116. Chemistry of the Metal Carbonyls. Part XXI.[1] New Complexes Derived from Manganese Pentacarbonyl Hydride, π-Cyclopentadienylmolybdenum Tricarbonyl Hydride, and π-Cyclopentadienyltungsten Tricarbonyl Hydride.

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Manganese pentacarbonyl hydride and π-cyclopentadienyl-molybdenum and -tungsten tricarbonyl hydride react with alkyl disulphides to afford the new dimeric series of compounds $[Mn(CO)_4{\cdot}SR]_2$ and $[\pi\text{-}C_5H_5{\cdot}M(CO)_2{\cdot}SR]_2$ (M = Mo or W), respectively. The addition of π-cyclopentadienylmolybdenum and -tungsten tricarbonyl hydride to tetrafluoroethylene is also reported.

A number of metal complexes of general formulæ $[Fe(CO)_3{\cdot}SR]_2$ and $[Co(CO)_3{\cdot}SR]_2$ (R = alkyl or C_6H_5) are known.[2] More recently the related complexes $[\pi\text{-}C_5H_5{\cdot}Fe(CO){\cdot}SCH_3]_2$,[3] $[\pi\text{-}C_5H_5{\cdot}Co{\cdot}SCH_3]_2$,[3] and $[\pi\text{-}C_5H_5{\cdot}V(SCH_3)_2]_2$ [1] have been described. In these dimeric complexes it is reasonable to assume that the alkylthio- or arylthio-groups function as bridging groups between two metal carbonyl portions and are bonded symmetrically to both metal atoms. Indeed, for the compound $[Fe(CO)_3{\cdot}SC_2H_5]_2$ this has been confirmed by an X-ray crystallographic study, which in addition to establishing the presence of two C_2H_5S groups shows the presence of an iron–iron bond.[4]

In this paper we report the organosulphur-manganese, -molybdenum, and -tungsten compounds $[Mn(CO)_4{\cdot}SR]_2$ (R = CH_3, C_2H_5, and n-C_4H_9) and $[\pi\text{-}C_5H_5{\cdot}M(CO)_2{\cdot}SCH_3]_2$ (M = Mo or W), which are prepared by treating the alkyl disulphide with the metal carbonyl hydrides $MnH(CO)_5$, $\pi\text{-}C_5H_5{\cdot}MoH(CO)_3$, and $\pi\text{-}C_5H_5{\cdot}WH(CO)_3$, respectively.

The new organosulphur-metal compounds are air-stable crystalline solids, the proton magnetic resonance spectra of which are described below. The character of this spectrum of $[\pi\text{-}C_5H_5{\cdot}Mo(CO)_2{\cdot}SCH_3]_2$ suggests that the compound is produced as a mixture of two geometrical isomers. If we assume a co-ordination number 5 for molybdenum, isomers could occur differing in the orientation of the $\pi\text{-}C_5H_5$ and CH_3S groups. Interestingly, the compound $[Fe(CO)_3{\cdot}SCH_3]_2$ has recently been resolved into two isomeric forms which apparently differ in the orientation of the methyl groups.[5] If geometrical isomers are present in $[\pi\text{-}C_5H_5{\cdot}Mo(CO)_2{\cdot}SCH_3]_2$ this would also explain the large number of observed carbonyl stretching frequencies.

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[1] Part XX, Holm, King, and Stone, *Inorg. Chem.*, 1962, **1**, in the press; Part XIX, Plowman and Stone, *Z. Naturforsch*, 1962, **17**b, 575.

[2] (*a*) Hieber and Scharfenberg, *Ber.*, 1940, **73**, 1012; (*b*) Reihlen. Friedolsheim, and Oswald, *Annalen*, 1928, **465**, 72; (*c*) Hieber and Beck, *Z. anorg. Chem.*, 1960, **305**, 265; (*d*) Hieber and Spacu, *Z. anorg. Chem.*, 1937, **233**, 359; (*e*) Kettle and Orgel, *J.*, 1960, 3890.

[3] King, Treichel, and Stone, *J. Amer. Chem. Soc.*, 1961, **83**, 3600.

[4] Dahl, personal communication.

[5] King, *J. Amer. Chem. Soc.*, 1962, **84**, 2460.

When π-cyclopentadienylmolybdenum tricarbonyl hydride and tetrafluoroethylene were brought together under conditions similar to those recently described[6] for adding manganese pentacarbonyl hydride to fluoro-olefins, the compound π-C_5H_5·$Mo(CO)_3$·CF_2·CHF_2 was obtained, as a yellow-orange, air-stable solid. The tungsten analogue, π-C_5H_5·$W(CO)_3$·CF_2·CHF_2 was also prepared, but appeared to be much less stable thermally and was light-sensitive.

The infrared spectra of the compounds show absorptions due to the perfluoroalkyl group in the region 1400—1000 cm.$^{-1}$ similar to those observed for CHF_2·CF_2·$Mn(CO)_5$.[6,7] The ^1H and ^{19}F nuclear magnetic resonance spectra of the molybdenum and tungsten compounds, similar to those of the analogous manganese compound,[6] are described below.

EXPERIMENTAL

Reactants.—Preparations of manganese pentacarbonyl hydride[8] and π-cyclopentadienylmolybdenum and -tungsten tricarbonyl hydrides[9] have been described. Tetrafluoroethylene was obtained by pyrolysis of Teflon resin at 600°.[10]

Apparatus and Instruments.—Experiments were conducted in a vacuum-system of conventional design. Infrared spectra were obtained by using a Perkin-Elmer model 21 double-beam spectrophotometer. Carbonyl stretching bands were recorded, unless otherwise stated, with the spectrophotometer equipped with a calcium fluoride prism. Other bands were measured by using sodium chloride optics. ^{19}F nuclear magnetic resonance spectra were recorded at 56·4 Mc./sec., with a Varian V4300B spectrometer equipped with superstabiliser. ^1H measurements were made on a Varian A-60 spectrometer.

Organosulphur Derivatives of Manganese, Molybdenum, and Tungsten.—(*a*) $[Mn(CO)_4$·$SCH_3]_2$. A Pyrex reaction bulb (300 ml.) was attached to the high-vacuum system, evacuated, and cooled to −196°. Then manganese pentacarbonyl hydride (2·5 g., 12·7 mmoles) and methyl disulphide (3·0 g., 32 mmoles) were distilled into the bulb, and the bulb was sealed. As the mixture warmed gas evolution was noted and the solution became yellow. After 12 hr. yellow crystals were observed. The bulb was opened to the vacuum-system and the volatile products were fractionated. Carbon monoxide (2·6 mmoles), methanethiol (53 c.c., 2·36 mmoles), and the excess of methyl disulphide were removed from the bulb. The golden-yellow solid remaining was recrystallised from pentane [2·1 g., 77% based on $Mn(CO)_5$·H used]; this solid *complex* [Found: C, 28·1; H, 1·6; Mn, 26·0; S, 14·8%; *M* (isopiestic), 427. $C_{10}H_6Mn_2O_8S_2$ requires C, 28·0; H, 1·3; Mn, 25·7; S, 14·9%; *M*, 428] decomposed without melting at 120°.

(*b*) $[Mn(CO)_4$·$SC_2H_5]_2$. From a reaction run in a similar manner to (*a*), with 1·05 g. of manganese pentacarbonyl hydride (5·36 mmoles) and 0·80 g. of ethyl disulphide, 1·0 g. of the yellow crystalline *compound* $[Mn(CO)_4$·$SC_2H_5]_2$ [Found: C, 31·7; H, 2·5; Mn, 24·1; S, 13·8%; *M* (isopiestic), 463. $C_{12}H_{10}Mn_2O_8S_2$ requires C, 31·6; H, 2·2; Mn, 24·1; S, 14·0%; *M*, 456], m. p. 80—81°, was obtained, representing an 82% yield based on manganese pentacarbonyl hydride used.

(*c*) $[Mn(CO)_4$·$SC_4H_9]_2$. From the reaction of 0·60 g. of manganese pentacarbonyl hydride (3·06 mmoles) and 1·0 g. of n-butyl disulphide (6·5 mmoles) in a Pyrex bulb, 0·65 g. of the *complex* $[Mn(CO)_4$·$SC_4H_9]_2$ [83% based on $Mn(CO)_5$·H used] was obtained as yellow crystals [Found: C, 37·8; H, 3·8; Mn, 21·3; S, 12·2%; *M* (isopiestic), 485. $C_{16}H_{18}Mn_2O_8S_2$ requires C, 37·5; H, 3·5; Mn, 21·5; S, 12·5%; *M*, 512], m. p. 66·5—67·5°.

(*d*) π-$[C_5H_5$·$Mo(CO)_2$·$SCH_3]_2$. Freshly sublimed π-cyclopentadienylmolybdenum tricarbonyl hydride (6·2 g., 25·2 mmoles) was placed in a 100-ml. round-bottomed flask under nitrogen. Then methyl disulphide (2·0 g., 32·3 mmoles) in pentane (25 ml.) was added. The reaction was allowed to proceed for 3 days. The solvent was evaporated at 20 mm. and the product recrystallised from pentane, giving a black crystalline *complex* (6·2 g., 95% based on the cyclopentadienylmetal hydride taken) [Found: C, 36·2; H, 3·1; Mo, 35·9; S, 12·0%; *M* (isopiestic), 518. $C_{16}H_{16}Mo_2O_4S_2$ requires C, 36·4; H, 3·0; Mo, 36·4; S, 12·1%; *M*, 528], m. p. 130° with decomp.

[6] Treichel, Pitcher, and Stone, *Inorg. Chem.*, 1962, **1**, 511.
[7] Pitcher and Stone, *Spectrochim. Acta*, 1962, **18**, 585.
[8] Hieber and Wagner, *Z. Naturforsch.*, 1958, **13**b, 338.
[9] Piper, Cotton, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1955, **1**, 165.
[10] Lewis and Naylor, *J. Amer. Chem. Soc.*, 1947, **69**, 1968.

If oxygen is not rigorously excluded from this reaction system some π-cyclopentadienylmolybdenum tricarbonyl dimer is formed. This species is very difficult to separate from the product, but this separation can be attained by careful chromatography on alumina with hexane as eluant.

(*e*) $[\pi\text{-}C_5H_5\cdot W(CO)_2\cdot SCH_3]_2$. Freshly sublimed π-cyclopentadienyltungsten tricarbonyl hydride (0·9 g., 2·8 mmoles) was placed in a 100-ml. round-bottomed flask under nitrogen, and the flask was evacuated. Methyl disulphide (0·6 g., 6·4 mmoles) and pentane (22 ml.) were cold-distilled in from a vacuum-system, and the mixture allowed to warm to room temperature. π-Cyclopentadienyltungsten tricarbonyl hydride was much less reactive than the corresponding molybdenum hydride and required a period of several weeks for satisfactory reaction, the solution becoming dark red during this time. The solvent was removed very slowly, to yield a dark red crystalline *complex* (0·7 g., 63% based on cyclopentadienylmetal hydride used) (Found: C, 27·1; H, 2·1; W, 51·9; S, 8·8. $C_{16}H_{16}W_2O_4S_2$ requires C, 27·3; H, 2·3; W, 52·5; S, 9·1%), which decomposed at 187°.

Spectroscopic Studies.—The infrared spectra of the new organosulphur-manganese, -molybdenum, and -tungsten compounds are listed in the Table.

The proton magnetic resonance spectra of the manganese compounds showed bands (τ) as follows: $[Mn(CO)_4\cdot SCH_3]_2$, 8·04; $[Mn(CO)_4\cdot SC_2H_5]_2$, 7·46 (quartet, separations 15 c./sec.), and 8·60 (triplet, separations 15 c./sec.), as expected for an ethyl group bonded to sulphur;[3] $[Mn(CO)_4\cdot SC_4H_9]_2$, multiplets at 7·45, 8·72, and 9·13 of relative intensity 2 : 4 : 3. The spectrum of $[\pi\text{-}C_5H_5\cdot W(CO)_2\cdot SCH_3]_2$ showed peaks at 4·51 and 8·11 τ (relative intensity 5 : 3), assignable to the cyclopentadienyl protons and the methylthio-protons, respectively. The spectrum of $[\pi\text{-}C_5H_5\cdot Mo(CO)_2\cdot SCH_3]_2$ showed single peaks at 4·53, 4·70, 8·13, and 8·18 τ. The peaks at 4·53 and 8·13 τ were of intensities 5 : 3 relative to each other, as were the other two peaks at 4·70 and 8·18 τ.

Reactions of π-Cyclopentadienylmolybdenum Tricarbonyl Hydride and π-Cyclopentadienyltungsten Tricarbonyl Hydride with Tetrafluoroethylene.—(*a*) Freshly sublimed π-cyclopentadienylmolybdenum tricarbonyl hydride (2·0 g., 8·15 mmoles) was transferred under nitrogen to a stainless-steel bomb of 150-ml. capacity. This vessel was then charged with tetrafluoroethylene (418 c.c. at N.T.P.; 18·7 mmoles) and pentane (20 ml.). The bomb was sealed and kept at room temperature for 24 hr.; then it was opened, and its contents were evaporated at 20 mm. The residue was sublimed at 25°/0·1 mm., affording 0·3 g. (11% yield based on hydride taken) of yellow crystals of the *compound* $\pi\text{-}C_5H_5\cdot Mo(CO)_3\cdot CF_2\cdot CHF_2$ [Found: C, 34·9; H, 1·7; F, 21·9; Mo, 27·5%; *M* (isopiestic), 341. $C_{10}H_6F_4MoO_3$ requires C, 34·7; H, 1·7; F, 22·0; Mo, 27·5%; *M*, 346], m. p. 53—54°.

Compound	Carbonyl stretching frequencies	Other bands
$[Mn(CO)_4\cdot SCH_3]_2$	(a) 2095w, 2074s, 2016vs, 2002vs, 1985m, 1969s, 1937w	(b) 2915w, 1428m, 1315w, 935w
$[Mn(CO)_4\cdot SC_2H_5]_2$	(a) 2094w, 2073s, 2015vs, 2000vs, 1985m, 1966s, 1935w	(b) 2978m, 2935m, 2885w, 1454m, 1436m, 1378m, 1258m, 1044m, 1024m, 973m
$[Mn(CO)_4\cdot SC_4H_9]_2$	(a) 2093w, 2072s, 2014vs, 1999vs, 1986m, 1966s, 1934w	(b) 2940m, 2875w, 1428w, 1339m, 1266m, 1212m
$[\pi\text{-}C_5H_5\cdot Mo(CO)_2\cdot SCH_3]_2$	(a) 1965s, 1947s, 1877s, 1869s, 1852m, sh	(b) 2960w, 1420w
$[\pi\text{-}C_5H_5\cdot W(CO)_2\cdot SCH_3]_2$	(c) 2034s, 1948s	(d) 3099vw, 2892vw, 1424w, 1351vw, 1306w, 1009w, 947w, 893w, 823m

(a) Cyclohexane solution. (b) Tetrachloroethylene solution. (c) Carbon tetrachloride solution. (d) Potassium bromide disc.

(*b*) A reaction under similar conditions with π-cyclopentadienyltungsten tricarbonyl hydride (5 g., 15 mmoles) and tetrafluoroethylene (1780 c.c. at N.T.P.), gave the yellow crystalline *compound*, $\pi\text{-}C_5H_5\cdot W(CO)_3\cdot CF_2\cdot CHF_2$ (0·5 g., 8%) [Found: C, 28·7; H, 1·4; F, 17·0; W, 42·4%; *M* (isopiestic), 414. $C_{10}H_6F_4O_3W$ requires C, 27·7; H, 1·4; F, 17·5; W, 42·4%; *M*, 434], m. p. 65—65·5° with decomp., that is best purified by recrystallisation from pentane.

The infrared spectrum of $\pi\text{-}C_5H_5\cdot Mo(CO)_3\cdot CF_2\cdot CHF_2$ (NaCl optics, CS_2 solution) showed bands at 3080w, 2920w, 2045s, 2000vs, 1945s, 1350m, 1172m, sh, 1165m, 1100s, 1005s, 972s, 915m, 822s, and 780m cm.$^{-1}$. The spectrum of $\pi\text{-}C_5H_5\cdot W(CO)_3\cdot CF_2\cdot CHF_2$ (NaCl optics, CS_2

solution) showed bands at 3120w, 2942w, 2045s, 1990vs, 1945s, 1360m, 1315w, 1168m, 1130m, 1095s, 1005s, 968m, 920m, 830s, and 778m cm.$^{-1}$.

The ^{19}F nuclear magnetic resonance spectrum of π-$C_5H_5{\cdot}W(CO)_3{\cdot}CF_2{\cdot}CHF_2$ shows two sets of doublets at 57·1 p.p.m. and 123·4 p.p.m. upfield from the standard trichlorofluoromethane with splittings of 3·1 and 57 c./sec., respectively. The proton spectrum consists of two sets of peaks, a sharp absorption of relative intensity five at 4·37 τ due to the cyclopentadienyl ring protons and a set of three triplets (splittings 3·1 and 57 c./sec.) centred at 4·71 τ of relative intensity one, due to the proton in the fluoroalkyl group. Consistently with the positions of the fluorine resonances and the proton–fluorine spin coupling constants, we have assigned the downfield doublet in the ^{19}F spectrum to the CF_2 group adjacent to the metal, and the upfield doublet to the CF_2 group in the position on carbon removed from the metal.[11] The ^1H and ^{19}F spectra of the molybdenum compound π-$C_5H_5{\cdot}Mo(CO)_3{\cdot}CF_2{\cdot}CHF_2$ are similar to those of this tungsten compound. Thus the ^{19}F spectrum contains two sets of peaks at 59·9 (splitting <1 c./sec.) and at 128·0 p.p.m. (splitting 58 c./sec.) upfield from the standard trichlorofluoromethane. The proton magnetic resonance is consistent with the ^{19}F spectrum.

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[11] Pitcher, Buckingham, and Stone, *J. Chem. Phys.*, 1962, **36**, 124.