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Organosulfur Derivatives of the Metal Carbonyls. VI. Monomeric $CH_3SFe(CO)_2C_5H_5$ and Related Compounds[1,2]

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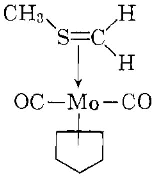
Brown monomeric $CH_3SFe(CO)_2C_5H_5$ has been obtained by the following two methods: (a) Treatment of a cold mixture of $NaFe(CO)_2C_5H_5$ and $(CH_3)_3CCl$ (*i.e.*, $C_5H_5Fe(CO)_2H$ *in situ*) with dimethyl disulfide; (b) irradiation of $[C_5H_5Fe(CO)_2]_2$ with dimethyl disulfide at room temperature. Methyl iodide reacts readily with $CH_3SFe(CO)_2C_5H_5$ to give yellow crystalline ionic $[C_5H_5Fe(CO)_2S(CH_3)_2]I$. Ethanolic mercuric chloride reacts with $CH_3SFe(CO)_2C_5H_5$ to form the orange adduct $CH_3SFe(CO)_2C_5H_5{\cdot}HgCl_2$. On pyrolysis at 70° $CH_3SFe(CO)_2C_5H_5$ readily loses carbon monoxide to form the previously reported[3] dimeric $[CH_3SFeCOC_5H_5]_2$, for which an improved preparation from $[C_5H_5Fe(CO)_2]_2$ and dimethyl disulfide is also described. Treatment of di-*t*-butyl disulfide with $Fe_3(CO)_{12}$ or $[C_5H_5Fe(CO)_2]_2$ gives red $[(CH_3)_3CSFe(CO)_3]_2$ or brown $[(CH_3)_3CSFeCOC_5H_5]_2$, respectively.

Introduction

Within the past few years numerous derivatives of transition metal carbonyls or cyclopentadienyls also containing either RS-*bridging* groups[2-4] or *chelating* dithiolate groups[5] (such as those derived from bis(trifluoromethyl)dithietene) have been discovered. However, until now no monomeric compounds containing a nonchelating, nonbridging RS group such as the CH_3S group have been described.

In an attempt to extend organosulfur–transition metal chemistry in still a different direction, the authors initiated in 1962 a study of the reactions between various chloroalkyl methyl sulfides and certain metal carbonyl anions hoping to obtain complexes with alkyl sulfide ligands with both metal–sulfur and metal–carbon bonds. This program was moderately successful, leading to the discovery of compounds such as $CH_3SCH_2Mo(CO)_2C_5H_5$ (I) and $CH_3SCH_2CH_2COMn(CO)_4$ (II).[1,6] However, during the course of this research, it was also noted that one of the predominant products of the irradiation of $CH_3SCH_2CH_2Fe(CO)_2C_5H_5$ was *monomeric* $CH_3SFe(CO)_2C_5H_5$, the first transition metal compound where a CH_3S group clearly does not serve a bridging function.

This initial discovery of $CH_3SFe(CO)_2C_5H_5$ prompted studies directed toward its synthesis from dimethyl disulfide and cyclopentadienyliron carbonyls by more conventional reactions. This paper reports the results of these studies as well as some reactions of $CH_3SFe(CO)_2C_5H_5$ and some further work on the closely related dimeric $[RSFeCOC_5H_5]_2$ compounds first reported in 1961 by King, Treichel, and Stone.[3]



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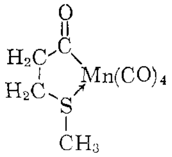

II

Experimental

In general infrared spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 21 double beam spectrometer with sodium chloride optics. In addition, the metal carbonyl regions of selected compounds (Table I) were taken in halocarbon oil mulls and recorded on a Beckman Model IR-9 spectrometer with grating optics. Ultraviolet and visible spectra were taken in spectral grade cyclohexane solution and recorded on a Cary Model 14 spectrometer. Proton n.m.r. spectra were taken in carbon disulfide, chloroform, or acetone-d_6 solution on a Varian Associates Model A-60 machine using hexamethyldisiloxane (τ 9.95) as an internal standard. Microanalyses and molecular weight determinations (Mechrolab vapor pressure osmometer in benzene solution) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany; Dr. A. Bernhardt, Mikroanalytisches Laboratorium, Max-Planck Institut für Kohlenforschung, Mülheim (Ruhr), Germany; and Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Melting points were taken in capillaries and are uncorrected. All materials used in this work were either commercial samples or prepared by well-established procedures.

(A) Preparation of $CH_3SFe(CO)_2C_5H_5$. (a) $C_5H_5Fe(CO)_2H$[7] and Dimethyl Disulfide.—A solution of 100 mmoles of $NaFe(CO)_2C_5H_5$[8] in 300 ml. of redistilled tetrahydrofuran was prepared under nitrogen from ~1% sodium amalgam and $[C_5H_5Fe(CO)_2]_2$ by the well-established procedure.[9] This solution was cooled to −78° and treated with 30 g. (320 mmoles) of dimethyl disulfide and 9.25 g. (100 mmoles) of *t*-butyl chloride. The cold reaction mixture was allowed to warm slowly to room temperature by the gradual evaporation of the Dry Ice in the metal pan serving as the cooling bath. After stirring ~16 hr. at room temperature, solvent was removed at ~25° (30 mm.). Nitrogen was admitted and the residue extracted with four 150-ml. portions of dichloromethane. The extracts were filtered by

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(1) For a preliminary communication of some of this work see R. B. King and M. B. Bisnette, *J. Am. Chem. Soc.*, **86**, 1267 (1964).

(2) For part V of this series see R. B. King, *ibid.*, **85**, 1587 (1963).

(3) R. B. King, P. M. Treichel, and F. G. A. Stone, *ibid.*, **83**, 3600 (1961).

(4) W. Hieber and P. Spacu, *Z. anorg. allgem. Chem.*, **233**, 353 (1937); W. Hieber and C. Scharfenberg, *Ber.*, **73**, 1012 (1940); W. Hieber and W. Beck, *Z. anorg. allgem. Chem.*, **305**, 265 (1960); S. F. A. Kettle and L. E. Orgel, *J. Chem. Soc.*, 3890 (1960).

(5) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **86**, 2799 (1964), and earlier papers cited therein.

(6) The next paper of this series gives details of this work (R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4**, 486 (1965)).

(7) The preparation of the hydride $C_5H_5Fe(CO)_2H$ from $NaFe(CO)_2C_5H_5$ and *t*-butyl chloride was first described by M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.*, **1**, 58 (1963).

(8) (a) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956); (b) E. O. Fischer and R. Böttcher, *Z. Naturforsch.*, **10B**, 600 (1955).

(9) Experimental details for the preparation of $NaFe(CO)_2C_5H_5$ as carried out in our laboratory are given in the article by R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **2**, 15 (1964), and need not be repeated here.

gravity under nitrogen and the dichloromethane removed from the filtrate at 25° (30 mm.). A brown solid residue remained consisting of a mixture of $[C_5H_5Fe(CO)_2]_2$ and $CH_3SFe(CO)_2C_5H_5$.

In order to separate these two materials a filtered solution of the residue in 200 ml. of pure benzene was chromatographed on a 5 × 50 cm. alumina column. The chromatogram was developed with benzene. A very weak brown band[10] was first observed which was discarded since it only contained a trace of material. This very weak band was followed by strong clearly separated red-brown bands[11] of $[C_5H_5Fe(CO)_2]_2$ and $CH_3SFe(CO)_2C_5H_5$. The red-brown band of $[C_5H_5Fe(CO)_2]_2$ was also eluted with benzene. The dark red eluate gave the characteristic red-violet crystals of $[C_5H_5Fe(CO)_2]_2$ after evaporation at 25° (30 mm.). Finally the remaining red-brown band of $CH_3SFe(CO)_2C_5H_5$ was eluted with dichloromethane. The brown dichloromethane eluate was filtered by gravity, collecting the filtrate under nitrogen. Removal of solvent at 25° (30 mm.) from this filtered eluate left behind brown crystals of $CH_3SFe(CO)_2C_5H_5$.

The chromatographed sample of $CH_3SFe(CO)_2C_5H_5$ was purified finally by crystallization from pentane. For this it was extracted with ~500 ml. of pentane in several portions, and the pentane extracts were filtered by gravity, collecting the brown air-sensitive filtrate under nitrogen. Cooling this filtrate to −78° for several hours precipitated brown crystals which were isolated by filtration in the usual manner to give a total of 2.92 g. (13% yield) of $CH_3SFe(CO)_2C_5H_5$, m.p. 68–70°.

(b) **Irradiation of $[C_5H_5Fe(CO)_2]_2$ with Dimethyl Disulfide.**—A mixture of 3.55 g. (10 mmoles) of $[C_5H_5Fe(CO)_2]_2$, 4.0 ml. (4.2 g., 45 mmoles) of dimethyl disulfide, and 50 ml. of benzene was irradiated in a quartz tube under nitrogen for 17 hr. with a 1000-watt ultraviolet source about 50 cm. from the reaction vessel. The filtered reaction mixture was chromatographed on a 2 × 50 cm. alumina column. After development with benzene, the first red-brown band of $[C_5H_5Fe(CO)_2]_2$ was eluted with benzene and the second red-brown band of $CH_3SFe(CO)_2C_5H_5$ with dichloromethane. Isolation of products from the eluates followed the procedure given in the previous experiment except that 80 ml. of pentane was sufficient for the recrystallization of the $CH_3SFe(CO)_2C_5H_5$. The red-violet crystals of $[C_5H_5Fe(CO)_2]_2$ after washing with pentane and drying weighed 1.12 g. (31.6% recovery). The brown crystals of $CH_3SFe(CO)_2C_5H_5$, m.p. 67–69°, after recrystallization weighed 0.68 g. (15% conversion; 22% yield based on unrecovered $[C_5H_5Fe(CO)_2]_2$). The infrared and n.m.r. spectra of $CH_3SFe(CO)_2C_5H_5$ obtained from this reaction were identical with those of $CH_3SFe(CO)_2C_5H_5$ obtained from $C_5H_5Fe(CO)_2H$ and dimethyl disulfide as described above.

(B) **Properties of $CH_3SFe(CO)_2C_5H_5$.** *Anal.* Calcd. for $C_8H_8O_2SFe$: C, 42.8; H, 3.6; S, 14.3; O, 14.3; Fe, 25.0; mol. wt., 244. Found: C, 42.7; H, 3.8; S, 13.9; O, 14.5; Fe, 24.8; mol. wt., 235.

Infrared Spectrum.—C–H bands at 3060–3010 (vw, br), 2920 (vvw), and 2860 (vvw) cm.$^{-1}$; see Table I for metal carbonyl bands; other bands at 1420 (m), 1310 (w), 1004 (w), 988 (w, br), 947 (w), 845 (w), and 835 (vw) cm.$^{-1}$.

Proton N.m.r. Spectrum.—Sharp singlet resonances at τ 5.11 (π-cyclopentadienyl protons) and 8.39 (methyl protons) of the expected relative intensities ~5:3.

(C) **Reactions of $CH_3SFe(CO)_2C_5H_5$. With Methyl Iodide.**—A clear brown filtered solution of 0.58 g. (2.6 mmoles) of $CH_3SFe(CO)_2C_5H_5$ in 20 ml. of anhydrous diethyl ether was treated under nitrogen with 1.0 ml. (2.3 g., 16.2 mmoles) of methyl iodide. A yellow precipitate soon formed. After ~15 min. at room temperature this precipitate was filtered, washed with three 15-ml. portions of diethyl ether, and dried. The crude product was extracted with 30 ml. of acetone and reprecipitated from the filtered yellow solution by addition of 20 ml. of hexane and concentration to 10 ml. at 25° (30 mm.) to give 0.26 g. (27.4% yield) of yellow solid $[C_5H_5Fe(CO)_2S(CH_3)_2]I$, m.p. 104° (decomposition with vigorous gas evolution).

Anal. Calcd. for $C_9H_{11}IO_2SFe$: C, 29.5; H, 3.0; O, 8.7; S, 8.7; I, 34.7; Fe, 15.3. Found: C, 29.8; H, 3.2; O, 9.2; S, 8.7; I, 35.0; Fe, 14.1.

Infrared Spectrum.—C–H bands at 3060 (w), 3000 (m), and 2950 (w) cm.$^{-1}$; see Table I for metal carbonyl bands; other bands at 1435 (w), 1412 (m), 1330 (w), 1307 (vw), 1106 (vw), 1067 (vw), 1042 (m), 998 (m), 964 (w), 922 (vw), 878 (m), and 830 (w) cm.$^{-1}$.

Proton N.m.r. Spectrum ($(CD_3)_2CO$ Solution).—Sharp resonances at τ 4.23 (π-cyclopentadienyl protons) and 7.39 (methyl protons) of the expected relative intensities ~5:6.

Conductivity.—A molar conductance of 205 ± 9 ohm^{-1} cm.^{2} mole^{-1} was found in acetone solution in the concentration range 7.5×10^{-4} to 1.32×10^{-3} *M*.

With Mercuric Chloride.—A filtered clear brown solution of 0.19 g. (0.85 mmole) of $CH_3SFe(CO)_2C_5H_5$ in 30 ml. of 95% ethanol was treated with a solution of ~0.5 g. (1.84 mmoles) of mercuric chloride in ~30 ml. of 95% ethanol. An orange precipitate formed almost immediately. After ~15 min. this precipitate was filtered, washed with three 20-ml. portions of ethanol, and dried. The crude product was purified by crystallization from a mixture of hexane and dichloromethane or preferably acetone at room temperature to give 0.15 g. (35% yield) of orange crystalline $CH_3SFe(CO)_2C_5H_5 \cdot HgCl_2$, m.p. 136–137° dec.

Anal. Calcd. for $C_8H_8Cl_2HgO_2SFe$: C, 19.3; H, 1.6; O, 6.4; S, 6.4; Cl, 14.3. Found: C, 18.9; H, 2.0; O, 6.9; S, 6.0; Cl, 12.9.

Infrared Spectrum.—C–H band at 3060 (vw) cm.$^{-1}$; see Table I for metal carbonyl bands; other bands at 1425 (m), 1306 (vw), 1020 (vw), 1017 (vw), 997 (w), 965 (m), 950 (w), 892 (vw), and 859 (m) cm.$^{-1}$.

(D) **Pyrolysis of $CH_3SFe(CO)_2C_5H_5$.**—A 0.5210-g. (2.325 mmoles) sample of $CH_3SFe(CO)_2C_5H_5$ was heated at 70–72° at 650–800 mm. for 18 hr. in a flask attached to a mercury-filled gas buret. A total of 33.63 ml. of gas [27.5° (733.5 mm.)] corresponding to 1.32 mmoles (~57% of the expected amount) was collected. After cooling to room temperature the brown residue was extracted with 50 ml. of pentane in three portions. Product was isolated from the filtered pentane extracts by cooling to −78° and filtration of the brown crystals which separated. A second crop of brown crystals was isolated by evaporation of the filtrate to ~10 ml. at 25° (25 mm.) and cooling again to −78°. In this manner a total of 0.12 g. (26% yield) of brown-black crystalline $[CH_3SFeCOC_5H_5]_2$, m.p. 103–104° (lit.[3] m.p. 104–105°), was obtained. The infrared spectrum of this material was identical with that of an authentic sample of $[CH_3SFeCOC_5H_5]_2$ obtained from the reaction between $[C_5H_5Fe(CO)_2]_2$ and dimethyl disulfide (see below).[3]

Improved Preparation of $[CH_3SFeCOC_5H_5]_2$.—Using the procedure given below, the yield of $[CH_3SFeCOC_5H_5]_2$ from $[C_5H_5Fe(CO)_2]_2$ and dimethyl disulfide was greatly improved over that previously reported by King, Treichel, and Stone.[3]

A mixture of 20 g. (56.5 mmoles) of $[C_5H_5Fe(CO)_2]_2$, 25 ml. (26.4 g., 270 mmoles) of dimethyl disulfide, and 200 ml. of methylcyclohexane was refluxed 19 hr. under nitrogen with magnetic stirring. After cooling the resulting brown mixture to room temperature, it was filtered by suction, discarding the black pyrophoric residue. The dark brown filtrate was chromatographed on a 5 × 60 cm. alumina column. The chromatogram was developed with benzene. The first large dark brown band[12] contained the $[CH_3SFeCOC_5H_5]_2$. It was eluted with benzene. Solvent was removed from the resulting brown eluate

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[10] The mobility and color of this very weak band suggest it to consist of trace quantities of $[CH_3SFeCOC_5H_5]_2$.

[11] The red-brown band of $[C_5H_5Fe(CO)_2]_2$ is noticeably more reddish than the red-brown band of $CH_3SFe(CO)_2C_5H_5$.

[12] A much weaker more strongly adsorbed black band was also observed on the column. Elution of this band with dichloromethane gave a black eluate which yielded about 0.17 g. of black crystals on evaporation. This compound, demonstrated by its infrared spectrum to contain no metal carbonyl groups, has not yet been characterized in detail.

at 25° (25 mm.) to give a mixture of brown crystals and liquid from which brown-black $[CH_3SFeCOC_5H_5]_2$ was isolated by crystallization from a mixture of dichloromethane and hexane, cooling the resulting concentrated hexane solution to $-78°$ before filtering the crystals. After heating at 70° (0.1 mm.) to remove ~1.2 g. (5.7% yield) of orange crystalline ferrocene by sublimation, the brown-black residue of $[CH_3SFeCOC_5H_5]_2$, m.p. 109–111° (lit.[3] m.p. 104–105°), weighed 8.3 g. (37% yield).

Anal. Calcd. for $C_{14}H_{16}O_2S_2Fe_2$: C, 42.8; H, 4.1; S, 16.3; Fe, 28.5. Found: C, 42.8; H, 4.3; S, 16.0; Fe, 28.1.

The infrared spectrum of $[CH_3SFeCOC_5H_5]_2$ corresponded very well to that reported previously.[3] More careful chemical shift measurements[13] on the two singlet resonances in the proton n.m.r. spectrum (CS_2 solution) resulted in the values τ 5.68 (lit.[3] 5.77) and 8.62 (lit.[3] 8.68) for the π-cyclopentadienyl and methyl peaks, respectively. The ultraviolet spectrum, reported here for the first time, exhibited maxima at 218 mμ (ϵ 48,100) and 321 mμ (ϵ 15,500).

Preparation of $[(CH_3)_3CSFeCOC_5H_5]_2$.—A mixture of 5.0 g. (14.1 mmoles) of $[C_5H_5Fe(CO)_2]_2$, 10 ml. (9.2 g., 51.7 mmoles) of di-*t*-butyl disulfide, and 40 ml. of ethylcyclohexane was refluxed 3 hr. under nitrogen at the boiling point. The reaction mixture was then cooled to room temperature and filtered. The black residue was extracted with 50 ml. of benzene. The filtered benzene extract was combined with the original ethylcyclohexane filtrate and chromatographed on a 2 × 60 cm. alumina column. Benzene was used both for developing the column and for eluting the large brown band[14] of $[(CH_3)_3CSFeCOC_5H_5]_2$. Evaporating the benzene eluate at 25° (25 mm.) gave brown oily crystals. These were purified by dissolving in 200 ml. of pentane and cooling the filtered solution to $-78°$ to give 2.33 g. (35% yield) of brown crystalline $[(CH_3)_3CSFeCOC_5H_5]_2$, m.p. 129–131°.

Anal. Calcd. for $C_{20}H_{28}O_2S_2Fe_2$: C, 50.4; H, 5.9; S, 13.4; Fe, 23.5. Found: C, 50.5; H, 6.0; S, 13.2; Fe, 23.2.

Infrared Spectrum.—C–H band at 2920–2820 (vw, br) cm.$^{-1}$; metal carbonyl band at 1920 (s) cm.$^{-1}$; other bands at 1440 (vw), 1418 (vw), 1355 (w), 1154 (m), 1008 (w, sh), 1000 (w), 840 (w, sh), 826 (w), 810 (w, sh), and 802 (m) cm.$^{-1}$.

Ultraviolet Spectrum.—Maxima at 216 mμ (ϵ 45,500) and 323 mμ (ϵ 10,300).

Proton N.m.r. Spectrum.—Sharp singlet resonances at τ 5.61 (π-cyclopentadienyl protons) and 8.97 (methyl protons) of the expected relative intensities ~5:9.

Preparation of $[(CH_3)_3CSFe(CO)_3]_2$.—A mixture of 10.8 g. (21.3 mmoles) of triiron dodecacarbonyl, 20 ml. of di-*t*-butyl disulfide, and 250 ml. of thiophene-free benzene was refluxed 5.5 hr. under nitrogen at the boiling point with magnetic stirring, the green color soon becoming red. After cooling to room temperature, the reaction mixture was filtered and the solvent removed from the filtrate at 25° (25 mm.). A filtered solution of the red liquid residue in ~60 ml. of hexane was cooled to $-78°$ to precipitate 4.7 g. (32% yield) of crude $[(CH_3)_3CSFe(CO)_3]_2$. Further purification was accomplished by a similar recrystallization from pentane to give 3.4 g. (23% yield) of pure red crystalline air-stable $[(CH_3)_3CSFe(CO)_3]_2$, m.p. 87–88°.

Anal. Calcd. for $C_{14}H_{18}O_6Fe_2S_2$: C, 36.7; H, 3.9; S, 14.0; Fe, 24.4. Found: C, 36.9; H, 4.1; S, 13.8; Fe, 24.1.

Infrared Spectrum.—Carbon–hydrogen stretching bands at 2940 (w), 2900 (w), and 2850 (sh) cm.$^{-1}$; metal carbonyl bands at 2060 (m), 2025 (s), 1990 (s), and 1970 (s) cm.$^{-1}$; other bands at 1470 (vw), 1455 (w), 1450 (w), 1360 (w), 1145 (m), and 1018 (vw) cm.$^{-1}$.

Proton N.m.r. Spectrum.—Two sharp methyl resonances at τ 8.62 and 8.72 of similar relative intensities.

TABLE I

INFRARED SPECTRA IN THE METAL CARBONYL REGION[a]

Compound	Metal carbonyl bands, cm.$^{-1}$
(1) $CH_3SFe(CO)_2C_5H_5$	2032 s, 1985 s
(2) $[C_5H_5Fe(CO)_2S(CH_3)_2]I$	2059 s, 2013 s
(3) $CH_3SFe(CO)_2C_2H_5 \cdot HgCl_2$	2047 s, $\begin{Bmatrix} 2011\ s \\ 1995\ s \end{Bmatrix}$

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

Discussion

Reactions of the metal carbonyl hydrides $C_5H_5M(CO)_3H$ (M = Mo and W) and $Mn(CO)_5H$ with dimethyl disulfide have been previously used by Treichel, Morris, and Stone[15] to prepare the *dimeric* derivatives $[C_5H_5M(CO)_2SCH_3]_2$ (M = Mo and W) and $[CH_3SMn(CO)_4]_2$ with loss of carbon monoxide as well as methanethiol. These workers failed to isolate any monomeric derivatives $C_5H_5M(CO)_3SCH_3$ or $Mn(CO)_5SCH_3$ analogous to the well-known carbonyl halides $C_5H_5M(CO)_3X$[8a] and $Mn(CO)_5X$.[16]

In contrast to these results with the carbonyl hydrides of molybdenum, tungsten, and manganese, the carbonyl hydride of iron, $C_5H_5Fe(CO)_2H$, although much less stable in other respects than the other hydrides, reacts with dimethyl disulfide to form the *monomeric* $CH_3SFe(CO)_2C_5H_5$ (II) without loss of carbon monoxide, according to the equation

$$C_5H_5Fe(CO)_2H + CH_3SSCH_3 \rightarrow CH_3SH + CH_3SFe(CO)_2C_5H_5$$

Only upon heating this monomeric compound (III) to ~70° is carbon monoxide lost to give dimeric $[CH_3SFeCOC_5H_5]_2$ (IV), analogous to the dimeric molybdenum, tungsten, and manganese compounds of Treichel, Morris, and Stone.[15]

The reluctance of $C_5H_5Fe(CO)_2H$ to lose carbon monoxide in its reactions is not unprecedented having been previously observed in unsuccessful attempts to prepare the unreported nitrosyl $C_5H_5FeCONO$. Thus reactions of the metal carbonyl hydrides $C_5H_5M(CO)_3H$ (M = Mo and W) and $Mn(CO)_5H$ with N-methyl-N-nitroso-*p*-toluenesulfonamide give the nitrosyls $C_5H_5M(CO)_2NO$[8a] and $Mn(CO)_4NO$[17] in good yields with loss of carbon monoxide. On the other hand, $C_5H_5Fe(CO)_2H$ reacts with N-methyl-N-nitroso-*p*-toluenesulfonamide to give the ubiquitous $[C_5H_5Fe(CO)_2]_2$ without loss of carbon monoxide.

The reaction between $[C_5H_5Fe(CO)_2]_2$ and dimethyl disulfide in boiling methylcyclohexane (~100°) has been previously shown[3] to give the same dimeric $[CH_3SFeCOC_5H_5]_2$ (IV) as that obtained by heating $CH_3SFe(CO)_2C_5H_5$. This reaction temperature of 100° is considerably above the decarbonylation temperature of ~70° for $CH_3SFe(CO)_2C_5H_5$ (III). By carrying out this reaction between $[C_5H_5Fe(CO)_2]_2$ and dimethyl disulfide at temperatures below ~40° using ultraviolet irradiation, it was found possible to isolate

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[13] In general, chemical shifts values obtained directly on the A-60 spectrometer appear to be more reliable than the values obtained by sidebanding techniques on the HR-60 spectrometer or its predecessor which were used for the original work on $[CH_3SFeCOC_5H_5]_2$ (ref. 3) reported in 1961.

[14] A weaker but more strongly adsorbed black band was also observed on the chromatogram from this reaction. Again the black crystalline carbonyl-free product has not yet been characterized in detail.

[15] P. M. Treichel, J. H. Morris, and F. G. A. Stone, *J. Chem. Soc.*, 720 (1963).

[16] E. W. Abel and G. Wilkinson, *ibid.*, 1501 (1959).

[17] P. M. Treichel, E. Pitcher, R. B. King, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 2593 (1961).

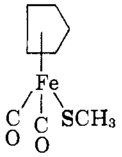
monomeric $CH_3SFe(CO)_2C_5H_5$ apparently formed according to the equation

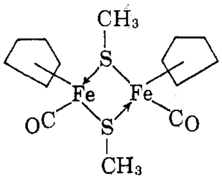
$$[C_5H_5Fe(CO)_2]_2 + CH_3SSCH_3 \rightarrow 2CH_3SFe(CO)_2C_5H_5$$

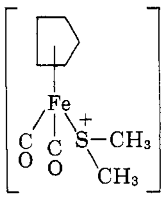
This reaction is entirely analogous to the preparation of the carbonyl halides $C_5H_5Fe(CO)_2X$ (X = I[18] and Br[19]) by treatment of $[C_5H_5Fe(CO)_2]_2$ with the appropriate free halogens.

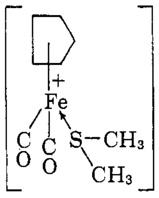
This new organosulfur compound $CH_3SFe(CO)_2C_5H_5$ is a brown crystalline solid appreciably more readily oxidized by air than the closely related halides $C_5H_5Fe(CO)_2X$. As expected, it is readily soluble in the usual organic solvents such as pentane, benzene, dichloromethane, carbon disulfide, ethanol, and acetone but insoluble in water. Its infrared and n.m.r. spectra are clearly in agreement with structure III and present no features of unusual interest.

The sulfur atom in $CH_3SFe(CO)_2C_5H_5$ possesses two lone pairs on the sulfur atom like the dialkyl sulfides and unlike all of the other known RS–transition metal derivatives where the sulfur is not part of a chelate dithiolate ring.[5] Treatment of the brown solutions of $CH_3SFe(CO)_2C_5H_5$ in pentane or similar inert solvent with active manganese dioxide or nickel peroxide in an attempt to prepare the corresponding sulfoxide or sulfone led instead to rapid destruction of the organometallic system with decolorization of the solution. On the other hand, $CH_3SFe(CO)_2C_5H_5$ was found to react immediately and exothermally with methyl iodide to give a yellow crystalline adduct $[C_5H_5Fe(CO)_2S(CH_3)_2]I$. Analogy with purely organic sulfur chemistry suggests this adduct to be the sulfonium salt Va with the positive charge on the sulfur atom. Nevertheless, the lower electronegativity of the iron atom relative to the sulfur atom favors location of the positive charge on the iron atom and formulation of this adduct as Vb, an adduct of dimethyl sulfide of the type $[C_5H_5Fe(CO)_2L]^+$ analogous to previously reported similar adducts of carbon monoxide,[20] ethylene,[20a] triphenyl phosphine,[20b] etc. The best description of $[C_5H_5Fe(CO)_2S(CH_3)_2]I$ is undoubtedly a resonance hybrid between Va and Vb, with Vb being greatly favored because of the positive charge on the iron atom.


III


IV


Va


Vb

A further illustration of the similarity of the reactivities of the sulfur atoms in $CH_3SFe(CO)_2C_5H_5$ and ordinary dialkyl sulfides is the formation of an adduct $CH_3SFe(CO)_2C_5H_5 \cdot HgCl_2$ by treatment of $CH_3SFe(CO)_2C_5H_5$ with ethanolic mercuric chloride analogous to the well-known adducts $R_2S \cdot HgCl_2$.[21]

Various observations suggested that $[CH_3SFeCOC_5H_5]_2$ decomposes significantly when sublimed under vacuum, the purification procedure used in the reported preparation of $[CH_3SFeCOC_5H_5]_2$ from $[C_5H_5Fe(CO)_2]_2$ and dimethyl disulfide.[3] It was found possible to raise the yield of pure $[CH_3SFeCOC_5H_5]_2$ from the originally reported[3] 9% to ~37% by substituting chromatography for sublimation during the product isolation using a procedure described in the Experimental section.

In order to examine the effect of substituting the methyl group in $[CH_3SFeCOC_5H_5]_2$ with the bulkier *t*-butyl group, the reaction between $[C_5H_5Fe(CO)_2]_2$ and di-*t*-butyl disulfide was investigated. The properties of the resulting brown crystalline $[(CH_3)_3CSFeCOC_5H_5]_2$ corresponded entirely to those of the analogous $[CH_3SFeCOC_5H_5]_2$.

The reaction between $Fe_3(CO)_{12}$ and di-*t*-butyl disulfide was also investigated and as expected gave a compound $[(CH_3)_3CSFe(CO)_3]_2$ analogous to other $[RSFe(CO)_3]_2$ compounds.[4,22] An attempt to separate this material into isomers by chromatography on alumina in pentane solution exactly analogous to the procedure successfully used for $[CH_3SFe(CO)_3]_2$[22] was unsuccessful, only a single red band being observed. Proton n.m.r. spectra of samples of $[(CH_3)_3CSFe(CO)_3]_2$ obtained in this work exhibited two methyl resonances of roughly equal relative intensities, suggesting this material to be the isomer containing two nonequivalent *t*-butyl groups analogous to the so-called "isomer A" of $[CH_3SFe(CO)_3]_2$[22] and the "*anti*" isomer of $[C_2H_5Fe(CO)_3]_2$.[23]

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