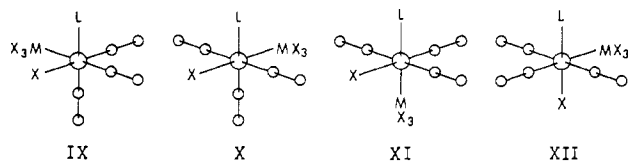some tentative conclusions about the nature of the triphenylphosphine adducts $(OC)_3LXFeMX_3$. Four isomers are possible (IX–XII), each with three infrared-active carbonyl stretching modes. Three bands are seen in the compounds reported here (Figure 3).

IX   X   XI   XII

Intensity considerations similar to those previously used in a related instance[30] lead us to expect one strong band and two bands of approximately equal intensity for isomer IX; in isomers X–XII, the mutually *trans*

(30) R. C. Taylor and W. D. Horrocks, Jr., *Inorg. Chem.*, **3**, 584 (1964).

arrangement of two carbonyls should give rise to a weak A' mode (also at highest frequency) and a very strong A'' mode, while the third carbonyl group should produce a strong A' mode. The observed intensities (Figure 3) certainly favor X, XI, or XII over IX but do not make possible an unambiguous choice. On other grounds, we tend to prefer XI or XII, with a *cis* placement of the X and SnX_3 ligands. Thus, these ligands are invariably *cis* in the $(OC)_4XFeSnX_3$ derivatives, and the fact that *trans*-$L_2Fe(CO)_3$ gives the same product as $LFe(CO)_4$ would tend to favor an isomer in which one of the new ligands (X or MX_3) is *trans* to the remaining L.

Organosulfur Derivatives of the Metal Carbonyls. XI. Some cis-1,2-Ethylenedithiolate Derivatives of Manganese Carbonyl and Related Compounds[1,2]

BY R. B. KING[3] AND C. A. EGGERS[4]

Reaction between $Mn(CO)_5Br$ and disodium *cis*-1,2-ethylenedithiolate in a mixture of acetone and methanol gives the deep red volatile complex $H_2C_2S_2Mn_2(CO)_6$. This compound reacts with various Lewis base ligands in inert solvents to form products of two types: (a) dark red-brown substitution products of the type $H_2C_2S_2Mn_2(CO)_4L_2$ (L = $(C_6H_5)_3P$ or $[(CH_3)_2-N]_3P$); (b) yellow addition products of the type $H_2C_2S_2Mn_2(CO)_6L$ (L = $(C_6H_5)_3P$, $0.5(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, or NH_3). Reaction between $Fe_2(CO)_9$ and disodium *cis*-1,2-ethylenedithiolate in methanol solution results in hydrogenation of the carbon–carbon double bond giving the saturated derivative $C_2H_4S_2Fe_2(CO)_6$ previously obtained from $Fe(CO)_5$ and 1,2-ethanedithiol.

Introduction

The previous paper of this series[2] discusses reactions between cyclopentadienylmetal halides and disodium *cis*-1,2-ethylenedithiolate. Reactions between metal carbonyl halides and disodium *cis*-1,2-ethylenedithiolate have also been investigated. This paper describes the reaction between disodium ethylenedithiolate[5] and bromopentacarbonylmanganese, $Mn(CO)_5Br$. This reaction was found to give a novel type of organosulfur derivative of manganese carbonyl, $H_2C_2S_2Mn_2(CO)_6$. This paper also describes some unusual reactions of this manganese complex.

Experimental Section

Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Molecular weight deter-

minations were carried out with a Mechrolab vapor pressure osmometer in benzene solution by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Infrared spectra were taken in either potassium bromide pellets or appropriate organic solvents and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Proton nmr spectra were taken in chloroform-*d* or acetone solutions and recorded on either a Varian A-60 or a Varian HA-100 spectrometer. Melting and decomposition points were determined in capillaries and are uncorrected.

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 vessels.

Reagents.—Sodium ethylenedithiolate, first reported by Schroth and Peschel,[6] was obtained by the procedure described in the previous paper.[2] Bromopentacarbonylmanganese was obtained from decacarbonyldimanganese[7] by the usual bromination procedure.[8] The phosphorus derivatives $[(CH_3)_2N]_3P$

(1) Portions of this work were presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

(2) Part X: R. B. King and C. A. Eggers, *Inorg. Chem.*, **7**, 340 (1968).

(3) Fellow of the Alfred P. Sloan Foundation, 1967–1969.

(4) Postdoctoral Research Associate supported by the Air Force Office of Scientific Research, Jan–Oct 1967.

(5) For brevity the *cis*-1,2-ethylenedithiolate dianion will be hereafter designated simply as "ethylenedithiolate."

(6) W. Schroth and J. Peschel, *Chimia*, **18**, 171 (1964).

(7) For a convenient preparation of decacarbonyldimanganese see R. B. King, J. C. Stokes, and T. F. Korenowski, *J. Organometal. Chem.* (Amsterdam), **11**, 641 (1968).

(8) E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959); R. B. King, *Organometal. Syn.*, **1**, 174 (1965).

TABLE I

ν(CO) FREQUENCIES OF NEW MANGANESE CARBONYL DERIVATIVES (CM⁻¹)

Compound	Medium[a]	ν(CO) frequencies
$H_2C_2S_2Mn_2(CO)_6$	CH_2Cl_2	2060 m, 2025 s, 1973 s, 1947 m
	KBr	2062 m, 2037 s, 1978 s, 1955 s, 1908 s
		2052 s, 1962 s, 1946 s
$H_2C_2S_2Mn_2(CO)_4[P(C_6H_5)_3]_2$	CH_2Cl_2	1962 s, 1926 s, 1897 m, 1868 m
	KBr	1958 s, 1922 s, 1896 s, 1859 s
$H_2C_2S_2Mn_2(CO)_4[P(N(CH_3)_2)_3]_2$	CH_2Cl_2	1953 s, 1913 s, 1882 m, 1859 m,
	KBr	1950 s, 1907 s, 1880 s, 1858 s
$H_2C_2S_2Mn_2(CO)_6 \cdot (C_6H_5)_3P$	CH_2Cl_2[c]	2037 s, 2009 s, 1962 s, 1935 br, s, 1887 m
	KBr	2032 s, 2005 s, 1958 s, 1919 br, s, 1887 m
		1948 s
$2H_2C_2S_2Mn_2(CO)_6 \cdot (C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$	KBr	2040 s, 2012 s, 1960 s, 1933 s, 1915 s
$H_2C_2S_2Mn_2(CO)_6 \cdot NH_3$	C_6H_6[b]	2043 w, 2012 s, 1960 w, 1925 s

[a] CH_2Cl_2, dichloromethane solution, KBr, potassium bromide pellet. [b] This spectrum was taken in a benzene solution saturated with ammonia. In benzene solution without added ammonia the complex breaks up to give the spectrum of $H_2C_2S_2Mn_2(CO)_6$. A KBr pellet again gives the latter spectrum indicating that the complex decomposes upon grinding. The color change from yellow to red during the grinding process is readily evident. [c] This dichloromethane solution was saturated with triphenylphosphine.

and $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ were prepared by standard methods.[9] Other materials were commercial samples.

Preparation of $H_2C_2S_2Mn_2(CO)_6$.—A mixture of 5.5 g (20 mmol) of $Mn(CO)_5Br$, 1.36 g (10 mmol) of disodium ethylenedithiolate, and 30 ml each of methanol and acetone was stirred 24 hr at room temperature. Solvent was then removed at ~25° (25 mm). The residue was subjected to sublimation at 40–50° (0.1 mm) to remove all of the yellow $Mn_2(CO)_{10}$. After removing this sublimate the residue was sublimed at 70–80° (0.2 mm) to give 1.3–2.0 g (35–54% yield) of a dark red sublimate of $H_2C_2S_2Mn_2(CO)_6$. The analytical sample, mp 147–148°, was sublimed a second time at 75–80° (0.07 mm). *Anal.* Calcd for $C_8H_2Mn_2O_6S_2$: C, 26.1; H, 0.5; O, 26.1; S, 17.4; Mn, 29.9; mol wt, 368. Found: C, 26.1; H, 0.6; O, 26.1; S, 17.3; Mn, 30.0; mol wt, 380.

Infrared spectrum: see Table I for ν(CO) frequencies; other bands at 1252 (w), 1097 (w), 821 (w), 812 (m), 668 (m), 643 (s), 624 (m), 610 (s), 598 (s) cm⁻¹.

Ultraviolet and visible spectra: maxima at 495 mμ (ε 1160), 336 mμ (ε 6450), and ~227 mμ (ε 84,000) in dichloromethane solution.

Reaction of $H_2C_2S_2Mn_2(CO)_6$ with Triphenylphosphine: (a) **Preparation of the Yellow Adduct $H_2C_2S_2Mn_2(CO)_6P(C_6H_5)_3$.**—A stirred solution of 0.063 g (~0.17 mmol) of $H_2C_2S_2Mn_2(CO)_6$ in 10 ml of dichloromethane was treated with 0.132 g (0.5 mmol) of triphenylphosphine at room temperature. A yellow precipitate formed upon evaporation under nitrogen and addition of petroleum ether (bp 30–60°). This precipitate was filtered and dried. Additional material was obtained by evaporating the filtrate in a nitrogen stream and then cooling back to −78°. The yellow solid could be recrystallized with difficulty from a mixture of diethyl ether and hexane to give yellow $H_2C_2S_2Mn_2(CO)_6P(C_6H_5)_3$, mp 105–107°. The yield of product before recrystallization was 0.087 g (81% based on $Mn_2(CO)_6S_2C_2H_2$). *Anal.* Calcd for $C_{26}H_{17}Mn_2O_6PS_2$: C, 49.6; H, 2.7; O, 15.2; P, 4.9; S, 10.2. Found: C, 50.1; H, 3.2; O, 16.0; P, 3.6; S, 9.4.

Infrared spectrum: see Table I for ν(CO) frequencies; ν(CH) at 3075 (vvw) and 3055 (vvw) cm⁻¹; other bands at 1470 (w), 1427 (m), 1356 (w), 1234 (vw), 1178 (w), 1153 (w), 1079 (m), 1020 (vw), 991 (w), 800 (w), 790 (w), 733 (m), 683 (m), 658 (w), 643 (m), 618 (m), 602 (m), and 532 (m) cm⁻¹.

(b) **Preparation of the Dark Red Substitution Product $H_2C_2S_2Mn_2(CO)_4[P(C_6H_5)_3]_2$.**—A mixture of 0.368 g (1 mmol) of $H_2C_2S_2Mn_2(CO)_6$, 1.048 g (4 mmol) of triphenylphosphine, 20 ml of hexane, and 10 ml of benzene was stirred at room temperature. The red color of the $H_2C_2S_2Mn_2(CO)_6$ became yellow immediately owing to formation of the adduct described above. The mixture was boiled under reflux for 4.2 hr. When heated,

the yellow solution became deep red-brown almost immediately. After the reaction period was over, the reaction mixture was cooled to room temperature and the solvent was removed at ~40° (40 mm). The residue was dissolved in a minimum of benzene and the product was precipitated by addition of excess hexane. The crude product was purified further by repeating three times this precipitation from benzene solution with excess hexane. In this manner a red-brown powder, mp 170–177° dec, of $H_2C_2S_2Mn_2(CO)_4[P(C_6H_5)_3]_2$ was obtained in a 10% yield. The low yield probably arose from losses during this purification process. *Anal.* Calcd for $C_{42}H_{32}Mn_2O_4P_2S_2$: C, 60.3; H, 3.9; O, 7.7; S, 7.7; P, 7.4. Found: C, 61.4; H, 4.4; O, 8.4; S, 7.6; P, 7.2.

Infrared spectrum: see Table I for ν(CO) frequencies; other bands at 1475 (m), 1429 (m), 1180 (vw), 1155 (vw), 1088 (m), 1067 (vw), 1024 (vw), 996 (vw), 749 (sh), 740 (m), 690 (s), 679 (m), 635 (m), 625 (w), and 584 (m) cm⁻¹.

Ultraviolet and visible spectra: maxima at ~533 mμ (ε 875), 434 mμ (ε 4270), 391 mμ (ε 5340), and 240 mμ (ε 32,300) in dichloromethane solution.

Reaction of $H_2C_2S_2Mn_2(CO)_6$ with Tris(dimethylamino)phosphine.—A mixture of 0.368 g (1 mmol) of $H_2C_2S_2Mn_2(CO)_6$, 0.8 g (*ca.* 4 mmol) of tris(dimethylamino)phosphine, 15 ml of hexane, and 10 ml of benzene was stirred for 21.5 hr at room temperature. The reaction mixture first became lighter in color, but soon darkened again. After the reaction period was over, solvent was removed from the reaction mixture at ~40° (25 mm). The resulting red-brown crystals were dried at 25° (0.1 mm). They were dissolved in a minimum of benzene, the solution was filtered under nitrogen, hexane was then added, and the solvent was removed at 40° (25 mm) until crystallization occurred. The resulting crystals were purified twice more in the same manner to give the deep red-brown crystalline $H_2C_2S_2Mn_2(CO)_4\{P[N(CH_3)_2]_3\}_2$, mp 138–141°, in 35% yield based on $H_2C_2S_2Mn_2(CO)_6$. *Anal.* Calcd for $C_{18}H_{38}Mn_2N_6O_4P_2S_2$: C, 33.9; H, 6.0; N, 13.2; O, 10.0; P, 9.7. Found: C, 32.3; H, 6.0; N, 12.8; O, 10.2; P, 9.9.

Infrared spectra: see Table I for ν(CO) frequencies; ν(CH) at 2915 (m), 2873 (m), 2832 (m), and 2790 (w) cm⁻¹; other bands at 1450 (m, br), 1260 (m), 1173 (s), 1053 (w), 965 (s), 951 (s), 802 (w), 686 (s), 642 (s), 584 (s), and 570 (w) cm⁻¹.

Ultraviolet and visible spectra: maxima at 522 mμ (ε 830), 402 mμ (ε 3750), and 350 mμ (ε 5050) in dichloromethane solution.

Reaction of $H_2C_2S_2Mn_2(CO)_6$ with $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$.—A mixture of 0.31 g (0.84 mmol) of $H_2C_2S_2Mn_2(CO)_6$, 0.33 g (1.65 mmol) of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, 20 ml of hexane, and 10 ml of benzene was stirred for 3 hr under nitrogen. The yellow solid which precipitated was filtered and washed thoroughly by shaking with mixtures of benzene, hexane, and petroleum ether to give up to 0.43 g (67% yield) of the diadduct $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2 \cdot 2H_2C_2S_2Mn_2(CO)_6$, mp 111–113°.

(9) (a) [(CH₃)₂N]₃P: A. B. Burg and P. J. Slota, Jr., *J. Am. Chem. Soc.*, **80**, 1107 (1958); (b) (C₆H₅)₂PCH₂CH₂P(C₆H₅)₂: J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

This compound soon became red upon standing particularly under vacuum. The red material could be extracted from partially decomposed material with benzene. It was shown to be $H_2C_2S_2Mn_2(CO)_6$ from its infrared spectrum. The compound $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2 \cdot 2H_2C_2S_2Mn_2(CO)_6$ was soluble in chloroform and acetone to give red solutions. It could not be recovered from these solutions without decomposition. No satisfactory method was found for the recrystallization of this material. *Anal.* Calcd for $C_{42}H_{28}Mn_4O_{12}P_2S_4$: C, 44.5; H, 2.5; O, 16.9; P, 5.5; S, 11.3. Found: C, 45.3, 45.9; H, 2.9, 3.4; O, 16.2; P, 4.2; S, 10.2.

Infrared spectrum: see Table I for ν(CO) frequencies; ν(CH) at 2960 (vw) and 2925 (vvw) cm^{-1}; other bands at 1470 (w), 1431 (m), 1354 (w), 1258 (vvw), 1167 (w), 1093 (m), 1023 (vw, br), 996 (vw), 803 (w), 747 (m), 724 (m), 708 (m), 690 (m), 675 (m), 662 (m), 653 (m), 626 (m), 615 (m), 605 (m), 538 (m), and 507 (m) cm^{-1}.

Reaction of $H_2C_2S_2Mn_2(CO)_6$ with Ammonia.—A solution of 0.17 g (0.46 mmol) of $H_2C_2S_2Mn_2(CO)_6$ in 5 ml of dichloromethane was treated with excess gaseous ammonia at room temperature. The originally red solution almost immediately became yellow. Yellow solid was precipitated by evaporation of the dichloromethane and addition of petroleum ether and hexane. This solid was filtered and dried in a stream of ammonia to give 0.137 g (77% yield) of yellow solid $H_2C_2S_2Mn_2(CO)_6 \cdot NH_3$.

Upon exposure to air or even nitrogen, this yellow ammonia adduct soon reverted to the dark red $H_2C_2S_2Mn_2(CO)_6$. This change was accelerated by heating or grinding. Thus, upon heating the ammonia adduct in a melting point capillary, it became red and exhibited the melting point (147°) characteristic of $H_2C_2S_2Mn_2(CO)_6$. The ammonia adduct also became red upon grinding with potassium bromide. The infrared spectrum of the pellet made from this mixture exhibited an infrared spectrum identical with that of pure $H_2C_2S_2Mn_2(CO)_6$. Satisfactory solution spectra of the adduct $H_2C_2S_2Mn_2(CO)_6 \cdot NH_3$ in the ν(CO) region could be obtained by using solvents saturated with ammonia to inhibit dissociation. In solvents not saturated with ammonia, the ammonia adduct soon reverted to $H_2C_2S_2Mn_2(CO)_6$. When stored at $-15°$ in a vial flushed with ammonia, the ammonia adduct decomposed in a more complex manner over a period of days.

The analyses were performed by the usual methods after evacuating a sample of the solid for 5 min at room temperature (0.1–0.5 mm). Under these conditions negligible ammonia was lost as indicated by persistence of the yellow color of the sample. *Anal.* Calcd for $C_8H_5Mn_2NO_6S_2$: C, 25.0; H, 1.3; O, 24.9; N, 3.6. Found: C, 25.2; H, 1.4; O, 25.1; N, 4.6.

Reaction between $Fe_2(CO)_9$ and Disodium Ethylenedithiolate. —A mixture of 3.64 g (10 mmol) of $Fe_2(CO)_9$, 1.36 g (10 mmol) of disodium ethylenedithiolate, and 50 ml of methanol was stirred until all of the solid $Fe_2(CO)_9$ had disappeared. This took 10–15 min. The methanol was then removed from the reaction mixture at 25° (40 mm). Sublimation of the residue at 40–50° (0.2 mm) gave a total of 1.0 g (27% yield) of red crystals of $C_2H_4S_2Fe_2(CO)_6$, mp 77–78° (lit.[14f] mp 76–77°). The proton nmr spectrum of this material in CDCl$_3$ solution exhibited a single sharp resonance at τ 7.61 $\pm$ 0.03 (lit.[14f] τ 7.64).

Attempts to prepare a deuterated compound $C_2H_2D_2S_2Fe_2(CO)_6$ by reaction between $Fe_2(CO)_9$ and disodium ethylenedithiolate in CH$_3$OD solution either with or without added D$_2$O were unsuccessful. Reaction proceeded only under reflux conditions and the product in each case contained no deuterium as indicated by nmr spectra.

Discussion

The compound $H_2C_2S_2Mn_2(CO)_6$ is a new type of organosulfur derivative of manganese carbonyl.[10] Its proton nmr spectrum in CDCl$_3$ solution exhibits a singlet resonance at τ 3.05, the normal region for ethylenic protons shifted slightly downfield by concurrent

bonding of the sp^2 carbon atom to a more electronegative sulfur atom. The normal proton nmr spectrum indicates $H_2C_2S_2Mn_2(CO)_6$ to be diamagnetic suggesting closed-shell rare gas configurations for the manganese atoms. The infrared spectrum of $H_2C_2S_2Mn_2(CO)_6$ exhibits no ν(CO) frequencies in the region associated with bridging carbonyl groups indicating that the sole bridging between the two Mn(CO)$_3$ groups occurs through the $H_2C_2S_2$ ligand and/or through metal–metal bonding.

The correct structure of $H_2C_2S_2Mn(CO)_6$ could not be deduced from the spectroscopic data. However, preliminary X-ray crystallographic results[11] indicate this manganese complex to have structure I (L = CO). This structure is similar to that recently[12] found for the iron complex $CF_2CF_2[(CH_3)_2As]C=CAs(CH_3)_2Fe_2(CO)_6$ (II). If only the outer electrons are considered, a four-atom system of two iron atoms and two arsenic atoms is isoelectronic with a four-atom system of two manganese atoms and two sulfur atoms. In structure I, both manganese atoms attain the favored rare gas
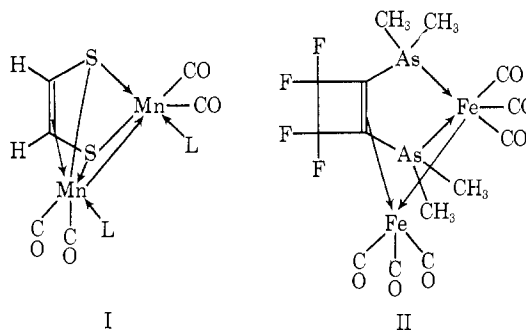
configuration by receiving a total of eleven electrons from the surrounding ligands.[13] In the case of both manganese atoms, six of these eleven electrons come from three carbonyl groups, three additional electrons from the two sulfur atoms, and the remaining two electrons from an additional electron pair donor. This additional electron pair donor is a carbon–carbon double bond in the case of one of the manganese atoms. This additional electron pair donor is a dative bond from the other manganese atom in the case of the second manganese atom. The structure of $H_2C_2S_2Mn_2(CO)_6$ is thus quite different from those of [RSFe(CO)$_3$]$_2$ compounds[14] including the apparently similar $H_2C_2S_2Fe_2(CO)_6$ (III).[15]

(10) For some related previously reported organosulfur derivatives of manganese carbonyl see the references: (a) [RSMn(CO)$_4$]$_2$ derivatives: P. M. Treichel, J. H. Morris, and F. G. A. Stone, *J. Chem. Soc.*, 720 (1963); (b) [RSMn(CO)$_3$]$_n$ derivatives: A. G. Osborne and F. G. A. Stone, *ibid.*, A, 1143 (1966); E. W. Abel and B. C. Crosse, *ibid.*, A, 1141 (1966).

(11) R. Vranka, R. B. King, and L. F. Dahl, unpublished results.

(12) F. W. B. Einstein, W. R. Cullen, and J. Trotter, *J. Am. Chem. Soc.*, 88, 5670 (1966).

(13) In this electron-counting process it is most convenient to consider both the metal atom and the surrounding ligands as neutral species. For further details see R. B. King, Advances in Chemistry Series, No. 62, American Chemical Society, Washington, D. C., 1967, p 203.

(14) The following papers discuss various aspects of the chemistry of [RSFe(CO)$_3$]$_2$ compounds: (a) W. Hieber and P. Spacu, *Z. Anorg. Allgem. Chem.*, 233, 353 (1937); (b) W. Hieber and C. Scharfenberg, *Ber.*, 73, 1012 (1964); (c) W. Hieber and W. Beck, *Z. Anorg. Allgem. Chem.*, 305, 265 (1960); (d) S. F. A. Kettle and L. E. Orgel, *J. Chem. Soc.*, 3890 (1960); (e) R. B. King, *J. Am. Chem. Soc.*, 84, 2460 (1962); (f) R. B. King, *ibid.*, 85, 1584 (1963); (g) R. B. King and M. B. Bisnette, *Inorg. Chem.*, 4, 1663 (1965).

(15) G. N. Schrauzer, V. P. Mayweg, H. W. Finck, and W. Heinrich, *J. Am. Chem. Soc.*, 88, 4604 (1966).

III
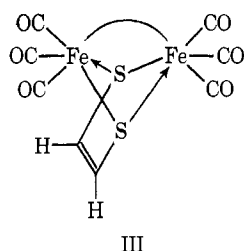
The mass spectrum of $H_2C_2S_2Mn_2(CO)_6$ (Table II) shows features typical of organosulfur derivatives of metal carbonyls.[16] The six carbonyl groups are lost stepwise from the parent ion until the monocarbonyl ion $H_2C_2S_2Mn_2CO^+$ (m/e 228) is obtained. Here loss of a C_2H_2 (acetylene: mass 26) fragment to form $Mn_2S_2CO^+$ (m/e 202) is competitive with the loss of the final carbonyl group to form the ion $H_2C_2S_2Mn_2^+$ (m/e 200). The tendency for this unsubstituted ethylenedithiolate derivative to lose an acetylene fragment appears to be related to the tendency for various $(CF_3)_2$-C_2S_2 complexes such as $C_5H_5W[S_2C_2(CF_3)_2]_7$ to lose hexafluorobutyne (C_4F_6) fragments in their mass spectra.[17] Further fragmentation of $H_2C_2S_2Mn_2^+$ (m/e 200) appears to occur by loss of a manganese atom giving $H_2C_2S_2Mn^+$ (m/e 145) as well as by loss of C_2H_2 giving $Mn_2S_2^+$ (m/e 174).

Hieber and Zeidler[18] have reported reactions of [RSFe(CO)$_3$]$_2$ compounds with Lewis bases. The unusual structure and bonding in $H_2C_2S_2Mn_2(CO)_6$ (I, L = CO) made related studies with this manganese complex of interest. In this connection triphenylphosphine was found to react readily with dark red $H_2C_2S_2Mn_2(CO)_6$ at room temperature to deposit a yellow precipitate. Analyses showed that triphenylphosphine had formed an *adduct* $H_2C_2S_2Mn_2(CO)_6 \cdot P(C_6H_5)_3$. The failure for metal–carbon monoxide bonds to rupture in this reaction thereby resulting in the retention of the six carbonyl groups is consistent with the mild conditions under which this reaction takes place. A possible structure for the adduct $H_2C_2S_2Mn_2(CO)_6 \cdot P(C_6H_5)_3$ is IV (L = (C$_6$H$_5$)$_3$P) in which the triphenylphosphine ligand has replaced the manganese–manganese dative bond. However, we cannot rigorously exclude for this adduct structure V (L = (C$_6$H$_5$)$_3$P) in which the triphenylphosphine ligand replaces the olefin–manganese bond. However, no cases are known where a metal–metal *dative* bond is the sole link between two halves of a molecule.
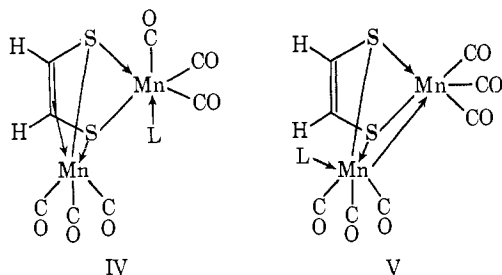
IV   V

(16) R. B. King, *J. Am. Chem. Soc.*, **90**, 1429 (1968).
(17) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **6**, 469 (1967).
(18) W. Hieber and A. Zeidler, *Z. Anorg. Allgem. Chem.*, **329**, 92 (1964).

TABLE II

MASS SPECTRUM OF $H_2C_2S_2Mn_2(CO)_6{}^a$

m/e	Ion	Rel intens	Calcd	Found
			— Exact mass —	
368	$H_2C_2S_2Mn_2(CO)_6{}^+$	15	367.805	367.804
340	$H_2C_2S_2Mn_2(CO)_5{}^+$	34	339.810	339.809
312	$H_2C_2S_2Mn_2(CO)_4{}^+$	120	311.816	311.814
284	$H_2C_2S_2Mn_2(CO)_3{}^+$	>300	283.821	283.822
256	$H_2C_2S_2Mn_2(CO)_2{}^+$	105	255.826	255.826
228	$H_2C_2S_2Mn_2CO^+$	>300	227.831	227.832
218		10		
202	$Mn_2S_2CO^+$	~50		
200	$H_2C_2S_2Mn_2{}^+$	>300	199.836	199.838
192		18		
186	$CS_2Mn_2{}^+$	11		
176		>300		
174	$Mn_2S_2{}^+$	>300	173.820	173.823
167	$C_2HSMn_2{}^+$	130	166.856	166.857
158		9		
155	$CHSMn_2{}^+$	23		
154	$CSMn_2{}^+$	16		
145	$H_2C_2S_2Mn^+$	300		
142	Mn_2S^+	>300	141.848	141.849
134	$Mn_2C_2{}^+$	46		
128		30		
126		17		
119	$MnS_2{}^+$	>300		
115		37		
114		55		
110	$Mn_2{}^+$	>300		
100	$MnCSH^+$	175		
99	$MnCS^+$	80		
87	MnS^+	>300		
83	$MnCO^+$	150		
80	C_2HMn^+	175		
71	$Mn_2S_2{}^{2+}$	40		
68	$MnCH^+$	22		
67	MnC^+	67		
58	$C_2H_2S^+$	29		
57	C_2SH^+	26		
56	C_2S^+	100		
55	Mn^+	>300		
45	CSH^+	34		
44	CS^+	16		

cule.[19] By contrast, a metal–olefin bond often is the sole link holding together rather stable metal–olefin complexes. A metal–metal dative bond therefore appears to be weaker than a metal–olefin bond and hence more likely to be replaced with triphenylphosphine or other ligands.

If the reaction between $H_2C_2S_2Mn_2(CO)_6$ and triphenylphosphine was carried out under more vigorous conditions (a boiling benzene–hexane mixture), the yellow adduct initially formed was converted into a dark red-brown derivative demonstrated by analysis to be the substitution product $H_2C_2S_2Mn_2(CO)_4[P(C_6H_5)_3]_2$. This substitution reaction resembles some reactions of certain [RSFe(CO)$_3$]$_2$ compounds with tertiary phosphines to give [RSFe(CO)$_2$PR$_3$]$_2$ derivatives.[18] The

(19) In this discussion it is important to differentiate between a metal–metal dative bond (where one metal donates both electrons of the bond) and a metal–metal covalent bond (where each metal donates one electron of the bond). Metal–metal covalent bonds are frequently the sole link between two halves of a molecule (*e.g.*, Mn$_2$(CO)$_{10}$ and [C$_5$H$_5$Mo(CO)$_3$]$_2$).

compound $H_2C_2S_2Mn_2(CO)_4[P(C_6H_5)_3]_2$ appears to have structure I (L = $(C_6H_5)_3P$) entirely analogous to the related structure for $H_2C_2S_2Mn_2(CO)_6$ discussed above.

The reaction between $H_2C_2S_2Mn_2(CO)_6$ and tris-(dimethylamino)phosphine[20] was also investigated. In this case, only the dark red substitution product $H_2C_2S_2Mn_2(CO)_4[P(N(CH_3)_2)_3]_2$ (I, L = $[(CH_3)_2N]_3P$) could be isolated. Initially the reaction mixture from the reaction between $H_2C_2S_2Mn_2(CO)_6$ and tris(dimethylamino)phosphine became a lighter color suggestive of transient formation of a yellowish $H_2C_2S_2Mn_2(CO)_6 \cdot$ $P(N(CH_3)_2)_3$ adduct. However, the solubility of this adduct appears to be so high that it remains in solution where it can undergo further change rather than precipitating out.

The normally chelating ditertiary phosphine 1,2-bis(diphenylphosphino)ethane, $(C_6H_5)_2PCH_2CH_2P$-$(C_6H_5)_2$, reacts with $H_2C_2S_2Mn_2(CO)_6$ to give a yellow precipitate of the diadduct $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2 \cdot$ $2H_2C_2S_2Mn_2(CO)_6$ which appears to be analogous to the yellow triphenylphosphine adduct $H_2C_2S_2Mn_2(CO)_6 \cdot$ $P(C_6H_5)_3$ discussed above. The infrared spectra of the two yellow adducts are similar in the $\nu(CO)$ region. Attempts to prepare a substitution product from $(C_6H_5)_2$-$PCH_2CH_2P(C_6H_5)_2$ and $H_2C_2S_2Mn_2(CO)_6$ under more vigorous conditions led first to a dark red compound and then to a green compound. Neither of these materials was isolated in a condition sufficiently pure for unambiguous identification.

The reaction between ammonia and $H_2C_2S_2Mn_2(CO)_6$ was explored in order to see whether non-π-accepting nitrogen Lewis bases like the π-accepting tertiary phosphine Lewis bases would form yellow adducts. Ammonia did form an analogous adduct $H_2C_2S_2Mn_2(CO)_6 \cdot$ NH_3 (IV, L = NH_3). In the absence of an ammonia atmosphere, this adduct was particularly unstable and gradually reverted to $H_2C_2S_2Mn_2(CO)_6$ (I, L = CO) with loss of the coordinated ammonia. Upon prolonged storage (even at $-10°$) in an ammonia atmosphere $H_2C_2S_2Mn_2(CO)_6 \cdot NH_3$ gradually decomposed in a more complex manner; in this latter case the recovery of $H_2C_2S_2Mn_2(CO)_6$ was far less than quantitative.

These studies thus indicate that $H_2C_2S_2Mn_2(CO)_6$ (I, L = CO) forms the following two types of products when treated with Lewis bases: (1) dark red-brown

(20) For a discussion of metal carbonyl complexes of tris(dimethylamino)-phosphine see R. B. King, *Inorg. Chem.*, **2**, 936 (1963).

products where the ligand has replaced carbonyl groups; (2) yellow addition products still containing the original six carbonyl groups. The dark red substitution products (type 1) prepared in this work are of the general formula $H_2C_2S_2Mn_2(CO)_4L_2$. The yellow addition products (type 2) are of the general formula $H_2C_2S_2Mn_2$-$(CO)_6 \cdot L$ with probable structure IV. In all cases the yellow addition products dissociate readily under certain conditions back into red $H_2C_2S_2Mn_2(CO)_6$ and the free ligand L.

Schrauzer and co-workers[15] have prepared the compound $H_2C_2S_2Fe_2(CO)_6$ (III) by treatment of M-$(S_2C_2H_2)_2$ (M = Fe, Co, or Ni) with excess $Fe(CO)_5$. In an attempt to prepare II from disodium ethylenedithiolate, its reaction with $Fe_2(CO)_9$ in methanol was investigated. This reaction did not give the expected $H_2C_2S_2Fe_2(CO)_6$ (II) with an unsaturated carbon bridge between the two sulfur atoms. Instead it gave $C_2H_4S_2$-$Fe_2(CO)_6$ (VI) with a *saturated* carbon bridge between the two sulfur atoms. This saturated derivative VI has been previously prepared in low yield from $Fe(CO)_5$ and 1,2-ethanedithiol.[14f]

VI
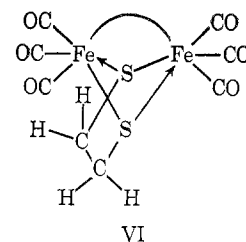
The reaction between disodium ethylenedithiolate and $Fe_2(CO)_9$ thus represents a novel means for hydrogenating a carbon–carbon double bond. In this reaction the dianion $H_2C_2S_2Fe_2(CO)_6{}^{2-}$ is presumably formed by a reaction such as

$$Fe_2(CO)_9 + Na_2S_2C_2H_2 \longrightarrow Na_2[H_2C_2S_2Fe_2(CO)_6] + 3CO$$
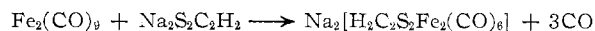
This dianion $H_2C_2S_2Fe_2(CO)_6{}^{2-}$ then can pick up two protons to form the neutral saturated derivative $C_2H_4S_2$-$Fe_2(CO)_6$. An attempt to identify a possible source of these protons by carrying out the reaction between disodium ethylenedithiolate and $Fe_2(CO)_9$ in CH_3OD rather than CH_3OH failed to yield a deuterated product and hence was inconclusive.