G. Wilkinson, *J. Chem. Soc.*, 602 (1961).

[20] E. W. Abel, M. A. Bennett, and G. Wilkinson, *ibid.*, 3178 (1959).

[21] R. G. Hayter, *Inorg. Chem.*, **3**, 711 (1964).

[22] We have found pure *anti*-$[CH_3SFe(CO)_3]_2$ to melt at 70–71° and pure *syn*-$[CH_3SFe(CO)_3]_2$ to melt at 112–114°. These values are somewhat higher than those previously reported[6] and were obtained on more highly purified samples of the two isomers.

ther purification of $[(CH_3S)_2Fe(CO)_2]_n$ was not possible owing to its insolubility. Upon heating above ~110°, $[(CH_3S)_2Fe(CO)_2]_n$ gradually darkened without melting.

Anal. Calcd. for $n(C_4H_6O_2S_2Fe)$: C, 23.3; H, 2.9; S, 31.0; Fe, 27.2; O, 15.5. Found: C, 23.3, 22.2; H, 3.1, 2.8; S, 31.0, 30.4; Fe, 26.6, 27.2; O, 15.8, 16.4.

Infrared Spectrum.[23]—Metal carbonyl bands at 2010 (vs), 1966 (m), 1956 (s), and 1945 (m) cm.$^{-1}$; other bands at 1418 (w), 1297 (w), and 940 (w) cm.$^{-1}$.

Preparation of $(CH_3S)_2Fe_2(CO)_4C_7H_8$.—A mixture of 3.74 g. (10 mmoles) of $[CH_3SFe(CO)_3]_2$ (~80% *anti* and ~20% *syn*), 5.0 ml. (4.5 g., 49 mmoles) of bicycloheptadiene, and 50 ml. of thiophene-free benzene was refluxed 70 hr. with stirring under nitrogen. Solvent was removed from the filtered reaction mixture at ~25° (35 mm.) leaving a dark red residue. After admitting nitrogen, the residue was extracted with 70 ml. of pentane in four portions and the filtered pentane extracts were chromatographed on a 2 × 50 cm. alumina column. The chromatogram was developed with pentane. The first two red to red-orange bands were eluted with pentane. Evaporation of the filtered eluates from these two bands gave 1.26 g. of *anti*-$[CH_3SFe(CO)_3]_2$ and 0.15 g. of *syn*-$[CH_3SFe(CO)_3]_2$, respectively; total recovery of both $[CH_3SFe(CO)_3]_2$ isomers, 1.41 g. (38%).

After removing both isomers of $[CH_3SFe(CO)_3]_2$ from the chromatography column, a brown band remained. This band was eluted with pentane. The dark brown pentane eluate (volume (~250 ml.) was filtered by gravity, collecting the filtrate under nitrogen. Removal of solvent (~25° (35 mm.)] from this filtrate left a brown liquid. This liquid was extracted with ~50 ml. of pentane in three portions. The filtered pentane extracts were concentrated to ~30 ml. and then cooled in a −78° bath. Separation of the dark brown crystalline product was slow and it was therefore advisable to keep the pentane solution at −78° for at least 40 hr. before filtering the product. After filtration and drying in the usual manner, 0.62 g. (15% conversion, 24% yield) of dark brown crystalline $(CH_3S)_2Fe_2(CO)_4C_7H_8$, m.p. 84–86°, was obtained.

Attempts to accelerate this reaction by carrying it out in boiling toluene or xylene rather than boiling benzene gave little or none of the desired product.

Anal. Calcd. for $C_{13}H_{14}O_4S_2Fe_2$: C, 38.1; H, 3.4; S, 15.6; O, 15.6; Fe, 27.3; mol. wt., 410. Found: C, 37.9, 37.7; H, 3.4, 3.3; S, 16.1, 15.3; O, 16.0, 16.5; Fe, 27.1, 26.9; mol. wt., 400.

Infrared Spectrum.[23]—Carbon–hydrogen stretching frequencies at 2910 (vvw) and 2875 (vw) cm.$^{-1}$; metal carbonyl bands at 2040 (s), 2029 (m), 1974 (s), 1963 (s), and 1943 (m) cm.$^{-1}$; other bands at 1417 (w), 1404 (w), 1300 (w), 1243 (vw), 1177 (w), 1154 (vw), 1077 (w), 1032 (vvw), 992 (vw), 947 (w), 942 (w), 893 (vw), 856 (vw), 800 (vw), 777 (w), 745 (vw), 730 (vw), 728 (vw), 697 (vw), and 685 (vw) cm.$^{-1}$.

Proton N.m.r. Spectrum.—(a) (CS_2 solution): Resonances at τ 6.39 (apparent triplet), 6.73 (apparent doublet), 8.80 (apparent singlet), and 8.98 (apparent singlet) of approximate relative intensities 4:2:5:3. (b) (C_6H_6 solution): Resonances at τ 6.80 (unclearly resolved), 7.14 (broad unresolved), 8.89 (sharp singlet), 9.26 (unresolved singlet), and 9.40 (sharp singlet) of approximate relative intensities 4:2:3:2:3. (c) (C_6F_6 solution): Resonances at τ 6.30 (complex with at least five discernible peaks), 6.58 (complex with at least four discernible peaks), 8.73 (unresolved singlet), 8.82 (sharp singlet), and 8.89 (sharp singlet) of approximate relative intensities 4:2:2:3:3.

Acknowledgment.—We are indebted to the U. S. Air Force Office of Scientific Research for partial support of this work under Grant AF-AFOSR-580-64.

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[23] The metal carbonyl region of this spectrum was studied in a halocarbon oil mull on a Beckman IR-9 double beam spectrometer with grating optics. The remainder of the spectrum is reported as obtained from a potassium bromide pellet on a Perkin-Elmer Model 21 double beam spectrometer.

CONTRIBUTION FROM THE ISTITUTO DI CHIMICA GENERALE E
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Infrared Spectra of Substituted Thiocyanate Complexes. The Effect of the Substituent on Bond Type. I

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Received June 7, 1965

Metal–thiocyanato complexes have been extensively investigated in order to solve the interesting problem of whether the thiocyanate group is bonded to the metal through the nitrogen atom (M–NCS), through the sulfur atom (M–SCN), or through both by means of bridging (M–NCS–M).[1] It has been found that metals classified by Ahrland, Chatt, and Davies[2] as class a are generally bonded to the nitrogen atom, whereas class b metals are bonded to the sulfur atom.

Turco and Pecile,[3] investigating compounds of the type $[ML_2(NCS)_2]$ with M = Pd or Pt, found that when L is an amine or a thiocyanate ion, the thiocyanate group is S-bonded, but when L is a trialkylphosphine the thiocyanate group is N-bonded. They suggested that, though the sulfur atom is a weaker σ donor than the nitrogen atom, M–S bonding is stabilized by π back bonding from metal to sulfur and that when L is a strong π acceptor, as for example triethylphosphine, the M–S π bond is so reduced in strength that the N-bonded isomer becomes the more stable one.

Burmeister and Basolo[4,5] widened the study of these compounds to include other organic ligands and were able to isolate both N- and S-bonded isomers of $[Pd(As(C_6H_5)_3)_2(NCS)_2]$ and $[Pd(dipy)(NCS)_2]$ by suitable adjustment of the conditions of preparation.

The criterion adopted until now to establish the bond type is that a C–S stretching frequency of 780–860 cm.$^{-1}$ is indicative of N– bonding, while a frequency of *ca.* 700 cm.$^{-1}$ indicates S– bonding. It had previously been noted that the NCS deformation mode can be used to characterize the bond type,[1b,6] being a single band at 460–490 cm.$^{-1}$ for N-thiocyanates and a band at 410–440 cm.$^{-1}$, with weaker satellites at higher frequencies, for S-thiocyanates. Furthermore the first overtone of the NCS deformation mode has an intensity comparable to that of the C–S stretching mode[7]: its value in S-thiocyanato complexes lies between 800 and 880 cm.$^{-1}$ so that it may be erroneously assigned as the C–S stretching band of an N-thiocyanato complex.

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