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Organosulfur Derivatives of the Metal Carbonyls. XII. Thenyl Derivatives of Metal Carbonyls[1,2]

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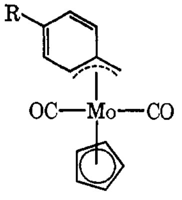
Reactions of 2-chloromethylthiophene and of 3-bromomethylthiophene with the sodium salts $NaM(CO)_3C_5H_5$ (M = Mo or W), $NaFe(CO)_2C_5H_5$, and $NaMn(CO)_5$ give the σ-thenyl derivatives σ-$C_4H_3SCH_2M(CO)_3C_5H_5$ (M = Mo or W, yellow crystals), σ-$C_4H_3SCH_2Fe(CO)_2C_5H_5$ (red-brown liquids), and σ-$C_4H_3SCH_2Mn(CO)_5$ (yellow liquids), respectively. In all cases, both σ-2-thenyl and σ-3-thenyl derivatives can be prepared. Ultraviolet irradiation of the molybdenum derivatives σ-$C_4H_3SCH_2Mo(CO)_3C_5H_5$ in hexane solution results in decarbonylation giving the red-orange π-thenyl derivatives π-$C_4H_3SCH_2Mo(CO)_2C_5H_5$. The nmr spectra of both the π-2-thenyl and the π-3-thenyl derivatives are temperature independent in the range −60 to +105° indicating the absence of fluxional properties in contrast to the corresponding π-benzyl derivative π-$C_6H_5CH_2Mo(CO)_2C_5H_5$. Vacuum distillation of the σ-$C_4H_3SCH_2Mn(CO)_5$ derivatives gives mixtures indicated by their proton nmr spectra to contain up to 50% of the corresponding π-$C_4H_3SCH_2Mn(CO)_4$ derivatives. The infrared and mass spectra of the new σ-thenyl and π-thenyl derivatives are described.

Fusion of a benzene ring to the π-allyl ligand gives the π-benzyl ligand which forms the molybdenum complex π-$C_6H_5CH_2Mo(CO)_2C_5H_5$ (I, R = H) with unusual fluxional properties.[5,6] Similar fusion of the thiophene ring to the π-allyl ligand gives either the π-2-thenyl (II) or the π-3-thenyl ligand (III) depending upon the point of fusion. This paper describes the synthesis of metal carbonyl complexes of both π-thenyl ligands II and III by the decarbonylation of appropriate σ-thenyl derivatives.



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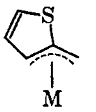

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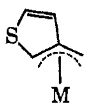

III

Experimental Section

Microanalyses (Table I) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Melting points were taken in capillaries and are uncorrected. Ultraviolet irradiations were performed by a water-jacketed Englehard-Hanovia 450-W lamp inserted into one neck of the reaction vessel. A nitrogen atmosphere was routinely provided for the following operations: (a) carrying out reactions; (b) handling filtered solutions of organometallic derivatives; and (c) admitting to evacuated vessels.

2-Chloromethylthiophene was prepared by treatment of thiophene with aqueous formaldehyde and hydrochloric acid.[7] 3-Bromomethylthiophene was prepared by treatment of 3-methylthiophene (Winthrop Laboratories, New York, N. Y.) with N-bromosuccinimide (Arapahoe Division of Syntex, Boulder, Colo.).[8] The sodium salts $NaMn(CO)_5$ and $NaFe(CO)_2C_5H_5$ were prepared by the standard procedure using the reactions of $Mn_2(CO)_{10}$[9] and $[C_5H_5Fe(CO)_2]_2$,[10] respectively, with ~1% sodium amalgam in tetrahydrofuran.[11,12] The sodium salts $NaM(CO)_3C_5H_5$ (M = Mo and W) were prepared by boiling the corresponding metal hexacarbonyl (Pressure Chemical Corp., Pittsburgh, Pa.) with sodium cyclopentadienide in tetrahydrofuran solution.[12,13] The reaction between sodium hydride and cyclopentadiene in tetrahydrofuran solution was used to prepare the sodium cyclopentadienide. The tetrahydrofuran used in this work was purified by redistillation over lithium aluminum hydride.

Preparation of the σ-$C_4H_3SCH_2M(CO)_3C_5H_5$ (M = Mo or W) Derivatives.—A solution of ~50 mmol of the sodium salt $NaM(CO)_3C_5H_5$ (M = Mo or W) in ~300 ml of tetrahydrofuran was stirred for ~25 hr with 60–70 mmol of the appropriate

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[2] Portions of this work were presented at the Fourth International Symposium on Organometallic Chemistry, Bristol, England, July 1969.

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Table I

New Compounds Prepared in This Work

Compound	Color	Mp, °C	Yield, %	Analyses, % C Calcd	C Found	H Calcd	H Found	S Calcd	S Found	O Calcd	O Found
σ-2-$C_4H_3SCH_2Mo(CO)_3C_5H_5$	Yellow	63–64	85	45.6	45.5	3.0	3.0	9.3	9.3	14.0	14.1
σ-3-$C_4H_3SCH_2Mo(CO)_3C_5H_5$	Yellow	85–86	75		44.7		2.9		8.6		14.3
π-2-$C_4H_3SCH_2Mo(CO)_2C_5H_5$	Red-orange	102–103	53	45.9	44.9	3.2	3.2	10.2	10.3	10.2	11.2
π-3-$C_4H_3SCH_2Mo(CO)_2C_5H_5$	Red-orange	125–127	35		44.5		3.3		10.2		10.1
σ-2-$C_4H_3SCH_2W(CO)_3C_5H_5$	Yellow	81–82	55	36.3	36.4	2.3	2.5	7.4	7.4	11.2	11.8
σ-3-$C_4H_3SCH_2W(CO)_3C_5H_5$	Yellow	86–87	52		36.4		2.5		7.3		11.0
σ-2-$C_4H_3SCH_2Fe(CO)_2C_5H_5$	Red-brown	Liquid	64	52.6	53.1	3.6	3.8	11.7	13.1	11.7	11.3
σ-3-$C_4H_3SCH_2Fe(CO)_2C_5H_5$	Red-brown	Liquid	55		52.3		3.8		12.1		11.1
σ-2-$C_4H_3SCH_2Mn(CO)_5$	Yellow	Liquid	60	41.1	40.9	1.7	2.0	11.0	11.1	27.4	27.4
σ-3-$C_4H_3SCH_2Mn(CO)_5$	Yellow	Liquid	66		40.6		1.9				

halomethylthiophene. Solvent was then removed at ~25° (40 mm). The residue was stirred for 4 hr with 400 ml of hexane to extract out the product. Concentrating and cooling the filtered hexane solution to −15° deposited yellow crystals of the product, which could be purified further by recrystallization from hexane.

Preparation of the σ-$C_4H_3SCH_2Fe(CO)_2C_5H_5$ Derivatives.—A solution of 50 mmol of the sodium salt $NaFe(CO)_2C_5H_5$ in ~250 ml of tetrahydrofuran was stirred for ~20 hr with 50 mmol of the appropriate halomethylthiophene. Solvent was then removed at ~25° (40 mm). The residue was stirred with 400 ml of deoxygenated hexane to extract out the product. Solvent was removed from the filtered hexane solution to give red-brown liquid crude σ-$C_4H_3SCH_2Fe(CO)_2C_5H_5$. This crude product was chromatographed on a 2 × 40 cm alumina column. The chromatogram was developed with hexane. A yellow band of σ-$C_4H_3SCH_2Fe(CO)_2C_5H_5$ followed by the characteristic red band of $[C_5H_5Fe(CO)_2]_2$ was observed. The yellow band was eluted with hexane. Evaporation of the hexane eluate at ~25° (40 mm) gave the pure σ-$C_4H_3SCH_2Fe(CO)_2C_5H_5$ as a yellow-brown liquid.

Preparation of the σ-$C_4H_3SCH_2Mn(CO)_5$ Derivatives.—A solution of 20 mmol of the sodium salt $NaMn(CO)_5$ in ~100 ml of tetrahydrofuran was stirred for ~16 hr with 20–30 mmol of the appropriate halomethylthiophene. Solvent was then removed at ~25° (40 mm). The residue was extracted with 400 ml of pentane. Solvent was removed from the filtered pentane extract at ~25° (40 mm) and the product was then dried 1 day at 25° (0.1 mm). The resulting yellow liquid froze upon cooling in a freezer at −15°. While being kept frozen around −15° this yellow product was washed two or three times with cold pentane and then dried further at 25° (0.1 mm) to give the σ-$C_4H_3SCH_2Mn(CO)_5$ derivative as a yellowish liquid. Vacuum distillation of this liquid at ~65° (0.2 mm) gave a dark yellow liquid shown by its nmr spectrum to be a mixture containing 10–50% of the corresponding π-$C_4H_3SCH_2Mn(CO)_4$ derivatives.

Preparation of π-3-$C_4H_3SCH_2Mo(CO)_2C_5H_5$.—A solution of 2.8 g (9.0 mmol) of σ-3-$C_4H_3SCH_2Mo(CO)_3C_5H_5$ in ~400 ml of hexane was exposed to ultraviolet irradiation for 30 hr. Solvent was then removed from the filtered reaction mixture at ~25° (40 mm). The residue was sublimed at 85° (0.1 mm) to give 0.9 g (35% yield) of red-orange π-3-$C_4H_3SCH_2Mo(CO)_2C_5H_5$. The analytical sample, mp 125–127°, was purified by a second sublimation.

Preparation of π-2-$C_4H_3SCH_2Mo(CO)_2C_5H_5$.—A solution of 3.5 g (11.1 mmol) of σ-2-$C_4H_3SCH_2Mo(CO)_3C_5H_5$ in ~400 ml of hexane was exposed to ultraviolet irradiation for 26 hr. Solvent was then removed from the filtered reaction mixture at ~25° (40 mm) to give 1.7 g (53% yield) of crude π-2-$C_4H_3SCH_2Mo(CO)_2C_5H_5$. This product was purified by sublimation at 85° (0.1 mm). Since the nmr spectrum of this product still indicated the presence of some unchanged σ-2-$C_4H_3SCH_2Mo(CO)_3C_5H_5$, this product was purified further by chromatography on an alumina column in hexane solution. The orange-red band was eluted with hexane. Evaporation of the filtered eluate gave pure π-2-$C_4H_3SCH_2Mo(CO)_2C_5H_5$, mp 102–103°.

Preparation of π-3-$C_4H_3SCH_2FeCOC_5H_5$.—A hexane solution containing the crude σ-3-$C_4H_3SCH_2Fe(CO)_2C_5H_5$ prepared from 25 mmol each of $NaFe(CO)_2C_5H_5$ and 3-bromomethylthiophene was exposed to ultraviolet irradiation for 36 hr. Solvent was removed from the filtered reaction mixture at ~25° (40 mm). The residue was chromatographed on a 2 × 40 cm alumina column. The column was developed with a mixture of dichloromethane and pentane. An orange band appeared followed by the characteristic red-purple band of $[C_5H_5Fe(CO)_2]_2$. Both bands were eluted with the dichloromethane–pentane mixture. Evaporation of the eluate from the first orange band gave liquid σ-3-$C_4H_3SCH_2Fe(CO)_2C_5H_5$ containing a small amount of crystalline π-3-$C_4H_3SCH_2FeCOC_5H_5$. This liquid was dissolved in pentane and the filtered pentane solution cooled to −78°. The red crystals which separated were filtered but melted upon warming to room temperature. This material was dissolved in 60–90° petroleum ether and the filtered solution again cooled to −78°. The red crystals which separated were filtered and remained solid upon warming to room temperature. By this procedure ~0.1 g (1.6% yield) of an air-sensitive red crystalline solid was obtained in one experiment. This was shown by its infrared and mass spectra to be π-3-$C_4H_3SCH_2FeCOC_5H_5$. Attempts to repeat this preparation were unsuccessful. Furthermore, an attempt to obtain a proton nmr spectrum of this compound in $CDCl_3$ solution failed owing to decomposition giving paramagnetic species.

Properties of π-3-$C_4H_3SCH_2FeCOC_5H_5$.—Infrared spectrum: $\nu(CO)$: 1955 (s) cm^{-1} (cyclohexane solution). Mass spectrum (relative intensities in parentheses): $C_4H_3SCH_2FeCOC_5H_5^+$ (20), $C_4H_3SCH_2FeC_5H_5^+$ (100), $C_2HSCH_2FeC_5H_5^+$ (9), $(C_5H_5)_2Fe^+$ (15), *m/e* 184 (48), $C_5H_5FeC_2HS^+$ (2), *m/e* 172 (4), $C_5H_5FeCHS^+$ (15), $C_5H_4FeS^+$ (33), $C_6H_6Fe^+$ (59), $C_3H_3FeSH^+$ (41), $C_3H_2SFe^+$ (17), $C_5H_5Fe^+$ (106), $FeSCH^+$ (13), $FeCS^+$ (20), $C_4H_3SCH_2^+$ (72), $C_3H_3Fe^+$ (13), $C_3H_2Fe^+$ (9), C_3HFe^+ (4) $FeSH^+$ (7), FeS^+ (11), C_2HFe^+ (11), Fe^+ (44).

Unsuccessful Decarbonylation Reactions. Iron Derivatives.—(a) Boiling a solution of σ-2-$C_4H_3SCH_2Fe(CO)_2C_5H_5$ in methylcyclohexane under reflux gave a mixture which deposited purple crystals upon cooling. These were identified as $[C_5H_5Fe(CO)_2]_2$ from their infrared spectrum. (b) Attempted vacuum distillation of σ-2-$C_4H_3SCH_2Fe(CO)_2C_5H_5$ at ~0.1 mm resulted in decomposition giving ferrocene, $[C_5H_5Fe(CO)_2]_2$, and unidentified dirty brown materials which did not appear to contain any π-$C_4H_3SCH_2$ derivatives.

Manganese Derivatives.—(a) Boiling a solution of σ-2-$C_4H_3SCH_2Mn(CO)_5$ in hexane under reflux gave only $Mn_2(CO)_{10}$ and a pyrophoric yellow-brown solid. (b) Distillation of σ-2-$C_4H_3SCH_2Mn(CO)_5$ at 65° (0.2 mm) caused partial decarbonylation, but the product was a mixture containing mostly unchanged σ-2-$C_4H_3SCH_2Mn(CO)_5$ with only up to ~35% of π-2-$C_4H_3SCH_2Mn(CO)_4$. The residue from the distillation was a brown solid similar to the yellow-brown solid obtained in (a). (c) Ultraviolet irradiation of σ-2-$C_4H_3SCH_2Mn(CO)_5$ in hexane gave either unchanged starting material or brown decomposition products depending upon the severity of the conditions.

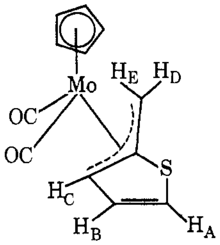
Tungsten Derivatives.—A solution of σ-3-$C_4H_3SCH_2W(CO)_3C_5H_5$ in a mixture of hexane and benzene was exposed to ultraviolet irradiation for 40 hr. An infrared spectrum of the resulting solution showed mainly the presence of unchanged σ-3-$C_4H_3SCH_2W(CO)_3C_5H_5$. Similar results were obtained when σ-3-$C_4H_3SCH_2W(CO)_3C_5H_5$ was refluxed for 10 hr in methylcyclohexane solution.

Discussion

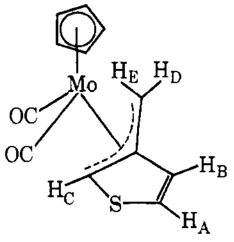
The preparations of the σ-thenyl derivatives from metal carbonyl anions and halomethylthiophenes resemble those of other σ-alkyl derivatives of the same metal carbonyls.[14] Attempts were made to decarbonylate these σ-thenyl derivatives by both photochemical and thermal methods, but these were only completely successful for the conversion of the σ-thenylmolybdenum derivatives σ-$C_4H_3SCH_2Mo(CO)_3C_5H_5$ to the π-thenylmolybdenum derivatives π-$C_4H_3SCH_2Mo(CO)_2C_5H_5$. In one experiment a low yield of the π-thenyliron derivative π-$C_4H_3SCH_2FeCOC_5H_5$ was obtained by ultraviolet irradiation of σ-$C_4H_3SCH_2Fe(CO)_2C_5H_5$ but this result could not be repeated. In other cases (*e.g.*, pyrolysis of σ-2-$C_4H_3SCH_2Fe(CO)_2C_5H_5$) cleavage of the metal–$\sigma$-thenyl bond occurred in preference to cleavage of the metal–carbonyl bond. The manganese derivatives σ-2-$C_4H_3SCH_2Mn(CO)_5$ and σ-3-$C_4H_3SCH_2Mn(CO)_5$ from the reaction between $NaMn(CO)_5$ and the halomethylthiophene were obtained mixed with small quantities of the corresponding π-$C_4H_3SCH_2Mn(CO)_4$ derivative. Some enrichment of this mixture in the π-thenyl derivatives by vacuum distillation could be effected. However, attempts to prepare pure π-$C_4H_3SCH_2Mn(CO)_4$ derivatives by pyrolysis or photolysis were unsuccessful. The relative ease of obtaining π-thenyl derivatives of the $C_5H_5Mo(CO)_2$ system parallels the relative ease of obtaining π-benzyl[5] and π-CH_3SCH_2[15] derivatives of this system.

The ν(CO) infrared frequencies of the new σ- and π-thenyl derivatives prepared in this work (Table II) are similar to the ν(CO) frequencies of related derivatives of the same metal carbonyls. The σ-$C_4H_3SCH_2Fe(CO)_2C_5H_5$ derivatives exhibit the expected two ν(CO) frequencies in the expected region. The σ-$C_4H_3SCH_2M(CO)_3C_5H_5$ (M = Mo and W) derivatives exhibit the three ν(CO) frequencies in similar positions to those recently[16] found for other $RM(CO)_3C_5H_5$ derivatives. The σ-$C_4H_3SCH_2Mn(CO)_5$ derivatives exhibited the expected two A_1 modes and the very strong E modes in the ν(CO) region; these frequencies were close to those reported for $CH_3Mn(CO)_5$.[17] Furthermore, the band around 2040 cm^{-1} may arise from the B mode which has gained some infrared activity from the asymmetry of the σ-thenyl group. The π-$C_4H_3SCH_2Mo(CO)_2C_5H_5$ derivatives exhibit a pair of strong ν(CO) frequencies as expected for a $C_5H_5Mo(CO)_2$ derivative. The additional weaker ν(CO) frequencies of the π-$C_4H_3SCH_2Mo(CO)_2C_5H_5$ derivatives indicated in Table II may arise from the presence of a second stereoisomer in quantities too small to be detected in the nmr spectra. (See below.) Other π-allylic $Mo(CO)_2C_5H_5$ derivatives exhibit two pairs of ν(CO) frequencies[18] which have been shown to arise from the presence of two stereoisomers.[19] The presence of the single ν(CO) frequency at 1955 cm^{-1} in the infrared spectrum of the monocarbonyl π-3-$C_4H_3SCH_2FeCOC_5H_5$ was useful for the identification of this rare and relatively unstable compound.

The proton nmr spectra of the new compounds were useful for their identification as σ- or π-thenyl derivatives. The spectra of the σ-thenyl derivatives exhibit complex aromatic resonances from the C_4H_3S protons in the range τ 2.9–3.3 and a singlet resonance due to the two equivalent CH_2 protons in the range τ 6.8–7.7. The proton nmr spectra of the π-thenyl derivatives are more complex since all five protons of the π-thenyl ligands are nonequivalent. Thus the proton nmr spectrum of π-2-$C_4H_3SCH_2Mo(CO)_2C_5H_5$ (IV) (Table III) exhibits resonances at τ 3.33 (H_A), 3.65 (H_B), 5.49 (H_C), 6.49 (H_D), and 8.08 (H_E) arising from the five π-2-thenyl protons and assigned as indicated in structure IV. The splittings indicate the following coupling constants (cps): $J_{AB} = 6$; $J_{BC} = 2$; $J_{DE} = 4$; others ~ 0. Similarly the proton nmr spectrum of π-3-$C_4H_3SCH_2Mo(CO)_2C_5H_5$ (V) (Table III) exhibits resonances at τ 3.50 (H_A), 3.97 (H_B), $\sim$5.3 (H_C), 6.82 (H_D), and 8.47 (H_E) arising from the five π-3-thenyl protons and assigned as indicated in structure V. The splittings indicate the following coupling constants (cps): $J_{AB} = 6$; $J_{AC} = 2$; $J_{DE} = 4$; others ~ 0. No unequivocal evidence for stereoisomers was found in the proton nmr spectra of either π-$C_4H_3SCH_2Mo(CO)_2C_5H_5$ derivative IV or V as is found in the nmr spectra of certain π-allyl derivatives including the closely related π-$C_3H_5Mo(CO)_2C_5H_5$ (VI).[19] Evidently the fusion of the thiophene nucleus to the π-allyl system causes one of the two possible stereoisomers to be greatly favored. The steric requirements of the thiophene ring favor the isomers corresponding to Davison and Rode's configuration A[19] rather than the alternatives corresponding to Davison and Rode's configuration B[19] which have the thiophene ring in the way of the π-cyclopentadienyl ring. A recent X-ray crystallographic study by Cotton and LaPrade[20] on the π-benzyl derivative p-$CH_3C_6H_4CH_2Mo(CO)_2C_5H_5$ (I, R = CH_3) likewise indicates it to be the single isomer corresponding to Davison and Rode's configuration A.[19] The proton nmr spectra of both π-$C_4H_3SCH_2Mo(CO)_2C_5H_5$ derivatives IV and V are temperature independent in the range −60 to +105°. This indicates that neither π-$C_4H_3SCH_2Mo(CO)_2C_5H_5$ derivative IV nor V has fluxional properties in an accessible temperature range



IV



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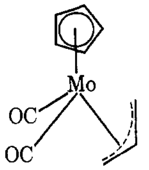

VI

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TABLE II

INFRARED SPECTRA OF NEW COMPOUNDS PREPARED IN THIS WORK[a]

Compound	ν(CO) frequencies[b]	Other bands[c]
σ-2-$C_4H_3SCH_2Mo(CO)_3C_5H_5$	2027 s, 1944 s, sh, 1940 s	3105 w,[d] 3040 vw,[d] 1418 s, 1350 m, 1236 w, 1082 vw, 1056 m, 1020 w, 1000 w, 838 m, 815 s, 798 s, 676 s, 635 vw
σ-3-$C_4H_3SCH_2Mo(CO)_3C_5H_5$	2025 s, 1945 s, 1935 s	3114 w,[d] 2990 vw,[d] 1440 m, 1395 m, 1256 m, 1172 w, 1098 w, 1076 m, 1030 w, 1017 w, 945 vw, 900 vw, 877 w, 870 w, 837 s, 830 s, 790 s, 695 w, 680 w, 652 m
π-2-$C_4H_3SCH_2Mo(CO)_2C_5H_5$[e]	1967 s, 1963 sh, 1895 s, 1882 m	1417 w, 1228 vw, 1200 vw, 1081 vw, 1003 w, 910 vw, br, 888 w, sh, 828 w, 810 m, 742 vw, 710 s, 660 w
π-3-$C_4H_3SCH_2Mo(CO)_2C_5H_5$	1970 s, 1897 s, 1884 m, sh	3090 vw,[d] 3065 vw,[d] 3030 vw,[d] 1510 m, 1422 w, 1358 m, 1250 w, 1163 w, 1080 m, 1040 w, 1000 w, 855 vw, 802 s, 795 s, 775 m, sh, 748 s, 700 m
σ-2-$C_4H_3SCH_2W(CO)_3C_5H_5$	2024 s, 1934 sh, 1930 s	2995 w,[d] 2970 vw,[d] 2950 w,[d] 1417 s, 1350 w, 1252 vw, 1230 vw, 1075 w, 1055 w, 1020 w, 1000 m, 837 m, sh, 823 s, 798 m, 676 s, 635 vw
σ-3-$C_4H_3SCH_2W(CO)_3C_5H_5$	2010 s, 1941 s, 1928 s	3110 w,[d] 3075 w,[d] 2925 vw,[d] 1518 w, 1420 m, 1400 w, 1377 m, 1240 w, 1155 w, 1078 w, 1057 w, sh, 1010 w, 1000 w, 927 w, 859 w, 850 w, 825 vs, 773 vs, 737 vw
σ-2-$C_4H_3SCH_2Fe(CO)_2C_5H_5$	2005 s, 1966 s	3125 w,[d] 3100 vw,[d] 2960 vw,[d] 2920 w,[d] 1518 w, 1435 m, 1422 m, 1364 w, 1248 m, 1176 vw, 1120 w, sh, 1088 m, 1065 m, 1028 m, 1020 m, 1005 m, 935 vw, 852 s, 837 vs, 822 m, 760 vw, 745 vw, 690 vs, 675 m, 625 vs
σ-3-$C_4H_3SCH_2Fe(CO)_2C_5H_5$	2004 s, 1963 s	3115 w,[d] 3110 w, sh,[d] 3065 vw,[d] 2960 w, sh,[d] 2925 w,[d] 1620 vw, 1580 vw, 1515 w, 1430 m, 1420 m, sh, 1355 w, 1260 w, sh, 1240 m, 1170 w, 1080 m, sh, 1060 m, 1014 m, 995 m, 935 w, 920 vw, 835 m, sh, 825 m, 805 m, 670 m, 650 m
σ-2-$C_4H_3SCH_2Mn(CO)_5$	2102 [A_1] m, 2062 w,[f] 2040 [B_1] m, 2005 [E] vs, 1987 [A_1] s, 1962 m[f]	3108 w,[d] 3064 w,[d] 3030 vw,[d] 2960 w, sh,[d] 2930 w,[d] 2865 vw,[d] 1525 w, 1445 m, 1435 m, 1362 vw, 1268 w, 1252 m, 1237 vw, 1210 w, 1200 w, 1185 w, 1132 w, 1097 s, 1090 s, sh, 1070 m, 1033 s, 940 vw, 930 w, 900 vw, 855 s, 840 w, 823 s, 762 w, 748 w, 695 vs, 670 vs
σ-3-$C_4H_3SCH_2Mn(CO)_5$	2104 [A_1] m, 2065 m,[f] 2037 [B_1] m, 2007 [E] vs, 1987 [A_1] s, 1965 m[f]	3100 vw,[d] 3085 vw,[d] 2960 w, sh,[d] 2935 w,[d] 2845 vw,[d] 1525 w, 1510 w, sh, 1427 vw, 1404 w, 1378 w, 1345 vw, 1255 w, 1235 w, 1172 vw, 1165 w, 1120 w, 1087 m, 1072 m, 1048 m, 1010 m, 985 w, 930 w, 865 w, 826 m, 800 w, 763 s, 715 w, 690 w, 655 vs, 625 vs

[a] These spectra were taken in the indicated media using a Perkin-Elmer Model 621 spectrometer with grating optics. All frequencies are given in cm^{-1}. [b] These frequencies were obtained from calibrated spectra taken in cyclohexane solution. [c] These frequencies were obtained from spectra taken in potassium bromide pellets. [d] ν(CH) frequency. [e] The spectrum of this compound was too weak for the ν(CH) frequencies to be unequivocally observed. [f] These relatively weak ν(CO) frequencies may arise from a π-$C_4H_3SCH_2Mn(CO)_4$ impurity. The π-allyl derivative π-$C_3H_5Mn(CO)_4$ exhibited the following ν(CO) frequencies in cyclohexane solution: 2046 (s), 2013 (vs), 1977 (m) cm^{-1}.

TABLE III

PROTON NMR SPECTRA

σ-$C_4H_3SCH_2$ derivatives	Solvent	Proton nmr chemical shifts, τ[a]		
		C_4H_3S	CH_2	π-C_5H_5
σ-2-$C_4H_3SCH_2Mo(CO)_3C_5H_5$	$CDCl_3$	3.10, 3.17, 3.23	6.88 s	4.77 s
σ-2-$C_4H_3SCH_2W(CO)_3C_5H_5$	$CDCl_3$	3.07, 3.14, 3.20, 3.23, 3.29	6.82 s	4.71 s
σ-2-$C_4H_3SCH_2Fe(CO)_2C_5H_5$[b]	$CDCl_3$	~3.2	~7.1	~5.4
σ-2-$C_4H_3SCH_2Mn(CO)_5$	$CDCl_3$	3.14, 3.20, 3.28	7.35 s	. . .
σ-3-$C_4H_3SCH_2Mo(CO)_3C_5H_5$	$CDCl_3$	2.9–3.0, 3.22 br	7.12 s	4.90 s
σ-3-$C_4H_3SCH_2W(CO)_3C_5H_5$	$CDCl_3$	~2.9, 3.05 d, 3.25	7.05 s	4.80 s
σ-3-$C_4H_3SCH_2Fe(CO)_2C_5H_5$[b]	$CDCl_3$	~3.2	7.15	~6.0
σ-3-$C_4H_3SCH_2Mn(CO)_5$	$CDCl_3$	~2.9, 3.14 d, 3.28	7.64 s	. . .

π-$C_4H_3SCH_2$ derivatives	Solvent	Proton nmr chemical shifts					
		C_4H_3S			CH_2		
		H_A	H_B	H_C	H_D	H_E	π-C_5H_5
π-2-$C_4H_3SCH_2Mo(CO)_2C_5H_5$	$C_6D_5CD_3$	3.33 d (6)	3.65 dd (6, 2)	5.49 d (2)	6.49 d (4)	8.08 d (4)	5.36 s
π-2-$C_4H_3SCH_2Mn(CO)_4$	$CDCl_3$	2.84 d (6)	*c*	5.17 d (4)	6.38 d (6)	8.08 d (6)	. . .
π-3-$C_4H_3SCH_2Mo(CO)_2C_5H_5$	$C_6D_5CD_3$	3.50 dd (6, 2)	3.97 d (6)	~5.3	6.82 d (3)	8.47	5.44 s
π-3-$C_4H_3SCH_2Mn(CO)_4$	$CDCl_3$	2.47 dd (5, 2)	*c*	4.77 s	6.61 d (4)	8.34 d (4)	. . .

[a] These spectra were taken in the indicated solvents and recorded on a Varian HA-100 spectrometer at 100 Mc or a Perkin-Elmer Hitachi R-20 spectrometer at 60 Mc. The coupling constants in cycles per second are given in parentheses. Abbreviations: d, doublet; dd, double doublet; s, singlet; br, broad. [b] These spectra were broad and poorly resolved owing to decomposition giving paramagnetic material. [c] These resonances were obscured by the stronger resonances arising from the σ-$C_4H_3SCH_2Mn(CO)_5$ derivative present in excess in the mixture investigated.

in contrast to the π-benzyl derivative π-$C_6H_5CH_2Mo(CO)_2C_5H_5$ (I, R = H) and derivatives thereof with various substituents on the benzene ring.

The proton nmr spectra of the σ-thenyl derivatives of manganese σ-$C_4H_3SCH_2Mn(CO)_5$, besides exhibiting strong resonances arising from the σ-$C_4H_3SCH_2$ protons, exhibited relatively weak resonances with the chemical shifts and fine structures expected for the presence of some of the corresponding π-$C_4H_3SCH_2Mn(CO)_4$ derivative (Table III). The amount of π-$C_4H_3SCH_2Mn(CO)_4$

derivative present in the σ-$C_4H_3SCH_2Mn(CO)_5$ derivative could be found by simple integration. A sample of σ-2-$C_4H_3SCH_2Mn(CO)_5$ prepared from 2-chloromethylthiophene and $NaMn(CO)_5$ without heating was shown by its nmr spectrum to contain none of the π-2-$C_4H_3SCH_2Mn(CO)_4$ derivative, but after vacuum distillation samples containing up to ~35% of π-2-$C_4H_3SCH_2M(CO)_4$ could be obtained. Similarly a sample of σ-3-$C_4H_3SCH_2Mn(CO)_5$ prepared from 3-bromomethylthiophene and $NaMn(CO)_5$ without heating contained ~10% of π-3-$C_4H_3SCH_2Mn(CO)_4$, but after vacuum distillation samples containing up to ~50% of π-3-$C_4H_3SCH_2Mn(CO)_4$ could be obtained. An attempt to obtain an nmr spectrum of the iron compound π-3-$C_4H_3SCH_2FeCOC_5H_5$ failed owing to its instability in $CDCl_3$ solution which led to rapid decomposition giving paramagnetic materials which obliterated the spectrum.

Table IV compares the positive ion mass spectra of the various thenyl derivatives of the cyclopentadienylmolybdenum carbonyl systems. In the mass spectra of the π-$C_4H_3SCH_2Mo(CO)_2C_5H_5$ derivatives stepwise losses of the two carbonyl groups occur followed by two C_2H_2 eliminations. Further fragmentation gives ions with molybdenum–sulfur bonds, notably MoS^+, which may arise by C_6H_6 elimination from $C_5H_5MoCHS^+$. Since the original thenylmolybdenum derivative contains no molybdenum–sulfur bond, this bond must have been formed some time during the fragmentation process. The mass spectra of the σ-thenyl derivatives σ-$C_4H_3SCH_2Mo(CO)_3C_5H_5$ exhibit the molecular ions but these are relatively weak compared with the other ions of the mass spectra. Decarbonylation of the σ-thenyl derivatives to the corresponding π-thenyl derivatives thus may occur in the mass spectrometer.[21] The σ-thenyl derivatives also undergo fission of the σ-thenyl group in the mass spectrometer giving the family of ions $C_5H_5Mo(CO)_n^+$ (n = 3, 2, and 1) not observed at all in the mass spectra of the π-thenyl derivatives. The metal-free ion $C_4H_3SCH_2^+$ (m/e 97) is intense in all of the mass spectra except that of π-2-$C_4H_3SCH_2Mo(CO)_2C_5H_5$ (IV) where it is not observed at all. Otherwise the ions observed in the mass spectra of all of the thenylmolybdenum derivatives are similar and occur in approximately similar abundances. The higher m/e ions in the mass spectrum of the iron derivative π-3-$C_4H_3SCH_2FeCOC_5H_5$ are similar to those in the mass spectra of the molybdenum derivatives but some differences are found among the lower m/e metal-containing ions. Thus, a major ion in the mass spectrum of the molybdenum derivatives but not in that of the iron derivative was $C_5H_5MS^+$. Attempts to obtain mass spectra of the σ-$C_4H_3SCH_2Fe(CO)_2C_5H_5$ and σ-$C_4H_3SCH_2Mn(CO)_5$ derivatives failed owing to decomposition within the mass spectrometer.

TABLE IV

MASS SPECTRA OF THENYL DERIVATIVES OF CYCLOPENTADIENYLMOLYBDENUM CARBONYLS[a]

	Relative abundance[b]			
Ion	σ-2-$C_4H_3SCH_2Mo(CO)_3C_5H_5$	σ-3-$C_4H_3SCH_2Mo(CO)_3C_5H_5$	π-2-$C_4H_3SCH_2Mo(CO)_2C_5H_5$	π-3-$C_4H_3SCH_2Mo(CO)_2C_5H_5$
$C_4H_3SCH_2Mo(CO)_3C_5H_5^+$	1	2	...	...
$C_4H_3SCH_2Mo(CO)_2C_5H_5^+$	35	33	26	28
$C_4H_3SCH_2MoCOC_5H_5^+$	9	7	7	6
$C_4H_3SCH_2MoC_5H_5^+$	100	100	100	100
$C_5H_5Mo(CO)_3^+$	6	5		
$C_2HSCH_2MoC_5H_5^+$	17	15	27	23
$C_5H_5MoC_2HS^+$			6	
$C_5H_5Mo(CO)_2^+$	27	24		
$C_5H_5MoCHS^+$	32	29	40	39
$C_5H_5MoS^+$	23	16	26	23
$C_5H_5MoCO^+$	42	27		
$C_3H_3MoS^+$			11	
$C_5H_5Mo^+$	65	55	16	15
$C_3H_3Mo^+$	29	20	10	14
MoS^+	22		27	52
C_2HMo^+			3	
$CHMo^+$	6	4	3	11
Mo^+	12		9	16
$C_4H_3SCH_2^+$	170	110	0	110

[a] These spectra were taken at 70 eV on a Perkin-Elmer Hitachi Model RMU-6 mass spectrometer. The inlet temperatures were kept at ~70°. [b] The relative abundance of the ion $C_4H_3SCH_2MoC_5H_5^+$ is assumed to have the arbitrary value of 100. The relative abundances of ions for which no figures are given were insignificant compared with the background.

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