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Organosulfur Derivatives of the Metal Carbonyls. VII. Reactions between Chloroalkyl Sulfides and Metal Carbonyl Anions[1,2]

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Treatment of $NaMo(CO)_3C_5H_5$ with chloromethyl methyl sulfide at room temperature gives the yellow crystalline *tri*carbonyl σ-$CH_3SCH_2Mo(CO)_3C_5H_5$. Upon heating or ultraviolet irradiation this tricarbonyl is converted to a yellow-orange crystalline *di*carbonyl π-$CH_3SCH_2Mo(CO)_2C_5H_5$, with the CH_3SCH_2 group bonded to the metal atom both by metal–carbon and metal–sulfur bonds. The related π-$CH_3SCH_2W(CO)_2C_5H_5$ and yellow liquid π-$CH_3SCH_2Mn(CO)_4$ may be obtained from chloromethyl methyl sulfide and $NaW(CO)_3C_5H_5$ or $NaMn(CO)_5$, respectively, at 65–85°. Treatment of $NaFe(CO)_2C_5H_5$ with chloromethyl methyl sulfide at room temperature gives brown liquid σ-$CH_3SCH_2Fe(CO)_2C_5H_5$. Treatment of $NaFe(CO)_2C_5H_5$ with 2-chloroethyl methyl sulfide gives yellow-brown liquid $CH_3SCH_2CH_2Fe(CO)_2C_5H_5$. Irradiation of this compound in benzene solution gives the red crystalline isomeric acyl compound $CH_3SCH_2CH_2COFeCOC_5H_5$ (V) as well as the known compounds $[CH_3SFeCOC_5H_5]_2$,[3] $CH_3SFe(CO)_2C_5H_5$,[2] and $[C_5H_5Fe(CO)_2]_2$. Treatment of $NaMn(CO)_5$ with 2-chloroethyl methyl sulfide in boiling tetrahydrofuran gives the yellow crystalline acyl compound $CH_3SCH_2CH_2COMn(CO)_4$. The structures of the new compounds are discussed.

Introduction

Within the past few years numerous organosulfur transition metal compounds also containing carbonyl and/or cyclopentadienyl groups have been prepared from metal carbonyl derivatives and mercaptans, sulfides, disulfides, and dithietenes.[4] In all of these compounds the sulfur-containing ligand is attached to the metal atom only with metal–sulfur bonds.

In an entirely new approach to the synthesis of new types of organosulfur derivatives of transition metal carbonyls, we initiated in 1962 a study of reactions between chloroalkyl methyl sulfides, $Cl(CH_2)_nSCH_3$, and various metal carbonyl anions, especially $[Mn(CO)_5]^-$, $[Fe(CO)_2C_5H_5]^-$, and $[Mo(CO)_3C_5H_5]^-$. Analogy with reactions between alkyl halides and metal carbonyl anions[5,6] predicted the primary products of these reactions to be the σ-bonded alkyl derivatives of general formula $CH_3S(CH_2)_nM(CO)_x(C_5H_5)_y$ ($M = Mn$, $x = 5$, $y = 0$; $M = Mo$ or W, $x = 3$, $y = 1$; and $M = Fe$, $x = 2$, $y = 1$) with no metal–sulfur bonds and entirely analogous to the alkyl derivatives $RMn(CO)_5$,[6] $RM(CO)_3C_5H_5$ ($M = Mo$ or W),[5] and $RFe(CO)_2C_5H_5$.[5] As such, these sulfur-containing σ-bonded alkyl derivatives are not particularly interesting, being merely new representatives of well-established series of compounds. However, the ease of formation of transition metal–sulfur bonds as indicated by the plethora of very stable compounds obtained by heating metal carbonyls with organosulfur compounds[4] suggested that these sulfur-containing organometallic compounds $CH_3S(CH_2)_nM(CO)_x(C_5H_5)_y$ on heating or ultraviolet irradiation might lose carbon monoxide to form compounds with the organosulfur group bonded to the metal atom both with a carbon atom and with a sulfur atom, possibly of the type $CH_3S(CH_2)_nM(CO)_{x-1}(C_5H_5)_y$. Moreover, the number of methylene groups separating the sulfur atom from the metal atom in the compounds $CH_3S(CH_2)_nM(CO)_x(C_5H_5)_y$ might be expected to influence the type of compound formed upon decarbonylation.

This paper describes the reactions of certain metal carbonyl anions with chloromethyl methyl sulfide ($ClCH_2SCH_3$) and 2-chloroethyl methyl sulfide ($ClCH_2CH_2SCH_3$).

Experimental

In general, infrared spectra of solid compounds were taken as potassium bromide pellets and liquid compounds as liquid films. They were 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 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 (Table II) were taken in carbon disulfide solution (unless otherwise indicated) on a Varian Associates Model A-60 spectrometer using hexamethyldisiloxane (τ 9.95) as an internal standard. Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Molecular weight determinations (Mechrolab vapor pressure osmometer in 0.02 to 0.04 *M* benzene solution) were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Melting points were taken in capillaries and are uncorrected.

Reagents.—Chloromethyl methyl sulfide, b.p. 104–106°, was prepared from thionyl chloride and dimethyl sulfoxide by the published procedure.[7] 2-Chloroethyl methyl sulfide was purchased from Columbia Organic Chemicals, Columbia, S. C.[8]

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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 VI of this series see R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4**, 482 (1965).

[3] R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3600 (1961).

[4] W. Hieber and W. Beck, *Z. anorg. allgem. Chem.*, **305**, 265 (1960), and earlier references cited therein; S. F. A. Kettle and L. E. Orgel, *J. Chem. Soc.*, 3890 (1960); R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3600 (1961); R. B. King, *ibid.*, **85**, 1587 (1963), and earlier papers of this series; A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **86**, 2799 (1964), and earlier papers cited therein.

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

[6] R. D. Closson, J. Kozikowski, and T. H. Coffield, *J. Org. Chem.*, **22**, 598 (1957).

[7] F. G. Bordwell and B. M. Pitt, *J. Am. Chem. Soc.*, **77**, 572 (1955).

[8] Although we have experienced no difficulties in handling 2-chloroethyl methyl sulfide apart from the usual obnoxious odor of divalent sulfur compounds, we advise caution in handling this compound due to its probable high toxicity based on its close chemical relationship to bis(2-chloroethyl) sulfide, the highly toxic "mustard gas."

TABLE I

INFRARED SPECTRA[a] OF NEW ORGANOSULFUR TRANSITION METAL–CARBONYL DERIVATIVES AND RELATED COMPOUNDS IN THE METAL CARBONYL REGION

	Compound	Metal carbonyl bands, cm.$^{-1}$
	(A) CH_3SCH_2 Derivatives	
(1)	σ-$CH_3SCH_2Mo(CO)_3C_5H_5$	2029 s, 1952–1943 vs
(2)	$ClHgMo(CO)_3C_5H_5$	2015 s, 1999 s, 1931 s, 1901 s
(3)	π-$CH_3SCH_2Mo(CO)_2C_5H_5$	1922 s, 1838 s
(4)	π-$CH_3SCH_2W(CO)_2C_5H_5$	1910 s, 1825 s
	(B) $CH_3SCH_2CH_2$ Derivatives	
(5)	$CH_3SCH_2CH_2COFeCOC_5H_5$[b]	1935 s
(6)	$CH_3SCH_2CH_2COMn(CO)_4$[c]	2068 s, 2001 vs, 1981 vs, 1975 vs, 1961 vs

[a] Beckman IR-9 spectrometer, grating optics, halocarbon oil mulls. [b] Acyl carbonyl band at 1618 (s) cm.$^{-1}$. [c] Acyl carbonyl band at 1631 (vs) cm.$^{-1}$.

TABLE II

PROTON N.M.R. SPECTRA OF COMPOUNDS DISCUSSED IN THIS PAPER (τ)

(A) σ-CH_3SCH_2 Compounds

Compound	C_5H_5	CH_2	CH_3
CH_3SCH_2Cl	...	5.35	7.75
σ-$CH_3SCH_2Mo(CO)_3C_5H_5$	4.62	7.62	7.82
σ-$CH_3SCH_2Mn(CO)_5$	...	8.12	7.82
σ-$CH_3SCH_2Fe(CO)_2C_5H_5$	5.21	7.68	7.91

(B) π-CH_3SCH_2 Compounds

		CH_2			
Compound	C_5H_5	A	B	J_{AB}, c.p.s.	CH_3
π-$CH_3SCH_2Mo(CO)_2C_5H_5$	4.85	7.33	8.11	6.0	8.12
π-$CH_3SCH_2W(CO)_2C_5H_5$	4.71	7.36	7.95	6.0	7.96
π-$CH_3SCH_2Mn(CO)_4$	...	7.65	8.15	5.5	7.94

(C) $CH_3SCH_2CH_2$ Compounds

		CH_2[a]			
Compound	CH_3	A	B	J_{AB}, c.p.s.	C_5H_5
$CH_3SCH_2CH_2Cl$	7.86	6.41	7.27	8	...
$(ClCH_2CH_2SCH_3)_2PdCl_2$	7.53	6.06	6.74	7	...
$CH_3SCH_2CH_2Fe(CO)_2C_5H_5$ (IV)	7.98	7.45	8.48	9	5.31
$CH_3SCH_2CH_2COFeCOC_5H_5$ (V)	7.78	7.7 to 7.8[b]			5.60
$CH_3SCH_2CH_2COMn(CO)_4$	7.41	~7.6[b]			...

[a] Except where otherwise indicated, two triplets with the indicated coupling constants were observed for the two CH_2 groups. [b] In these two compounds a broad resonance was observed corresponding to both CH_2 groups.

The metal carbonyls required as ultimate starting materials ($Fe(CO)_5$, $Mn_2(CO)_{10}$, $Mo(CO)_6$, and $W(CO)_6$) were commercial samples.[9] $[C_5H_5Fe(CO)_2]_2$[10] and $[C_5H_5Mo(CO)_3]_2$[11] were prepared from $Fe(CO)_5$ and $Mo(CO)_6$, respectively, by well-established procedures. The techniques used here for preparing the sodium salts $NaFe(CO)_2C_5H_5$,[5,12] $NaMn(CO)_5$,[7] $NaMo(CO)_3C_5H_5$,[5,11,12] and $NaW(CO)_3C_5H_5$[5,12] are adequately described in the literature.

Tetrahydrofuran and 1,2-dimethoxyethane were purified by distillation over lithium aluminum hydride. A nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions, (b) handling all filtered solutions of metal complexes, and (c) admitting to evacuated flasks.

Preparation of σ-$CH_3SCH_2Mo(CO)_3C_5H_5$.—A solution of 100 mmoles of $NaMo(CO)_3C_5H_5$ in ~300 ml. of tetrahydrofuran was prepared either from molybdenum hexacarbonyl and sodium cyclopentadienide or from $[C_5H_5Mo(CO)_3]_2$ and dilute sodium amalgam and treated dropwise with 9.6 g. (100 mmoles) of chloromethyl methyl sulfide. After stirring for 15 to 60 hr. at room temperature solvent was removed at 25° (25 mm.). The residue was extracted with three 100-ml. portions of dichloromethane and the solvent removed from the filtered extracts at 25° (25 mm.). The yellow crystals of the product were extracted with ~400 ml. of pentane in several portions. The filtered pentane extracts were cooled to −78° to precipitate 22.8 g. (74.5% yield) of dirty yellow crystalline σ-$CH_3SCH_2Mo(CO)_3C_5H_5$. The pure yellow analytical sample, m.p. 66–67°, was obtained after a second similar recrystallization from pentane. It gradually darkened upon storage at room temperature in vials flushed with nitrogen. Storage in the freezer is therefore recommended.

Anal. Calcd. for $C_{10}H_{10}O_3SMo$: C, 39.2; H, 3.3; S, 10.4; Mo, 31.4; O, 15.7. Found: C, 39.6; H, 3.6; S, 10.4; Mo, 30.6; O, 16.0.

Infrared Spectrum.—C–H stretching frequencies at 3100 (w), 2925 (vw), 2875 (w), and 2850 (vw) cm.$^{-1}$; see Table I for metal carbonyl bands; other bands at 1415 (m), 1300 (w), 1106 (vw), 1080 (m), 1008 (w), 954 (w), 825 (s), 728 (vw), 693 (w), and 684 (w) cm.$^{-1}$.

Ultraviolet Spectrum.—Maxima at 221 mμ (ϵ 18,500) and 313 mμ (ϵ 4250).

Reaction between σ-$CH_3SCH_2Mo(CO)_3C_5H_5$ and Mercuric Chloride.—Filtered solutions of 1.0 g. (3.26 mmoles) of σ-$CH_3SCH_2Mo(CO)_3C_5H_5$ in 50 ml. of 95% ethanol and of 1.0 g. (3.69 mmoles) of mercuric chloride in 50 ml. of 95% ethanol were mixed and kept at room temperature for 1 hr. A fine pale yellow precipitate formed initially and pale yellow crystals gradually separated during the reaction period. These were removed by filtration, washed with two 20-ml. portions of ethanol, two 20-ml. portions of pentane, and dried. Recrystallization from a mixture of acetone and hexane gave 0.946 g. (~60% yield) of yellow crystalline $ClHgMo(CO)_3C_5H_5$, m.p. 183–185° dec.

Anal. Calcd. for $C_8H_5ClO_3HgMo$: C, 20.0; H, 1.0; Cl, 7.4; O, 10.0; S, 0.0. Found: C, 21.3; H, 1.3; Cl, 7.3; O, 10.4; S, 0.0.

Infrared Spectrum.—C–H band at 3080 (w) cm.$^{-1}$; see Table I for metal carbonyl bands; other bands at 1415 (m), 1005 (m), 872 (vw), 848 (w), and 825 (s) cm.$^{-1}$.

Proton N.m.r. Spectrum.—Single sharp resonance at τ 4.20 due to the five cyclopentadienyl protons.

Conversion of σ-$CH_3SCH_2Mo(CO)_3C_5H_5$ into π-$CH_3SCH_2Mo(CO)_2C_5H_5$. (A) By Ultraviolet Irradiation.—A solution of 6.0 g. (19.6 mmoles) of σ-$CH_3SCH_2Mo(CO)_3C_5H_5$ in 200 ml. of nitrogen-saturated benzene was irradiated for 112 hr. with magnetic stirring using an unfiltered 1000-watt ultraviolet source about 40 cm. from the quartz reaction vessel. The resulting black reaction mixture was filtered by gravity and the solvent removed from the black filtrate at 25° (25 mm.). The resulting brown residue was extracted with ~250 ml. of pentane in five portions, and the filtered pentane extracts were cooled 3 hr. in a −78° bath. Filtration of the cold solution gave 0.95 g. (17.4% yield) of yellow-brown crystalline π-$CH_3SCH_2Mo(CO)_2C_5H_5$. Sublimation of this crude material at 60° (0.1 mm.) gave 0.61 g. (64% recovery) of the pure yellow-orange crystalline product, m.p. 65–67°.

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(9) Iron pentacarbonyl was purchased from the Antara Division of General Aniline and Film; dimanganese decacarbonyl from the Ethyl Corporation; and molybdenum and tungsten hexacarbonyls from the Climax Molybdenum Co.

(10) R. B. King and F. G. A. Stone, *Inorg. Syn.*, **7**, 110 (1963).

(11) R. G. Hayter, *Inorg. Chem.*, **2**, 1031 (1963).

(12) R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **2**, 15 (1964).

(B) **By Pyrolysis.**—A 2.0-g. (6.5 mmoles) sample of σ-$CH_3SCH_2Mo(CO)_3C_5H_5$ was heated at 70–80° (0.5 mm.) in a sublimation apparatus with an uncooled probe. An orange-yellow liquid collected on the probe and periodically dripped back into the heated liquid. After 2 hr. the probe was filled with water at room temperature and an orange-yellow crystalline sublimate of π-$CH_3SCH_2Mo(CO)_2C_5H_5$ free from the tricarbonyl derivative collected on the probe. The recovery of somewhat sticky crystals was 1.283 g. (64%).

For further purification the crude sublimate was extracted with 100 ml. of pentane in five portions. The volume of the filtered extracts was reduced to ~60 ml. in a nitrogen stream and the product then recovered by cooling in a −78° bath and filtering the resulting crystals. After sublimation at 60–80° (0.1 mm.), 0.81 g. (~45% yield) of yellow-orange crystalline π-$CH_3SCH_2Mo(CO)_2C_5H_5$ was obtained.

(C) **Properties of π-$CH_3SCH_2Mo(CO)_2C_5H_5$.**—*Anal.* Calcd. for $C_9H_{10}O_2SMo$: C, 38.8; H, 3.6; S, 11.5; Mo, 34.5; O, 11.5; mol. wt., 278. Found: C, 38.9, 38.3; H, 3.6, 3.7; S, 11.2, 11.6; Mo, 33.5, 34.5; O, 11.1, 11.6; mol. wt., 262.

Infrared Spectrum.—C–H band at 3060 (vw); see Table I for metal carbonyl bands; other bands at 1415 (m), 1305 (w), 1055 (w), 1003 (w), 963 (w), 807 (m), 778 (w), 715 (vw), and 686 (vw) cm.$^{-1}$.

Ultraviolet Spectrum.—Maxima at 220 mμ (ϵ 18,100), 254 mμ (ϵ 11,750), and 419 mμ (ϵ 705).

Preparation of π-$CH_3SCH_2W(CO)_2C_5H_5$.—A solution of 20 mmoles of $NaW(CO)_3C_5H_5$ in 175 ml. of 1,2-dimethoxyethane was treated with 1.93 g. (20 mmoles) of chloromethyl methyl sulfide. The resulting mixture was heated ~16 hr. under reflux at the boiling point. After cooling to room temperature the solvent was removed at 25° (25 mm.) using a rotary evaporator. The residue was extracted with three 75-ml. portions of dichloromethane. The extracts were first filtered by suction through ~20 g. of chromatography grade alumina. After a second filtration by gravity, solvent was removed from the filtrate at 25° (25 mm.), leaving a yellow crystalline residue of crude π-$CH_3SCH_2W(CO)_2C_5H_5$. Extraction of this residue with 200 ml. of pentane in seven portions and cooling the filtered extract in a −78° bath deposited 0.374 g. of yellow crystalline π-$CH_3SCH_2W(CO)_2C_5H_5$, m.p. 80–81.5°. A purer sample of this compound (1.198 g.) was obtained as an orange crystalline sublimate, m.p. 87–88°, by sublimation of the residue from the pentane extraction at 100° (1 mm.). The total yield of π-$CH_3SCH_2W(CO)_2C_5H_5$ thus obtained from this experiment was 1.572 g. (21.5%).

The analytical sample, m.p. 87–88°, was obtained by resublimation of the sublimed material at 80° (0.025 mm.).

Anal. Calcd. for $C_9H_{10}O_2SW$: C, 29.5; H, 2.7; S, 8.7; O, 8.7; W, 50.3; mol. wt., 366. Found: C, 29.8; H, 2.8; S, 8.6; O, 9.0; W, 50.0; mol. wt., 394.

Infrared Spectrum.—C–H bands at 3060 (w) and 2890 (vw) cm.$^{-1}$; see Table I for metal carbonyl bands; other bands at 1415 (m), 1375 (vw), 1300 (m), 1100 (w), 1056 (vw, br), 1004 (w), 967 (w), 920 (vw, br), 832 (w), 817 (m), 768 (w), 717 (vw), and 685 (w) cm.$^{-1}$.

Ultraviolet Spectrum.—Maxima at 213 mμ (ϵ 16,300), 246 mμ (ϵ 13,450), and 417 mμ (ϵ 734).

Preparation of σ-$CH_3SCH_2Fe(CO)_2C_5H_5$.—A solution of 100 mmoles of $NaFe(CO)_2C_5H_5$ in 250 ml. of tetrahydrofuran was treated dropwise with 9.6 g. (100 mmoles) of chloromethyl methyl sulfide. An exothermic reaction occurred with relatively little color change. After stirring overnight at room temperature the solvent was removed at 25° (25 mm.). The residue was extracted with three 100-ml. portions of dichloromethane. The extracts were first filtered by suction through ~20 g. of chromatography grade alumina and then by gravity. Solvent was removed from the final filtrate at 25° (25 mm.), leaving an orange-brown liquid residue. This residue was extracted with 50 ml. of pentane in three portions. The filtered extracts were cooled for several hours in a −78° bath. Yellow crystals separated. While keeping the mixture cold, supernatant liquid was removed with a syringe and the crystals were warmed to room temperature in a vigorous stream of nitrogen. They melted below room temperature to give a yellow-brown liquid. After drying for ~1 hr. at room temperature in a vigorous stream of nitrogen, yellow-brown malodorous liquid σ-$CH_3SCH_2Fe(CO)_2C_5H_5$ was obtained in about 25% yield.

Anal. Calcd. for $C_9H_{10}O_2SFe$: C, 45.3; H, 4.2; S, 13.5; O, 13.5. Found: C, 44.8; H, 4.2; S, 13.8; O, 15.0.

Infrared Spectrum.—C–H bands at 3050 (vw), 2935 (sh), and 2870 (w) cm.$^{-1}$; metal carbonyl lands at 2000 (vs) and 1940 (vs) cm.$^{-1}$; other bands at 1425 (w), 1415 (w), 1395 (vw), 1355 (vw), 1300 (vw), 1085 (m), 1012 (vw), 998 (w), 944 (vw), 839 (m), 828 (s), 730 (w, br), and 695 (vw, br) cm.$^{-1}$.

Preparation of π-$CH_3SCH_2Mn(CO)_4$.—A solution of 10 mmoles of $NaMn(CO)_5$ in 100 ml. of redistilled tetrahydrofuran was treated with 0.96 g. (10 mmoles) of chloromethyl methyl sulfide. The resulting mixture was heated under reflux at the boiling point for 18 hr. After cooling to room temperature, the solvent was removed from the reaction mixture at ~25° (25 mm.). The residue was extracted with three 50-ml. portions of dichloromethane. Solvent was removed from the filtered extracts at 25° (25 mm.). A filtered solution of the liquid residue in 50 ml. of pentane was chromatographed on a 2 × 50 cm. alumina column. The chromatogram was developed with pentane and the single yellow band eluted with pentane. Solvent was removed from the filtered pentane eluate at 25° (25 mm.).

The resulting liquid residue of crude π-$CH_3SCH_2Mn(CO)_4$ was extracted with 20 ml. of pentane in three portions, and the filtered extracts were concentrated to 10 ml. in a vigorous stream of nitrogen. Yellow crystals separated upon cooling overnight in a −78° bath. While keeping the mixture cold, supernatant liquid was removed with a syringe and the crystals were dried in a stream of nitrogen while warming to room temperature. During this process they melted to a golden yellow liquid. After drying for ~1 hr. in a vigorous stream of nitrogen to ensure removal of pentane, the liquid π-$CH_3SCH_2Mn(CO)_4$ weighed 0.578 g. (25.2% yield).

Anal. Calcd. for $C_6H_5O_4SMn$: C, 31.6; H, 2.2; S, 14.0; Mn, 24.1; O, 28.1. Found: C, 31.4; H, 2.4; S, 13.8; Mn 24.5; O, 27.7.

Infrared Spectrum.—C–H bands at 2930 (vw) and 2910 (vw) cm.$^{-1}$; metal carbonyl bands at 2050 (s), 1990 (sh), 1970 (sh), 1930 (sh), and 1915 (vs) cm.$^{-1}$; other bands at 1425 (m), 1313 (m), 1010 (w), 960 (m), 928 (w), 768 (m), 722 (m), and 690 (m) cm.$^{-1}$.

Preparation of σ-$CH_3SCH_2Mn(CO)_5$.—The reaction between 10 mmoles of $NaMn(CO)_5$ and 10 mmoles of chloromethyl methyl sulfide in 100 ml. of redistilled tetrahydrofuran was repeated exactly as described above for the π-$CH_3SCH_2Mn(CO)_4$ preparation except that the reaction mixture was never heated above room temperature (~28°). Chromatography and low-temperature crystallization exactly as described above gave 0.4 g. (16% yield) of a yellow liquid suggested by its proton n.m.r. spectrum (Table II) to consist of σ-$CH_3SCH_2Mn(CO)_5$ free from π-$CH_3SCH_2Mn(CO)_4$ but containing other unidentified impurities. Analytical data given below although not unreasonable for an impure sample of σ-$CH_3SCH_2Mn(CO)_5$ confirmed the presence of an unidentified impurity and were too crude to be a sole basis for distinction between a tetracarbonyl and a pentacarbonyl. Attempts at further purification of this yellow liquid, much more weakly colored than the yellow π-$CH_3SCH_2Mn(CO)_4$ described above, were not made owing to the scarcity of the dimanganese decacarbonyl required as a starting material for the preparation of larger quantities of this substance.

Anal. Calcd. for $C_7H_5O_5SMn$: C, 32.8; H, 2.0; S, 12.5; Mn, 21.5; O, 31.2. Found: C, 33.8; H, 2.7; S, 13.1; Mn, 23.2; O, 27.3.

Infrared Spectrum.—C–H band at 2900 (s) cm.$^{-1}$; metal carbonyl bands at 2100 (s) and 2060–1915 (vvs) cm.$^{-1}$; acyl carbonyl bands at 1625 (m) and 1610 (w) cm.$^{-1}$; other bands at 1455 (w), 1425 (m), 1405 (sh), 1310 (sh), 1305 (m), 1190 (w), 1090 (s), 1010 (w), 960 (w), 945 (w), 935 (w), 768 (w), 740 (m), 723 (m), and 700 (m) cm.$^{-1}$.

Preparation of σ-$CH_3SCH_2CH_2Fe(CO)_2C_5H_5$.—A solution of 50 mmoles of $NaFe(CO)_2C_5H_5$ in 200 ml. of tetrahydrofuran was treated with 5.5 g. (50 mmoles) of 2-chloroethyl methyl sulfide. After stirring overnight at room temperature, solvent was removed at 25° (30 mm.). The resulting gray-brown residue was extracted with three 100-ml. portions of dichloromethane. Solvent was removed from the filtered extracts at 25°(30 mm.). A filtered solution of the yellow-brown liquid residue in ~100 ml. of pentane or diethyl ether was chromatographed on a 2 × 50 cm. alumina column. The yellow band of the product was eluted with diethyl ether. Solvent was removed from the filtered eluate at ~25° (30 mm.), leaving a yellow-brown liquid. A filtered solution of this residue in 50 ml. of pentane was cooled overnight in a −78° bath. Yellow crystals separated. The supernatant liquid was removed from the cold mixture with a syringe. The remaining crystals were dried in a rapid stream of nitrogen while warming to room temperature. They melted somewhat below room temperature to give 1.79 g. (~14% yield) of air-sensitive orange-brown liquid malodorous $CH_3SCH_2CH_2Fe(CO)_2C_5H_5$. The product was solid in a freezer at ~−15°.

Anal. Calcd. for $C_{10}H_{12}SFeO_2$: C, 47.6; H, 4.8; S, 12.7; Fe, 22.2; O, 12.7. Found: C, 47.4; H, 4.9; S, 12.4; Fe, 22.0; O, 12.7.

Infrared Spectrum.—C–H bands at 3070 (w), 2910 (sh), 2880 (m), and 2825 (w) cm.$^{-1}$; metal carbonyl bands at 1990 (vs) and 1930 (vs) cm.$^{-1}$; band at 1765 (w) due to bridging carbonyls from a trace of $[C_5H_5Fe(CO)_2]_2$ present as an impurity; other bands at 1428 (m), 1355 (w), 1310 (w), 1240 (w), 1200 (vw), 1100 (m), 1089 (m), 1060 (w), 1013 (w), 998 (w), 950 (w), 923 (vw), 840 (s), 830 (s), and 728 (vw, br) cm.$^{-1}$.

Irradiation of $CH_3SCH_2CH_2Fe(CO)_2C_5H_5$.—A solution of 100 mmoles of $NaFe(CO)_2C_5H_5$ in 250 ml. of tetrahydrofuran was treated with 11 g. (100 mmoles) of 2-chloroethyl methyl sulfide. After stirring overnight at room temperature the solvent was removed at 25° (30 mm.). As before the resulting gray-brown residue was extracted with three 100-ml. portions of dichloromethane. The dichloromethane extracts were filtered first by suction through alumina and then by gravity. Solvent was removed from the filtrate at 25° (30 mm.), leaving a yellow-brown liquid residue of crude $CH_3SCH_2CH_2Fe(CO)_2C_5H_5$.

This product was dissolved in 150 ml. of thiophene-free benzene. The solution was charged into a quartz tube and deaerated by evacuating and refilling with nitrogen. It was then irradiated for at least 24 hr. with the radiation from a 1000-watt mercury ultraviolet lamp about 40 cm. from the reaction vessel.

After the irradiation period was over, the resulting benzene solution was filtered, washing the residue with benzene. The combined filtrate and washings were chromatographed on a 5 × 50 cm. alumina column prepared in benzene. The chromatogram was developed with benzene. A brown band (A) overlapping slightly with a less mobile red-brown band (B) was observed. Another still less mobile brown band (C) was observed, followed finally by a much more strongly adsorbed orange band (D) which remained near the top of the column during the entire benzene development.

The first (brown) band (A) was eluted with benzene. Removal of solvent from the filtered eluate left a brown viscous liquid. This liquid was extracted with 50-ml. portions of 95% ethanol in three portions. The filtered brown ethanol extracts were cooled overnight in a −78° bath. The resulting mixture of yellow and brown crystals was filtered. The yellow crystals (probably unchanged σ-$CH_3SCH_2CH_2Fe(CO)_2C_5H_5$) melted below room temperature and passed through the filter. The sticky brown crystals remaining on the filter were washed with a few ml. of ethanol to remove the oily impurities. They were then extracted with 50 ml. of pentane in three portions. Cooling the filtered extracts several hours in a −78° bath precipitated brown crystals which were filtered and dried. This brown crystalline solid, m.p. 100–105°, was shown to be $[CH_3SFeCOC_5H_5]_2$ (lit.[8] m.p. 104–105°) by elemental analyses and its infrared and n.m.r. spectra. The yield of $[CH_3SFeCOC_5H_5]_2$ ranged from 0.2 to 0.6 g. (1.0 to 3.1% based on $[C_5H_5Fe(CO)_2]_2$).

The second (red-brown) band (B) was also eluted with benzene. Removal of solvent from the filtered eluate at 25° (30 mm.) left the characteristic red-violet crystals of $[C_5H_5Fe(CO)_2]_2$. After washing with several portions of pentane and drying, these crystals weighed 0.7 to 1.2 g. (4.0 to 6.8% yield based on $[C_5H_5Fe(CO)_2]_2$ used as a starting material).

The third (brown) band (C) was eluted with dichloromethane. Removal of solvent from the filtered eluate at 25° (30 mm.) left brown crystals. These were extracted with 200 to 400 ml. of pentane (about 150 ml. of pentane required for each gram of product) in many 25–50 ml. portions. The filtered pentane extracts were cooled several hours in a −78° bath. The resulting brown crystals were filtered and dried. This brown crystalline solid, m.p. 68–70°, was shown to be $CH_3SFe(CO)_2C_5H_5$ (lit.[2] m.p. 67–69°) by its infrared and proton n.m.r. spectra and by the elemental analyses given below. The yield was about 2.4 g. (10.7% based on $[C_5H_5Fe(CO)_2]_2$).

Anal. Calcd. for $C_8H_8O_2SFe$: C, 42.8; H, 3.6; S, 14.3; O, 14.3; Fe, 25.0. Found: C, 42.2; H, 3.7; S, 14.4; O, 14.5; Fe, 25.2.

The fourth (orange) band (D) was eluted with acetone. Removal of solvent from the filtered eluate at 25° (30 mm.) left oily orange crystals of $CH_3SCH_2CH_2COFeCOC_5H_5$ which were washed with pentane and dried. The yield at this stage ranged from 0.3 to 1.1 g. (1.2 to 4.4% based on $[C_5H_5Fe(CO)_2]_2$).

Further purification of this compound was somewhat difficult. On attempted sublimation at 70° (0.1 mm.) a dark red liquid collected on the probe in reasonable quantity. However, this liquid failed to crystallize, even during persistent cooling of the probe to −78° with Dry Ice. Finally a pure sample of $CH_2SCH_2CH_2COFeCOC_5H_5$, m.p. 71–73°, was obtained by crystallization from diethyl ether. The crude product was dissolved in diethyl ether (~100 ml./g. of product) and the filtered solution cooled overnight in a −78° bath. Well-formed air-sensitive orange crystals slowly separated. These were filtered, washed with a minimum of cold pentane, and dried.

Properties of $CH_3SCH_2CH_2COFeCOC_5H_5$.—*Anal.* Calcd. for $C_{10}H_{12}SFeO_2$: C, 47.6; H, 4.8; S, 12.7; Fe, 22.2; O, 12.7; mol. wt., 252. Found: C, 47.3; H, 5.1; S, 12.9; Fe, 21.6; O, 12.8; mol. wt., 232.

Infrared Spectrum.—C–H bands at 3060 (vw) and 2880 (vw) cm.$^{-1}$; see Table I for metal and acyl carbonyl bands; other bands at 1415 (m), 1405 (m), 1315 (w), 1269 (vw), 1250 (vw), 1105 (vw), 1054 (w), 1026 (m), 988–978 (w, br), 948 (m), 910 (w), 835 (m), 818 (m), 790 (vw), and 778 (m) cm.$^{-1}$.

Irradiation of $CH_3S(CH_2)_3Fe(CO)_2C_5H_5$.—Crude yellow-brown liquid $CH_3S(CH_2)_3Fe(CO)_2C_5H_5$ was prepared from 100 mmoles each of $NaFe(CO)_2C_5H_5$ and 3-chloropropyl methyl sulfide in 300 ml. of tetrahydrofuran. This material was irradiated under nitrogen in 100 ml. of benzene for 70 hr. exactly as described above for $CH_3SCH_2CH_2Fe(CO)_2C_5H_5$. Chromatography on alumina gave only unchanged $CH_3S(CH_2)_3Fe(CO)_2C_5H_5$, $[C_5H_5Fe(CO)_2]_2$, and $CH_3SFe(CO)_2C_5H_5$. The yield of brown crystalline $CH_3SFe(CO)_2C_5H_5$, m.p. 65–67° (lit.[2] m.p. 67–69°), was only 0.32 g. (1.4%).

Reaction between $NaMn(CO)_5$ and $CH_3SCH_2CH_2Cl$.—A solution of 25 mmoles of $NaMn(CO)_5$ in 150 ml. of tetrahydrofuran was treated at −78° with 2.8 g. (25 mmoles) of 2-chloroethyl methyl sulfide. The reaction mixture was stirred ~16 hr. at room temperature. Solvent was then removed at 25° (30 mm.). The residue was extracted with three 75-ml. portions of dichloromethane. Removal of solvent from the filtered dichloromethane extracts left a yellow liquid. A filtered solution of this liquid in ~75 ml. of benzene was chromatographed on a 2 × 50 cm. alumina column. The chromatogram was developed with benzene. Two yellow bands appeared.

The first yellow band was eluted with benzene. Solvent was removed from the filtered eluate at 25° (30 mm.). The remaining yellow crystals were extracted with 40 ml. of pentane in three portions. The filtered extracts were cooled to −78°. The resulting yellow crystals were filtered and dried to give 0.4 g. (~8% recovery) of $Mn_2(CO)_{10}$, identified by its infrared spectrum.

The second more weakly colored yellow band was eluted with dichloromethane. Solvent was removed from the filtered eluate at 25° (30 mm.). A pale yellow liquid remained which crystallized on treatment with 100 ml. of pentane, scratching the flask, and brief immersion in a −78° bath. These crystals of the desired $CH_3SCH_2CH_2COMn(CO)_4$ were removed by filtration. Further purification could be accomplished by dissolving the crystals in pentane at room temperature and cooling the filtered solution to −78° to reprecipitate the product. However, the product was only sparingly soluble in pentane, 60 ml. of pentane serving for the purification of only about 0.15 g. A more satisfactory technique for purifying $CH_3SCH_2CH_2COMn(CO)_4$ was sublimation at ~60° (0.1 mm.). During sublimation of $CH_3SCH_2CH_2COMn(CO)_4$ under these conditions, there was some tendency for the product to condense onto the probe as a liquid rather than a solid. To induce crystallization the probe was cooled briefly to −78° with few pieces of Dry Ice. Once the material had crystallized on the probe it remained crystalline on warming back to room temperature. Product obtained in this manner formed pale yellow crystals, m.p. 56–58°. Unlike the analogous iron compound $CH_3SCH_2CH_2COFeCOC_5H_5$, the manganese compound $CH_3SCH_2CH_2COMn(CO)_4$ was stable to air oxidation. From 5.0 g. of dimanganese decacarbonyl, 1.75 g. (26% yield) of $CH_3SCH_2CH_2COMn(CO)_4$ was obtained.

Anal. Calcd. for $C_8H_7O_5SMn$: C, 35.6; H, 2.6; S, 11.8; Mn, 20.3; O, 29.6; mol. wt., 270. Found (two different preparations): C, 36.3, 35.9; H, 3.0, 2.8; S, 11.6, 11.5; Mn, 19.8, 20.4; O, 29.1, 29.8; mol. wt., 284.

Infrared Spectrum.—C–H bands at 2960 (vw), 2930 (vw), 2900 (vw), and 2850 (vw) cm.$^{-1}$; see Table I for metal and acyl carbonyl bands; other bands at 1435 (m), 1425 (s), 1403 (m), 1328 (m), 1280 (w), 1259 (w), 1178 (w), 1111 (m), 1024 (s), 978 (m), 973 (m), 952 (s), 910 (m), 796 (w), and 784 (s) cm.$^{-1}$.

Preparation of $(ClCH_2CH_2SCH_3)_2PdCl_2$.—A filtered solution of 1.5 g. (~5 mmoles) of "sodium palladous chloride" (36.1% palladium) in 25 ml. of methanol was treated with 2.0 ml. (2.2 g., 20 mmoles) of 2-chloroethyl methyl sulfide. Initially a fine yellow precipitate formed but after standing 27 hr. in the air orange crystals had also separated. They were filtered, washed with two 10-ml. portions of methanol, and dried. After one crystallization from a mixture of dichloromethane and hexane, 0.93 g. (47% yield) of orange crystalline $(ClCH_2CH_2SCH_3)_2PdCl_2$, m.p. 69–70°, was obtained.

Anal. Calcd. for $C_6H_{14}Cl_4S_2Pd$: C, 18.0; H, 3.5; S, 16.0; Cl, 35.6; Pd, 26.7. Found: C, 18.0; H, 3.5; S, 15.8; Cl, 32.1; Pd, 26.9.

Infrared Spectrum.—C–H bands too weak to be observed; other bands at 1427 (m), 1410 (w), 1400 (w), 1312 (w), 1300 (vw), 1260 (m), 1126 (vw), 1020 (w), 980 (w), 971 (m), 928 (w), and 855 (m) cm.$^{-1}$.

Discussion

(A) The σ-CH_3SCH_2 Compounds.—The two σ-CH_3SCH_2 derivatives characterized in detail in this work, σ-$CH_3SCH_2Mo(CO)_3C_5H_5$ and σ-$CH_3SCH_2SCH_2Fe(CO)_2C_5H_5$, possess properties entirely analogous to those of the corresponding σ-bonded methyl, ethyl, and phenyl derivatives first studied in detail by Piper and Wilkinson.[5] The carbonyl region of the infrared spectra of the two new compounds and the ultraviolet spectrum of the molybdenum compound are entirely analogous to those of the other σ-bonded derivatives of these metals, providing evidence for the proposed structures. The proton n.m.r. spectra (Table II) of these two compounds, besides exhibiting the expected sharp resonance due to the five π-cyclopentadienyl protons, exhibit two additional sharp singlet resonances, one due to the CH_2 group and the other due to the CH_3 group. These are readily identified by their relative intensities. Of particular significance as will be seen below is the equivalence of the two CH_2 protons in the n.m.r. spectrum. As expected the chemical shifts of the CH_2 groups σ-bonded to the molybdenum or iron atom fall in the range τ 7.6–7.7, at much higher field than the corresponding CH_2 protons in chloromethyl methyl sulfide at τ 5.35.

In further confirmation of the proposed structure of σ-$CH_3SCH_2Mo(CO)_3C_5H_5$, in which the sulfur atom possesses two lone pairs like the dialkyl sulfides and $CH_3SFe(CO)_2C_5H_5$,[2] reactions characteristic of such sulfur atoms were investigated on this new molybdenum complex. Methyl iodide, which reacts rapidly and exothermally with $CH_3SFe(CO)_2C_5H_5$ to form $[C_5H_5Fe(CO)_2S(CH_3)_2]I$,[2] reacts only very slowly over many days with σ-$CH_3SCH_2Mo(CO)_3C_5H_5$ to form a yellow-brown ether-insoluble product demonstrated by its infrared spectrum to contain metal carbonyl groups. It thus appears that the lone pairs on the sulfur atom are less basic in $CH_3SCH_2Mo(CO)_3C_5H_5$ than in $CH_3SFe(CO)_2C_5H_5$. Ethanolic mercuric chloride, which reacts rapidly with $CH_3SFe(CO)_2C_5H_5$ to form the adduct $C_5H_5Fe(CO)_2SCH_3 \cdot HgCl_2$[2] analogous to other adducts of the type $R_2S \cdot HgCl_2$[13] with a mercury–sulfur bond, reacts with σ-$CH_3SCH_2Mo(CO)_3C_5H_5$ to give a yellow crystalline product clearly demonstrated by elemental analyses including the absence of sulfur to be the chloromercuri derivative $ClHgMo(CO)_3C_5H_5$ rather than the expected adduct σ-$CH_3SCH_2Mo(CO)_3C_5H_5 \cdot HgCl_2$. This synthesis of a derivative with a molybdenum–mercury bond is similar to some syntheses recently reported by Nyholm and Vrieze[14] of chloromercuri derivatives of iridium with iridium–mercury bonds from mercuric chloride and certain tertiary phosphine iridium carbonyl halides. Interestingly enough, the ethyl derivative $C_2H_5Mo(CO)_3C_5H_5$ did not form $ClHgMo(CO)_3C_5H_5$ on treatment with mercuric chloride; instead an orange rather insoluble material was formed. The trifluoromethyl derivative $CF_3Mo(CO)_3C_5H_5$[12] failed to react with ethanolic mercuric chloride even after several hours; this behavior is hardly surprising in view of the great stability of metal–carbon bonds in polyfluoroalkyl transition metal compounds.

(B) π-$CH_3SCH_2Mo(CO)_2C_5H_5$.—One of the most stable, highest melting, and most readily purified of the known π-allyl derivatives is the molybdenum compound π-$C_3H_5Mo(CO)_2C_5H_5$ prepared by Cousins and Green[15] by ultraviolet irradiation of the σ-allyl derivative σ-$C_3H_5Mo(CO)_3C_5H_5$. This suggested that if π-CH_3SCH_2 derivatives were reasonably stable, ultraviolet irradiation of σ-$CH_3SCH_2Mo(CO)_3C_5H_5$ would give the π-CH_3SCH_2 derivative π-$CH_3SCH_2Mo(CO)_2C_5H_5$. Ultraviolet irradiation of the yellow crystalline σ-$CH_3SCH_2Mo(CO)_3C_5H_5$, m.p. 66–67°, gave a dark-colored reaction mixture from which a yellow solid of almost iden-

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[13] W. F. Faragher, J. C. Morrell, and S. Comay, *J. Am. Chem. Soc.*, **51**, 2774 (1929).

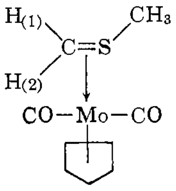
[14] R. S. Nyholm and K. Vrieze, *Chem. Ind.* (London), 318 (1964).

[15] M. Cousins and M. L. H. Green, *J. Chem. Soc.*, 889 (1963).

tical melting point was isolated. However, the infrared spectrum and especially the proton n.m.r. spectrum of this new yellow material differed from the corresponding spectra of authentic σ-$CH_3SCH_2Mo(CO)_3C_5H_5$. Complete elemental analyses of this new compound indicated it to have the required composition for the sought π-$CH_3SCH_2Mo(CO)_2C_5H_5$. The monomeric formulation was confirmed by the molecular weight determination.

To an untrained observer the color and melting points of σ-$CH_3SCH_2Mo(CO)_3C_5H_5$ and π-$CH_3SCH_2Mo(CO)_2C_5H_5$ are practically identical. Both are readily soluble in organic solvents. Both compounds even have a similar tendency to turn black gradually over a period of weeks on storage at room temperature in closed vials flushed with nitrogen. Only after some experience with these compounds did the appreciably greater intensity of the yellow color of the dicarbonyl as compared with that of the tricarbonyl become apparent.

The most significant feature of π-$CH_3SCH_2Mo(CO)_2C_5H_5$ is *the nonequivalence of the two CH_2 protons in the proton n.m.r. spectrum.* Besides the two sharp singlet resonances due to the C_5H_5 group and the CH_3 group, a characteristic AX pattern of two doublets, $J = 6.0$ c.p.s., is observed. This nonequivalence of the two CH_2 protons in π-$CH_3SCH_2Mo(CO)_2C_5H_5$ is consistent with either the preferred structure I with a carbon–sulfur double bond π-bonded to the molybdenum atom or with the alternative structure II with a carbon–sulfur–molybdenum three-membered ring. In both structures I and II the two CH_2 hydrogen atoms, $H_{(1)}$ and $H_{(2)}$, are oriented differently with respect to the molybdenum atom. Structures I and II represent different modes of bonding for the same or at least very similar physical arrangements of atoms. No evidence has been obtained in the present work which permits an unequivocal decision between these two structures. Indeed, it is doubtful whether the distinction between structures I and II is really meaningful, since they may really be extreme canonical forms of which the "actual" structure of π-$CH_3SCH_2Mo(CO)_2C_5H_5$ is a resonance hybrid. Analogous structural dilemmas have been recognized for certain π-complexes of dienes.[16]



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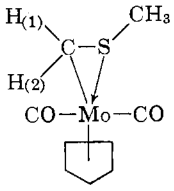
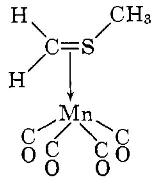


II



III

A useful technique for the purification of π-$CH_3SCH_2Mo(CO)_2C_5H_5$ is vacuum sublimation at 80° (0.1 mm.). Indeed the relatively high volatility of this compound is in accord with the monomeric formulation. However, when attempts were made to purify σ-$CH_3SCH_2Mo(CO)_3C_5H_5$ by vacuum sublimation, unexpected difficulties were encountered. Yellow-orange liquid sublimates were obtained which crystallized only with great reluctance. An explanation for this difficulty was obtained when the n.m.r. spectrum and analysis of the crystals obtained during the sublimation of σ-$CH_3SCH_2Mo(CO)_3C_5H_5$ revealed them not to be recovered *tri*carbonyl as expected but instead the *di*carbonyl formed by decarbonylation during the sublimation. The compound σ-$CH_3SCH_2Mo(CO)_3C_5H_5$ thus decarbonylates during attempted sublimation like the perfluoroacyl derivatives $R_fCOMo(CO)_3C_5H_5$ (R_f = CF_3 and C_3F_7),[12] but unlike the σ-allyl derivative σ-$C_3H_5Mo(CO)_3C_5H_5$, which is converted mainly to $[C_5H_5Mo(CO)_3]_2$.[15] On the basis of this observation, a procedure described in the Experimental section was developed for the preparation of π-$CH_3SCH_2Mo(CO)_2C_5H_5$ by the pyrolysis of σ-$CH_3SCH_2Mo(CO)_3C_5H_5$. This procedure was found to be considerably superior to the photochemical procedure discussed above.

In view of the obvious involvement of one of the lone pairs of the sulfur atom in π-$CH_3SCH_2Mo(CO)_2C_5H_5$ in the bonding with the molybdenum atom, it is scarcely surprising that this compound failed to react with either ethereal methyl iodide or ethanolic mercuric chloride under conditions where $CH_3SFe(CO)_2C_5H_5$ reacts rapidly.

(C) Other π-CH_3SCH_2 Compounds.—The success in the synthesis of π-$CH_3SCH_2Mo(CO)_2C_5H_5$ stimulated attempts to synthesize other π-CH_3SCH_2 compounds. In an attempt to prepare σ-$CH_3SCH_2W(CO)_3C_5H_5$, the sodium salt $NaW(CO)_3C_5H_5$ was allowed to react with chloromethyl methyl sulfide at room temperature in a manner analogous to the successful preparation of σ-$CH_3SCH_2Mo(CO)_3C_5H_5$. However, in several experiments it was mysteriously impossible to isolate any of the tungsten compound from the reaction mixture using techniques effective for the molybdenum analog. On the other hand, when the reaction between $NaW(CO)_3C_5H_5$ and chloromethyl methyl sulfide was carried out at the boiling point of 1,2-dimethoxyethane (~85°), orange volatile crystals soluble in organic solvents of the expected composition for the *di*carbonyl π-$CH_3SCH_2W(CO)_2C_5H_5$ were obtained. The considerable similarities in the infrared, ultraviolet, and proton n.m.r. spectra of the new tungsten compound clearly indicated its similarity to the molybdenum compound π-$CH_3SCH_2Mo(CO)_2C_5H_5$ discussed above.

Treatment of $NaMn(CO)_5$ with allyl chloride at room temperature has been found to give the yellow liquid σ-allyl derivative σ-$C_3H_5Mn(CO)_5$, which may be decarbonylated on heating to ~80° to give the yellow crystalline π-allyl derivative π-$C_3H_5Mn(CO)_4$.[17] Since the π-allyl derivative of manganese was higher melting, it appeared more promising initially to seek the π-CH_3SCH_2 derivative π-$CH_3SCH_2Mn(CO)_4$ hoping

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[16] See, for example, M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3753 (1959), and O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 421 (1960).

[17] (a) H. D. Kaesz, R. B. King, and F. G. A. Stone, *Z. Naturforsch.*, **15b**, 682 (1960); (b) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *J. Am. Chem. Soc.*, **83**, 1601 (1961).

to obtain a higher melting and therefore more readily isolated and purified product. Thus the mixture resulting from the treatment of $NaMn(CO)_5$ with chloromethyl methyl sulfide was heated to the boiling point of tetrahydrofuran (~65°) for several hours before isolating the product. From the resulting solution a golden yellow liquid could be isolated by chromatography. This material, although liquid at room temperature, was crystalline at −78° and could be purified by low-temperature crystallization from pentane. The proton n.m.r. spectrum of this material (Table II) exhibited the familiar pattern for π-CH_3SCH_2 derivatives with the two nonequivalent but coupled CH_2 protons again exhibiting two doublets. Elemental analyses indicated it to be the expected π-$CH_3SCH_2Mn(CO)_4$ (III).

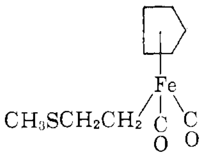
In an attempt to isolate an intermediate σ-$CH_3SCH_2Mn(CO)_5$ in the formation of π-$CH_3SCH_2Mn(CO)_4$, the reaction between $NaMn(CO)_5$ and chloromethyl methyl sulfide was repeated but the reaction mixture was not heated above room temperature. After chromatography a yellow liquid was isolated much paler in color than π-$CH_3SCH_2Mn(CO)_4$ but which was also crystalline at −78° and could be purified by low-temperature crystallization from pentane. The proton n.m.r. spectrum of this liquid exhibited singlet resonances at τ 8.12 and 7.82 (Table II) assigned on the basis of relative intensities to two *equivalent* CH_2 protons and three CH_3 protons, thus suggesting this yellow liquid to be the sought σ-$CH_3SCH_2Mn(CO)_5$. However, additional weaker n.m.r. resonances, the presence of acyl carbonyl bands in its infrared spectrum, and the elemental analyses suggested the presence of impurities. The scarcity of dimanganese decacarbonyl discouraged experiments as extensive as those carried out on the molybdenum derivatives.

Heck and Breslow prepared the first recognized π-allyl derivative, π-$C_3H_5Co(CO)_3$, by treatment of $NaCo(CO)_4$ with allyl chloride at room temperature.[17a,18] However, treatment of $NaCo(CO)_4$ with chloromethyl sulfide failed to yield a stable organocobalt compound. However, π-$C_3H_5Co(CO)_3$ appears to be less stable than the π-allyl derivatives analogous to the π-CH_3SCH_2 derivatives successfully prepared.

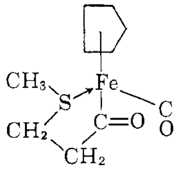
Green and Nagy have prepared the π-allyl derivative π-$C_3H_5FeCOC_5H_5$ by ultraviolet irradiation of the corresponding σ-allyl derivative σ-$C_3H_5Fe(CO)_2C_5H_5$.[19] However, chromatography of the mixture obtained by the irradiation of a benzene solution of σ-$CH_3SCH_2Fe(CO)_2C_5H_5$ resulted only in the recovery of unchanged starting material and the observation of trace amounts of a very intensely colored green substance. No π-$CH_3SCH_2FeCOC_5H_5$ was obtained. However, π-$C_3H_5FeCOC_5H_5$ from the description of its properties by Green and Nagy again appears to be less stable than the π-allyl derivatives analogous to the π-CH_3SCH_2 derivatives successfully prepared.

(D) Compounds from Metal Carbonyl Anions and 2-Chloroethyl Methyl Sulfide.—The orange malodorous air-sensitive liquid product $CH_3SCH_2CH_2Fe(CO)_2C_5H_5$ obtained from 2-chloroethyl methyl sulfide and $NaFe(CO)_2C_5H_5$ at room temperature is clearly the usual type of alkyl iron compound (IV) with an iron–carbon σ-bond and no iron–sulfur bonds. Its infrared spectrum exhibits no acyl carbonyl bands around 1600 cm.$^{-1}$ and two bands in the 2000 cm.$^{-1}$ metal carbonyl region similar to that of the other alkyl derivatives $RFe(CO)_2C_5H_5$.

One of the products obtained from the irradiation of $CH_3SCH_2CH_2Fe(CO)_2C_5H_5$ (IV) in benzene solution as described in the Experimental section is an isomeric red-orange crystalline solid (V), m.p. 71–73°. The infrared spectrum of this isomeric V is very different from that of IV, exhibiting only a single strong band in the metal carbonyl region at 1935 cm.$^{-1}$ and also a single strong band at 1618 cm.$^{-1}$, the expected carbonyl frequency for an *acyl* carbonyl group[20] bonded to a transition metal. This indicates structure V for this crystalline material, where only one of the two carbonyl groups clearly present from the analyses is a terminal metal carbonyl group and the other carbonyl group is an acyl carbonyl group. This structure contains a novel five-membered ring with two methylene groups, one acyl carbonyl group, one iron atom, and one sulfur atom. This chelate-type ring formally donates three electrons to the metal atom. Two of these three electrons arise from the iron–sulfur dative bond and the third electron from the bond between the iron atom and the carbon atom of the acyl group. The formula of V will be written as $CH_3SCH_2CH_2COFeCOC_5H_5$ in order to distinguish it readily from IV.[21]



IV



V

An even more predominant product in the irradiation of $CH_3SCH_2CH_2Fe(CO)_2C_5H_5$ is the monomeric methylthio derivative $CH_3SFe(CO)_2C_5H_5$.[2] This material is formed by an unusual shift of a CH_3S group from bonding with a carbon atom to bonding with an iron atom. A minor product is the dimeric $[CH_3SFeCOC_5H_5]_2$[3] known to be a decarbonylation product of $CH_3SFe(CO)_2C_5H_5$.[2]

Attempts were made to prepare compounds similar to V but containing metals other than iron. In this connection $NaMn(CO)_5$ was found to react with 2-chloroethyl methyl sulfide to give an air-stable pale yellow crystalline solid, m.p. 56–58°. Indeed this manganese compound was isolated, although only in

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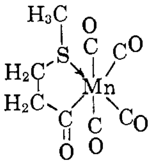
(18) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **82**, 750 (1960); **83**, 1097 (1961).

(19) M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 189 (1963).

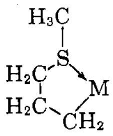
(20) E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, **18**, 585 (1962); R. B. King, *J. Am. Chem. Soc.*, **85**, 1918 (1963); R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **2**, 15 (1964).

(21) Strictly speaking, an arrow should be drawn from the sulfur atom to the iron atom in order to indicate the iron–sulfur bond. This bond is omitted from the formulas actually written for III in this paper for ease in printing the running text.

small quantities, about 1 year before any of the other metal carbonyl compounds described in this paper. The presence of a strong acyl carbonyl band at 1631 cm.$^{-1}$ and analyses for all five elements clearly indicate this manganese compound to be $CH_3SCH_2CH_2COMn(CO)_4$ of structure VI, entirely analogous to $CH_3SCH_2CH_2COFeCOC_5H_5$ (V). Unfortunately, the relative rarity of manganese carbonyl prevented studies on the manganese system as detailed as those carried out on the iron system.



VI



VII

An attempt to prepare a similar molybdenum compound ($CH_3SCH_2CH_2COMo(CO)_2C_5H_5$) from $NaMo(CO)_3C_5H_5$ and 2-chloroethyl methyl sulfide gave negative results. No reaction appeared to take place, suggesting that $NaMo(CO)_3C_5H_5$ is too unreactive[22] to react with 2-chloroethyl methyl sulfide, at least in tetrahydrofuran solution at room temperature.

The ability for the lone pair on the sulfur atom in 2-chloroethyl methyl sulfide to form more normal types of adducts with metal salts is demonstrated by the preparation by treatment of 2-chloroethyl methyl sulfide with methanolic Na_2PdCl_4 of the palladium compound $(ClCH_2CH_2SCH_3)_2PdCl_2$, completely analogous to other $(R_2S)_2PdCl_2$ compounds.[23]

The existence of cyclic acyl derivatives such as V with a five-membered ring containing a metal atom, a sulfur atom, two methylene groups, and an acyl carbonyl group suggested the existence of similar cyclic alkyl derivatives (VII) with a five-membered ring containing a metal atom, a sulfur atom, and three methylene groups. However, irradiation of the crude $CH_3SCH_2CH_2CH_2Fe(CO)_2C_5H_5$ obtained from $NaFe(CO)_2C_5H_5$ and 3-chloropropyl methyl sulfide in benzene solution as described in the Experimental section gave only $CH_3SFe(CO)_2C_5H_5$. This and the similar failure to obtain appreciable quantities of a manganese compound with the ring system VII from $NaMn(CO)_5$ and 3-chloropropyl methyl sulfide suggest the need for different synthetic techniques for such cyclic alkyl derivatives.

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

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[22] The work of T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956), suggests $NaMo(CO)_3C_5H_5$ to be less reactive than $NaFe(CO)_2C_5H_5$.

[23] F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1549 (1935).

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Crystal Structure of a 1:1 Mixture of Two Iron Carbonyl Sulfur Complexes, $S_2Fe_3(CO)_9$ and $S_2Fe_2(CO)_6$[1]

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The structure of $[S_2Fe_3(CO)_9][S_2Fe_2(CO)_6]$ (previously formulated incorrectly as $S_2Fe_3(CO)_9$) has been determined by X-ray diffraction. Three-dimensional isotropic least-squares refinement of all atoms yielded a final unweighted reliability index of $R_1 = 8.9\%$. The crystals contain four formula species in an orthorhombic unit cell of dimensions $a = 13.23 \pm 0.01$ Å., $b = 11.08 \pm 0.01$ Å., $c = 17.95 \pm 0.01$ Å. and of symmetry Pnma. The structure consists of an ordered array of two different molecular species of formulas $S_2Fe_3(CO)_9$ and $S_2Fe_2(CO)_6$, both of which possess crystallographic C_s-m symmetry. The molecular configuration of the $S_2Fe_2(CO)_6$ molecule is in close agreement with that of triclinic $S_2Fe_2(CO)_6$, prepared by the Hieber–Gruber reaction. The $S_2Fe_3(CO)_9$ molecule is found to be a conformer of the isomorphous Hieber–Gruber compounds $X_2Fe_3(CO)_9$ (X = S, Se).

Introduction

The preparation of $S_2Fe_3(CO)_9$ was first performed by Hieber and Gruber,[3] who allowed $HFe(CO)_4^-$ to react with sulfite ion to obtain a diamagnetic red-black crystalline compound, whose infrared spectrum possessed bands characteristic of only terminal carbonyl groups. Single crystal X-ray diffraction studies in this laboratory[4] showed the compound to be isomorphous with the Hieber–Gruber analog, $Se_2Fe_3(CO)_9$,[3] which contains a new type of seven-coordinated metal.[5] Recently King[6] isolated red-purple crystals with the presumably identical formula, $S_2Fe_3(CO)_9$, from the reaction between $Fe_3(CO)_{12}$ and cyclohexene sulfide or 3-chloropropylene sulfide. King[6] concluded from the

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[1] Presented in part at the National Meeting of the American Crystallographic Association, Montana State College, Bozeman, Mont., July 26–31, 1964.

[2] Fellow of the Alfred P. Sloan Foundation.

[3] W. Hieber and J. Gruber, *Z. anorg. allgem. Chem.*, **296**, 91 (1958).

[4] C. H. Wei, unpublished work (1963).

[5] L. F. Dahl and P. W. Sutton, *Inorg. Chem.*, **2**, 1067 (1963).

[6] R. B. King, *ibid.*, **2**, 326 (1963).