If pyridine is added to the reaction mixture before the solvent is removed, the nonvolatile residue has much $pyBH_2N(CH_3)_3^+$ present. For example, addition of PF_6^- to a 8.1 mmol size run led to precipitation of 1.3 g (58%) of salt. After recrystallization the salt had an infrared spectrum identical with that of an analyzed sample of $(CH_3)_3NBH_2py^+PF_6^-$. *Anal.* Calcd: C, 32.5; H, 4.8; N, 9.5. Found: C, 32.2; H, 5.3; N, 9.3.

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Transition Metal Dithiolene Complexes. IX.[1] Manganese π-Cyclopentadienyl(nitrosyl)dithiolene and Related Metal Complexes

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The preparation of new monodithiolene complexes $\pi\text{-}C_5H_4RMn(NO)(S\text{–}S)^z$, where R = H or CH_3 and $z = 0$ or -1 and where S–S represents $S_2C_2(CN)_2$, $S_2C_6H_3CH_3$, or $S_2C_6Cl_4$, is reported. The analogous dithiocarbamates, $\pi\text{-}C_5H_4RMn(NO)S_2CNR'_2{}^0$, where $R' = CH_3$ or C_2H_5, and 1,1-dicyanoethylene-2,2-dithiolenes, $\pi\text{-}C_5H_4RMn(NO)S_2C{=}C(CN)_2^-$, are also described. These complexes have been investigated by voltammetry and it is shown that the 1,2-dithiolenes exist as part of a three-membered electron-transfer series, $z = +1$, 0, or -1, the 1,1-dithiolene is part of at least a two-membered series, $z = 0$ or -1, and the dithiocarbamates can be oxidized to monocations; the complexes have been further characterized by ir and esr spectroscopy. The voltammetric properties of certain π-cyclopentadienyldicyano-1,2-dithiolenes, $(\pi\text{-}C_5H_5)_2TiS_2C_2(CN)_2$, $\pi\text{-}C_5H_5MS_4C_4(CN)_4^-$ (M = Mo, W, or Ti), and $\pi\text{-}C_5H_5CoS_2C_2(CN)_2$, are reported, and evidence for $\pi\text{-}C_5H_5CoS_2C_2(CN)_2^-$ is presented.

In this article, we describe the synthesis and electron-transfer reactions of manganese π-cyclopentadienyl-(nitrosyl)-1,2-dithiolenes and related sulfur complexes. The reduction of $\pi\text{-}C_5H_5Mn(NO)S_2C_2(CF_3)_2{}^0$ to $Mn(NO)S_4C_4(CF_3)_4{}^{2-}$ using ethanolic hydrazine[3] first drew our attention to this class of compounds, which we represent generally as $\pi\text{-}C_5H_4RMn(NO)(S\text{–}S)^z$,[4] as potential intermediates in the syntheses of manganese(nitrosyl)bisdithiolenes, $Mn(NO)(S\text{–}S)_2{}^z$. Because the latter group of compounds were of interest to us in a continuing study of five-coordinate nitrosylbisdithiolene complexes, but were relatively inaccessible synthetically, we initiated a program of research designed to produce and investigate the properties of the intended intermediates $\pi\text{-}C_5H_4RMn(NO)(S\text{–}S)^z$. At the same time, we prepared several similar compounds containing 1,1-dicyanoethylene-2,2-dithiolate and dimethyl- and diethyldithiocarbamates. Some of our results have been reported in a preliminary communication,[5] but the use of these cyclopentadienyl complexes in the preparation of $Mn(NO)(S\text{–}S)_2{}^z$ will be described elsewhere.

Bis- and tris-dithiolene complexes readily undergo electron-transfer reactions,[6] but this behavior is not well established in systems containing only one dithiolato ligand. Our voltammetric study of the new cyclopentadienyl complexes shows that these monodithiolenes can readily undergo reversible one-electron-transfer reactions, and we have used the electrochemical results to design synthetic routes to the various oxidized and reduced species which we have detected. In addition, we have investigated the electron-transfer properties of the π-cyclopentadienyldicyano-1,2-dithiolenes described in part I of this series.[7]

Experimental Section

Disodium *cis*-1,2-dicyanoethylene-1,2-dithiolate, $Na_2S_2C_2(CN)_2$,[8] tetrachlorobenzene-1,2-dithiol,[1] and disodium 1,1-dicyanoethylene-2,2-dithiolate[9] were prepared by published methods, as were $[\pi\text{-}C_5H_5Mn(NO)(CO)_2][PF_6]$ and $[\pi\text{-}C_5H_4CH_3Mn(NO)(CO)_2][PF_6]$.[10] Toluene-3,4-dithiol was purchased from Eastman Kodak, and sodium dimethyl- and diethyldithiocarbamate hydrates were from BDH.

Conductivity measurements were determined at room temperature (22°) using a Philips conductivity meter. Magnetic measurements were made at room temperature by the Gouy method, nmr spectra were obtained in solution using a Varian A-60 spectrometer, and esr spectra were obtained in solution at room temperature using a Varian V-4500 X-band spectrometer. Electronic and infrared spectra were recorded with Unicam SP700 and SP100 and Infracord 457 spectrophotometers.

Voltammetric data were obtained using a Heathkit Model EUW-401 polarograph with a platinum electrode rotating at 620 rpm. Dichloromethane was employed as the solvent and $[(C_2H_5)_4N][ClO_4]$ as the base electrolyte. All measurements were standardized against a saturated calomel electrode containing 1 *M* aqueous LiCl.

All melting points are uncorrected, and yields are calculated

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(1) Part VII: E. J. Wharton and J. A. McCleverty, *J. Chem. Soc., A*, in press.

(2) Supported by the Science Research Council of Great Britain.

(3) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **6**, 469 (1967).

(4) The use of the abbreviation (S–S) is meant to refer to a bidentate sulfur ligand and not to diatomic sulfur.

(5) J. A. McCleverty, T. A. James, E. J. Wharton, and C. J. Winscom, *Chem. Commun.*, 933 (1968).

(6) References in J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968); and also in G. N. Schrauzer, *Transition Metal Chem.*, **4**, 229 (1968).

(7) J. Locke and J. A. McCleverty, *Inorg. Chem.*, **5**, 1157 (1966).

(8) G. Bähr and G. Schleitzer, *Chem. Ber.*, **88**, 1771 (1955); an improved synthesis is described in ref 7.

(9) R. Gomper and E. Kutler, *Angew. Chem.*, **74**, 251 (1962).

(10) R. B. King, "Organometallic Syntheses," Vol. I, J. J. Eisch and R. B. King, Ed., Academic Press, New York, N. Y., 1965, p 111.

against $[\pi\text{-C}_5\text{H}_4\text{RMn(NO)(CO)}_2][\text{PF}_6]$, R = H or CH_3, where appropriate. Elemental analyses were determined by the microanalytical laboratory of this department.

$[(\text{C}_2\text{H}_5)_4\text{N}][\pi\text{-C}_5\text{H}_5\text{Mn(NO)S}_2\text{C}_2\text{(CN)}_2]$.—$[\pi\text{-C}_5\text{H}_5\text{Mn(NO)(CO)}_2][\text{PF}_6]$ (1.0 g) was dissolved in 20 ml of degassed acetone and heated on a steam bath. A warmed solution of $\text{Na}_2\text{S}_2\text{C}_2\text{(CN)}_2$ (0.53 g) in 15 ml of water was added and vigorous evolution of CO ensued while the solution became red-brown. The solution was warmed gently on the steam bath for 10 min and then filtered into 20 ml of water containing $[(\text{C}_2\text{H}_5)_4\text{N}]\text{Br}$ (0.6 g). After partial evaporation of the solvent mixture, brick red needles were formed. These were collected by filtration and recrystallized from acetone–water mixtures (3:2 v/v) affording 0.8 g of the complex (67%), mp >300°. The compound is soluble in acetone, dichloromethane, and chloroform giving red-brown solutions.

Infrared Spectra.—The spectra (cm^{-1}) were recorded in KBr disks and dichloromethane solution. In KBr disks: 3000 br, w, 2208 sh, 2198 vs (ν_{CN}), 1705 vs, 1488 m, 1480 m, 1455 w, 1440 w, 1368 w, 1175 m, 1145 m, 1108 m, 1060 w, 1000 w, 858 w, 840 w, 808 m, 782 m. In dichloromethane: 3000 br, w, 2206 sh, 2196 vs (ν_{CN}), 1699, 1480 s, 1396 m, 1370 w, 1218 m, 1184 w, 1172 m, 1144 s, 1110 m, 1000 m, 860 m, 810 m.

$[(\text{C}_6\text{H}_5)_4\text{P}][\pi\text{-C}_5\text{H}_5\text{Mn(NO)S}_2\text{C}_2\text{(CN)}_2]$.—This complex was prepared in the same way as its analog above, using $[(\text{C}_6\text{H}_5)_4\text{P}]\text{Br}$ (1.3 g) in 20 ml of ethanol. The complex was obtained as brown flakes, mp 135–140° (yield, 60%). It is soluble in acetone, dichloromethane, and chloroform giving red-brown solutions.

Infrared Spectra.—The spectra (cm^{-1}) were recorded in KBr disks and dichloromethane solution. In KBr disks: 3065 w, 2200 sh, 2190 vs (ν_{CN}), 1695 vs, 1595 m, 1486 s, 1448 sh, 1440 s, 1368 w, 1348 w, 1322 w, 1224 w, 1192 w, 1170 w, 1142 s, 1112 vs, 998 m, 864 m, 840 m, 800 m, 754 m, 725 s, 690 s. In dichloromethane: 3040 vw, 2208 sh, 2197 vs (ν_{CN}), 1700 vs, 1592 m, 1488 m, 1480 m, 1440 m, 1342 vw, 1320 vw, 1190 vw, 1145 m, 1111 vs, 1000 m, 860 m, 816 m.

$[(\text{C}_2\text{H}_5)_4\text{N}][\pi\text{-C}_5\text{H}_4\text{CH}_3\text{Mn(NO)S}_2\text{C}_2\text{(CN)}_2]$.—This complex was prepared in the same way as its $\pi\text{-C}_5\text{H}_5$ analog described above, using $[\pi\text{-C}_5\text{H}_4\text{CH}_3\text{Mn(NO)(CO)}_2][\text{PF}_6]$ (1.0 g). The compound was obtained as a brown microcrystalline powder (yield, *ca.* 60%), mp 108°.

Proton Magnetic Resonance Spectra.—These were recorded in CDCl_3 solution containing a few drops of hydrazine hydrate; resonances were observed a τ 5.40 (doublet, $\pi\text{-C}_5\text{H}_4$), *ca.* 7.00 (probably $-\text{CH}_2-$, largely obscured by $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$), 8.40 (singlet, $-\text{CH}_3$ of ring), and 8.72 (triplet, CH_3- of $(\text{C}_2\text{H}_5)_4\text{N}^+$). Satisfactory pmr spectra could be obtained only when $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ was present in the solutions.

Infrared Spectra.—The spectra (cm^{-1}) were recorded in KBr disks and in dichloromethane solution. In KBr disks: 3200 vw, 2980 vw, 2950 w, 2920 w, 2250 w, 2200 sh, 2180 vs (ν_{CN}), 1703, 1495 m, 1486 m, 1465 s, 1455 sh, 1000 m, 930 m, 860 m, 846 m, 830 w, 815 m, 782 m. In dichloromethane: 3000 br, w, 2920 w, 2280 w, 2256 w, 2200 sh, 2190 vs (ν_{CN}), 1725 w, 1690 vs, 1485 s, 1478 s, 1395 m, 1184 w, 1172 m, 1144 s, 1110 m, 1068 m, 1030 w, 1000 m, 860 m, 845 m, 817 m.

Electronic Spectra.—These were recorded in dichloromethane solution: λ_{max}, cm^{-1} (ϵ, $M^{-1}\ \text{cm}^{-1}$): 22,810 (3184 sh), 25,400 (4319), 39,600 (18,000 sh).

$\pi\text{-C}_5\text{H}_4\text{CH}_3\text{Mn(NO)S}_2\text{C}_2\text{(CN)}_2$. — To $[(\text{C}_2\text{H}_5)_4\text{N}][\pi\text{-C}_5\text{H}_4\text{CH}_3\text{Mn(NO)S}_2\text{C}_2\text{(CN)}_2]$ (0.5 g) dissolved in 40 ml of warm acetone was added dropwise I_2 (0.15 g) dissolved in 40 ml of hot ethanol. The solution changed from dark red-brown to green-black, and on partial evaporation of the solution after filtration, 0.15 g (43%) of black crystals mp >300°, was obtained. These were washed with ethanol–water and ether and air dried. The complex is partially soluble in acetone, dichloromethane, and chloroform giving unstable green-black solutions.

Infrared Spectra.—The spectra (cm^{-1}) were recorded in KBr disks and in dichloromethane solution. In KBr disks: 3200 w, 3180 w, 2220 s, 2208 vs, 1780 vs, 1485 m, 1454 m, 1410 w, 1373 w, 1240 w, 1150 m, 1115 w, 1045 w, 1035 w, 1030 w, 930 vw, 915 w, 855 m, 830 w. In dichloromethane: 2200 m, 1795 vs, 1485 m 1150 w, 1100 w, 1030 w, 840 m.

Electronic Spectra.—The spectra were recorded in dichloromethane solution: λ_{max}, cm^{-1} (ϵ, $M^{-1}\ \text{cm}^{-1}$): 9820 (650), 17,800 (1576), 22,380 (1817), 32,000 (1873 sh), 42,800 (22,790).

$\pi\text{-C}_5\text{H}_5\text{Mn(NO)S}_2\text{C}_6\text{H}_3\text{CH}_3$.—$[\pi\text{-C}_5\text{H}_5\text{Mn(NO)(CO)}_2][\text{PF}_6]$ (0.7 g) was dissolved in 40 ml of warm degassed acetone and treated dropwise, under nitrogen on a steam bath, with a solution of toluene-3,4-dithiol (0.31 g) in 30 ml of warm ethanol. CO gas was evolved and the solution became first brown and then purple. When no further color change and CO evolution could be detected, the solution was filtered and the filtrate was partially evaporated using a water pump, affording 0.6 g (69%) of purple crystals, mp 300°. These were collected by filtration, washed with ether, and air dried. The compound is soluble in acetone, dichloromethane, and chloroform giving purple solutions.

Infrared Spectra.—The spectra (cm^{-1}) were recorded in KBr disks and in dichloromethane solution. In KBr disks: 1770 vs, 1580 w, 1445 w, 1430 m, 1420 m, 1370 w, 1345 w, 1272 w, 1250 w, 1150 vw, 1090 w, 1056 w, 1038 w, 1015 m, 1005 w, 870 m, 830 s, 805 s. In dichloromethane: 1774 vs, 1585 w, 1440 br, w, 1220 w, 1210 w, 1091 w, 1015 w, 830 s, 807 m.

$\pi\text{-C}_5\text{H}_4\text{CH}_3\text{Mn(NO)S}_2\text{C}_6\text{H}_3\text{CH}_3$.—This complex was prepared in the same way as its $\pi\text{-C}_5\text{H}_5$ analog and was obtained as purple crystals, mp 95–98°.

Infrared Spectra.—The spectra (cm^{-1}) were recorded in KBr disks and in dichloromethane solution. In KBr disks: 3100 br, w, 1765 vs, 1580 w, 1530 w, 1480 m, 1440 m, 1400 w, 1375 m, 1270 w, 1248 w, 1240 w, 1203 w, 1080 w, 1060 w, 1030 m, 925 w, 877 m, 845 m, 800 s, 745 s. In dichloromethane: 3100 w, 3040 w, 2970 w, 2920 w, 1770 vs, 1585 m, 1530 w, 1485 w, 1445 br, 1375 m, 1230 br, w, 1205 w, 1080 w, 1065 w, 1050 w, 1030 m, 910 m, 835 s, 805 m.

Electronic Spectra.—The spectra were recorded in dichloromethane solution: λ_{max}, cm^{-1} (ϵ, $M^{-1}\ \text{cm}^{-1}$): 10,170 (1353), 17,600 (1984), 28,870 (4870), 36,800 (21,720).

$\pi\text{-C}_5\text{H}_5\text{Mn(NO)S}_2\text{C}_6\text{Cl}_4$.—$[\pi\text{-C}_5\text{H}_5\text{Mn(NO)(CO)}_2][\text{PF}_6]$ (1.0 g) was dissolved in 40 ml of warm degassed acetone and treated under nitrogen with a hot solution of tetrachlorobenzene-1,2-dithiol (0.8 g) in 40 ml of ethanol containing a few drops of triethylamine. After CO evolution, a purple solution was formed which was filtered and partially evaporated using a water pump. This afforded 0.6 g (49%) of purple crystals, mp >300°, which dissolved in acetone, dichloromethane, and chloroform giving purple solutions.

Infrared Spectra.—The spectra (cm^{-1}) were recorded in KBr disks and in dichloromethane solution. In KBr disks: 1790 vs, 1770 sh, 1431 m, 1423 m, 1325 s, 1290 m, 1245 m, 1160 m, 1100 m, 1060 w, 1018 m, 1008 w, 872 w, 838 s, 684 s. In dichloromethane: 1790 vs, 1327 s, 1290 br, m, 1240 m, 1160 m, 1100 m, 1015 br, w, 835 s.

$\pi\text{-C}_5\text{H}_4\text{CH}_3\text{Mn(NO)S}_2\text{C}_6\text{Cl}_4$.—$[\pi\text{-C}_5\text{H}_4\text{CH}_3\text{Mn(NO)(CO)}_2][\text{PF}_6]$ (1.0 g) was dissolved in 70 ml of hot degassed acetone and to this was added tetrachlorobenzene-1,2-dithiol (0.75 g) in 60 ml of hot ethanol containing 3 ml of 1% sodium amalgam[11] and a few drops of triethylamine. Vigorous evolution of CO took place, and a red-brown solution was formed. On addition of iodine in acetone, the solution became purple, and on evaporation of the solvent using a water pump, purple crystals were formed. These were collected by filtration and recrystallized from acetone–ethanol giving yields of *ca.* 60%, mp >300°. The complex dissolves in acetone, chloroform, and dichloromethane giving purple solutions.

Infrared Spectra.—The spectra (cm^{-1}) were recorded in KBr disks and in dichloromethane solution. In KBr disks: 1785 vs, 1480 m, 1450 w, 1375 w, 1322 s, 1290 m, 1240 w, 1175 w, 1160 w, 1098 w, 1065 w, 1048 w, 1030 m, 927 w, 860 w, 840 m, 835 w, 680 m. In dichloromethane: 1780 vs, 1485 m, 1375

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[11] The use of sodium amalgam is to be recommended if the tetrachlorobenzenedithiol has become oxidized, since fission of the S–S bond in $\text{C}_6\text{Cl}_4\text{(SH)(S–S(HS)C}_6\text{Cl}_4$ is necessary before complex formation can take place.

w, 1325 s, 1290 br, m, 1160 m, 1100 m, 1065 vw, 1050 vw, 1030 w, 920 vw, 970 w, 840 m.

Electronic Spectra.—The spectra were recorded in dichloromethane solution: λ_{max}, cm^{-1} (ϵ, M^{-1} cm^{-1}): 10,180 (1000), 17,560 (2362), 27,400 (4164), 34,590 (17,620 sh), 36,910 (19,600).

$[(C_2H_5)_4N][\pi\text{-}C_5H_4CH_3Mn(NO)S_2C_6Cl_4]$.—Tetrachlorobenzene-1,2-dithiol (1.6 g) was dissolved in 80 ml of ethanol and treated with three drops of triethylamine and 5 ml of 1% sodium amalgam.[11] The pale yellow mixture was shaken, decanted from the amalgam, heated briefly on a steam bath, and then added to $[\pi\text{-}C_5H_4CH_3Mn(NO)(CO)_2][PF_6]$ (2.0 g) dissolved in 60 ml of hot degassed acetone. The red-brown solution which was obtained after CO evolution had ceased was filtered and the filtrate was treated with $[(C_2H_5)_4N]Br$ (1.2 g) in 20 ml of water. In this way, 1.4 g of brown flaky crystals were obtained, mp 151°. The complex is soluble in acetone, dichloromethane, and chloroform giving red-brown solutions which gradually become purple when exposed to air.

Infrared Spectra.—The spectra (cm^{-1}) were recorded in KBr disks and in dichloromethane solution. In KBr disks: 3080 w, 3000 w, 2970 w, 2943 w, 2917 w, 1660 vs, 1485 m, 1480 s, 1452 m, 1440 m, 1393 m, 1385 w, 1378 w, 1325 s, 1308 s, 1281 w, 1271 m, 1251 m, 1188 w, 1170 m, 1157 w, 1081 m, 1068 w, 1051 w, 1038 w, 1030 w, 1000 m, 920 w, 826 w, 841 m, 780 m, 672 s. In dichloromethane: 3030 w, 2980 br, w, 1670 vs, 1480 m, 1450 w, 1390 m, 1362 w, 1322 s, 1309 s, 1240 w, 1180 w, 1170 m, 1080 w, 1030 w, 998 m, 840 w, 810 m, 668 m.

Electronic Spectra.—These were recorded in dichloromethane solution: λ_{max}, cm^{-1}(ϵ, M^{-1} cm^{-1}): 10,300 (221), 14,560 (282 sh), 20,700 (1337 sh), 28,400 (70,180 sh), 37,220 (21,380).

$[(C_2H_5)_4N][\pi\text{-}C_5H_5Mn(NO)S_2C{=}C(CN)_2$.—This complex was prepared in the same way as its dicyano-1,2-dithiolene analog, using $Na_2S_2C{=}C(CN)_2$ (0.53 g). The complex, mp 145–148°, was obtained in yields of 0.7 g (60%) as golden flaky crystals. The compound is soluble in acetone, chloroform, and dichloromethane giving red-brown solutions.

Infrared Spectra.—The spectra (cm^{-1}) were recorded in KBr disks and in dichloromethane solution. In KBr disks: 2980 w, 2210 vs, 1690 vs, 1487 m, 1410 s, 1385 m, 1240 w, 1172 m, 1060 w, 1000 m, 940 m, 895 m, 810 m, 789 w. In dichloromethane: 2980 w, 2204 vs (ν_{CN}), 1698 vs, 1487 m, 1399 s, 1375 w, 1173 w, 1000 m, 840 w, 815 m.

$[(C_2H_5)_4N][\pi\text{-}C_5H_4CH_3Mn(NO)S_2C{=}C(CN)_2]$.—This complex was prepared in the same way as its $\pi\text{-}C_5H_5$ analog and was obtained as a brown microcrystalline powder, mp 120°.

Infrared Spectra.—The spectra (cm^{-1}) were recorded in KBr disks and in dichloromethane solution. In KBr disks: 3290 w, 3270 vw, 2990 w, 2920 vw, 2188 vs (ν_{CN}), 2135 m. 1690 vs, 1485 m, 1480 s, 1450 m, 1435 m, 1400 s, 1360 s, 1337 m, 1242 m, 1173 m, 1068 m, 1055 w, 1028 w, 1000 w, 958 m, 900 s, 845 m, 830 m, 790 m, 780 m. In dichloromethane: 3020 w, 2920 vw, 2200 vs (ν_{CN}), 1690 vs, 1480 m, 1395 m, 1370 s, 1217 m, 1182 w, 1170 m, 1065 w, 1030 w, 1000 m, 950 m, 885 w, 840 w, 815 w.

Electronic Spectra.—These were recorded in dichloromethane solution: λ_{max}, cm^{-1} (ϵ, M^{-1} cm^{-1}): 21,300 (587 sh), 28,600 (18,500), 36,300 (12,130).

$\pi\text{-}C_5H_5Mn(NO)S_2CN(CH_3)_2$.—$[\pi\text{-}C_5H_5Mn(NO)(CO)_2][PF_6]$ (1.0 g) was dissolved in 30 ml of warm degassed acetone and treated with a solution of $NaS_2CN(CH_3)_2\cdot 3H_2O$ (0.45 g) in 20 ml of acetone–ethanol (1:1 v/v) containing 5 ml of water. After CO evolution, the solution had become red-brown and was filtered. The filtrate was partially evaporated using a water pump and afforded brown crystals. These were collected by filtration and recrystallized from acetone–water mixtures, washed with ether, and air dried. The complex was obtained in yields of 0.6 g (77%), mp >300°, as brown crystals. The compound is soluble in acetone, chloroform, and dichloromethane giving red-brown solutions.

Proton Magnetic Resonance Spectra.—The spectra were recorded in $CDCl_3$ solution and exhibited resonances at τ 5.10 (singlet, $\pi\text{-}C_5H_5$) and 6.20 (singlet, $-CH_3$); the relative areas were 5:6, respectively.

Mass Spectra.—These were recorded using an AEI MS9 spectrometer. The parent ion was observed at m/e 270 (P^+) and other major peaks were detected at m/e = 240 ($P^+ - NO$) and m/e 174 ($P^+ - C_5H_5NO$).

Infrared Spectra.—The spectra (cm^{-1}) were recorded in KBr disks and dichloromethane solution. In KBr disks: 3440 br, w, 1712 vs, 1697 vs, 1534 s, 1400 s, 1254 m, 1150 m, 1055 w, 1010 m, 985 m, 930 w, 838 m, 820 m. In dichloromethane: 3400 br, w, 1710 vs, 1530 s, 1400 s, 1150 s, 1054 m, 1010 m, 990 s, 920 m, 835 s, 815 s.

$\pi\text{-}C_5H_4CH_3Mn(NO)S_2CN(CH_3)_2$.—This compound was prepared in the same way as its $\pi\text{-}C_5H_5$ analog and was obtained as a brown microcrystalline solid, mp 119°.

Proton Magnetic Resonance Spectra.—The spectra were recorded in $CDCl_3$ solution and resonances were observed at τ 5.26 (singlet, $\pi\text{-}C_5H_4$), 6.80 (singlet, $-CH_3$ of $N(CH_3)_2$), and 8.22 (singlet, CH_3- of ring); the relative areas were 4:6:3, respectively.

Infrared Spectra.—The spectra (cm^{-1}) were recorded in KBr disks and in dichloromethane solution. In KBr disks: 3090 w, 2980 w, 2960 w, 2920 w, 1705 vs, 1790 vs, 1535 s, 1488 m, 1435 m, 1390 s, 1350 w, 1250 m, 1155 m, 1050 w, 1039 w, 1020 s, 982 s, 932 w, 912 w, 858 w, 845 m, 831 m, 818 s. In dichloromethane: 2925 m, 2860 w, 1798 vs, 1535 s, 1395 s, 1235 w, 1147 m, 1045 w, 1025 w, 985 m, 960 w, 842 m, 815 m.

Electronic Spectra.—These were recorded in dichloromethane solution: λ_{max}, cm^{-1} (ϵ, M^{-1} cm^{-1}): 21,100 (418 sh), 25,380 (1203), 33,700 (10,690 sh), 38,320 (15,370), 43,220 (17,160).

$\pi\text{-}C_5H_5Mn(NO)S_2CN(C_2H_5)_2$.—$[\pi\text{-}C_5H_5Mn(NO)(CO)_2][PF_6]$ (1.0 g) was dissolved in 30 ml of acetone and treated with $NaS_2CN(C_2H_5)_2\cdot 2H_2O$ (0.7 g) dissolved in 15 ml of acetone–ethanol (1:1 v/v) containing 5 ml of water. After vigorous evolution of CO, a red-brown solution had formed which was filtered and evaporated partially using a water pump. The brown solid which was formed was collected by filtration and recrystallized from acetone–water giving 0.5 g (59%) of brown crystals, mp 108°. The complex is soluble in acetone, chloroform, and dichloromethane, giving red-brown solutions.

Proton Magnetic Resonance Spectra.—The spectra were recorded in $CDCl_3$ and three groups of resonances were observed at τ 5.05 (singlet, $\pi\text{-}C_5H_5$), 6.34 (quartet, $-CH_2-$), and 8.78 (triplet, $-CH_3$); the relative areas were 5:4:6, respectively.

Mass Spectra.—The parent ion was observed at m/e 298 (P^+), and other major peaks were detected at m/e 268 ($P^+ - NO$) and m/e 203 ($P^+ - C_5H_5NO$).

Infrared Spectra.—The spectra (cm^{-1}) were recorded in KBr disks and in dichloromethane solution. In KBr disks: 3380 w, 3100 w, 2980 w, 2940 w, 2878 w, 1710 vs, 1500 vs, 1465 m, 1455 w, 1440 m, 1382 m, 1361 m, 1301 m, 1278 s, 1212 s, 1141 s, 1112 w, 1099 w, 1076 w, 931 w, 915 m, 835 m, 817 m, 779 m. In dichloromethane: 2980 w, 2940 w, 1710 vs, 1501 s, 1462 m, 1440 m, 1382 s, 1361 w, 1215 s, 1150 s, 1078 w, 1005 m, 915 w, 850 w, 835 w, 815 m.

$\pi\text{-}C_5H_4CH_3Mn(NO)S_2CN(C_2H_5)_2$.—This complex was prepared in the same way as its $\pi\text{-}C_5H_5$ analog and was obtained as brown crystals, mp 57–58°.

Proton Magnetic Resonance Spectra.—The spectra were recorded in $CDCl_3$ solution and consisted of four groups of signals at τ 5.30 (doublet, $\pi\text{-}C_5H_4$), 6.30 (quartet, $-CH_2-$), 8.20 (singlet, $-CH_3$ of ring), and 9.8 (triplet, $-CH_3$ of $N(C_2H_5)_2$); the relative areas were 4:4:3:6, respectively.

Mass Spectra.—The parent ion was observed at m/e 312 (P^+), and other major peaks included those at m/e 282 ($P^+ -$ NO) and m/e 203 ($P^+ - C_6H_7NO$).

Infrared Spectra.—The spectra (cm^{-1}) were recored in KBr disks and in dichloromethane solution. In KBr disks: 3080 w, 2980 w, 1706 vs, 1495 s, 1457 m, 1433 m, 1380 m, 1360 m, 1303 m, 1278 m, 1149 m, 1096 w, 1080 w, 1070 w, 1060 w, 1045 w, 1020 w, 1000 m, 935 w, 916 m, 860 w, 850 m, 820 m, 780 w. In dichloromethane: 3080 w, 2980 w, 2880 vw, 1708 vs, 1495 s, 1457 m, 1432 m, 1380 m, 1360 w, 1302 m, 1212 m, 1150 m, 1098 w,

TABLE I

ELEMENTAL ANALYSES AND CONDUCTIVITY DATA

		Analytical data, %								
		Calcd				Found				Λ,[a]
Complex	Cation	C	H	N	S	C	H	N	S	cm^{-1}
$C_5H_5Mn(NO)S_2C_2(CN)_2]^-$	$(C_2H_5)_4N^+$	48.6	6.0	13.3	15.2	48.5	6.3	13.1	15.4	147
	$(C_6H_5)_4P^+$	63.0	4.0	6.7	10.2	62.9	3.9	6.6	10.0	172
$C_5H_4CH_3Mn(NO)S_2C_2(CN)_2^-$	$(C_2H_5)_4N^+$	49.8	6.2	12.3	14.7	49.7	6.1	12.1	14.4	123
$C_5H_4CH_3Mn(NO)S_2C_2(CN)_2^0$	...	39.5	2.3	13.8	21.1	40.1	3.0	13.2	20.7	b
$C_5H_5Mn(NO)S_2C_6Cl_4^0$	...	30.8	1.2	3.5	15.0[c]	30.8	1.7	3.6	15.1[c]	b
$C_5H_4CH_3Mn(NO)S_2C_6Cl_4^-$	$(C_2H_5)_4N^+$	42.0	4.7	4.9	11.2[d]	41.8	4.8	5.0	11.5[d]	142
$C_5H_4CH_3Mn(NO)S_2C_6Cl_4^0$	...	32.6	1.6	3.2	14.5[e]	33.2	2.1	3.3	14.5[e]	b
$C_5H_5Mn(NO)S_2C_6H_3CH_3^0$	...	47.6	3.6	4.5	21.1	47.6	4.0	4.4	19.8	b
$C_5H_4CH_3Mn(NO)S_2C_6CH_3^0$	...	49.1	4.1	4.4	20.1	49.6	4.3	4.4	19.8	b
$C_5H_5Mn(NO)S_2C{=}C(CN)_2^-$	$(C_2H_5)_4N^+$	48.6	6.0	13.3	15.2	48.5	5.9	13.3	15.5	155
$C_5H_4CH_3Mn(NO)S_2C{=}C(CN)_2^-$	...	49.8	6.2	12.3	14.7	49.4	6.2	12.5	14.3	136
$C_5H_5Mn(NO)S_2CN(CH_3)_2^0$	...	35.6	4.3	10.4	22.8	35.6	4.1	10.4	22.7	b
$C_5H_4CH_3Mn(NO)S_2CN(CH_3)_2^0$	...	38.3	4.6	9.8	22.5	38.4	4.9	9.4	22.3	b
$C_5H_5Mn(NO)S_2CN(C_2H_5)_2^0$	...	40.3	5.0	9.4	21.5	40.1	5.2	9.8	21.8	b
$C_5H_4CH_3Mn(NO)S_2CN(C_2H_5)_2^0$	...	42.3	5.5	8.9	20.6	42.1	6.2	9.1	20.4	b

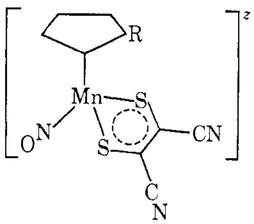
[a] Conductivity measurements in 10^{-4} *M* acetone solution. [b] Nonconducting in acetone. [c] Chlorine analyses: calcd, 33.2; found, 33.0. [d] Chlorine analyses: calcd, 24.8; found, 24.4. [e] Chlorine analyses: calcd, 32.2; found, 32.5.

1080 w, 1070 w, 1045 w, 1022 w, 1000 m, 935 w, 915 m, 862 w, 850 m, 820 m, 780 w.

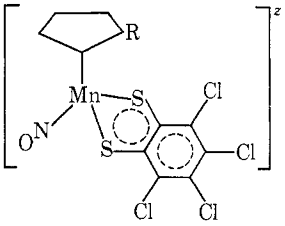
Electronic Spectra.—These were recorded in dichloromethane solution: λ_{max}, cm^{-1} (ϵ, M^{-1} cm^{-1}): 25,950 (1360 sh), 35,000 (11,980), 38,390 (15,280).

Results and Discussion

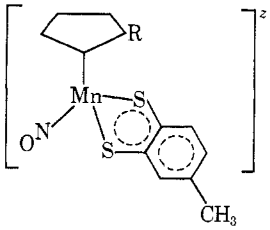
Manganese Monodithiolene Complexes.—The complexes discussed in this section are of the types I–V.



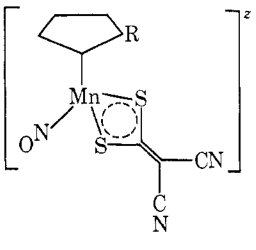
Ia, R = H
b, R = CH$_3$



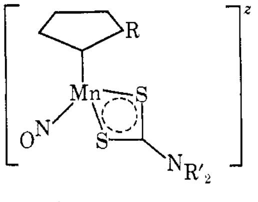
IIa, R = H
b, R = CH$_3$



IIIa, R = H
b, R = CH$_3$



IVa, R = H
b, R = CH$_3$



Va, R = H
b, R = CH$_3$
(R′ = CH$_3$ or C$_6$H$_5$)

We have isolated and purified the species Ia (z = −1), Ib (z = 0, −1), IIa (z = 0), IIb (z = 0, −1), IIIa, b (z = 0), IVa, b (z = −1), and Va, b (R′ = CH$_3$, C$_2$H$_5$; z = 0). The monoanionic species were isolated usually as the $(C_2H_5)_4N^+$ salts, although the $(C_6H_5)_4P^+$ salt of Ia (z = −1) was obtained. All complexes were obtained as crystalline materials and were satisfactorily characterized by elemental analyses and conductivity measurements (Table I). The dialkyldithiocarbamates IV were sufficiently volatile to allow characterization by mass spectrometry, and peaks corresponding to the parent ion, P$^+$, and to $\{P - NO\}^+$ and $\{P - (NO + C_5H_4R)\}^+$ were readily detected.

Synthetic Studies.—Treatment of [π-C$_5$H$_4$RMn(NO)(CO)$_2$][PF$_6$], R = H or CH$_3$, with Na$_2$S$_2$C$_2$(CN)$_2$ and its isomer Na$_2$S$_2$C=C(CN)$_2$ afforded the monoanions red-brown I (z = −1) and IV (z = −1). However, if the hexafluorophosphates were treated with $S_2C_6Cl_4^{2-}$ or $S_2C_6H_3CH_3^{2-}$ in the absence of reducing agents, the purple neutral complexes II (z = 0) and III (z = 0) were formed. Reaction of the hexafluorophosphates with $S_2CNR'_2{}^-$, R′ = CH$_3$ or C$_2$H$_5$, afforded the neutral dialkyldithiocarbamates V (z = 0).

When Ib (z = −1) was treated with iodine, oxidation to a green-black compound readily took place, and we were able to isolate the neutral complex Ib (z = 0). While similar treatment of IVb (z = −1) apparently also gave the neutral complex, we were unable to isolate and completely characterize the compound. Attempted oxidation of Vb (z = 0) with iodine or bromine in dichloromethane resulted in the decomposition of these compounds. The compounds II (z = 0) and III (z = 0) were resistant to iodine oxidation and decomposed when treated with bromine.

Reduction of IIb (z = 0) was readily accomplished using sodium amalgam, and the red-brown monoanion IIb (z = −1) was isolated; the latter was stable to aerial oxidation in the solid state but was rapidly reconverted to IIb (z = 0) by air or iodine in solution. Sodium amalgam reduction of IIIb (z = 0) in acetone or THF clearly gave the expected red-brown monoanion, but all of our attempts to isolate the salt were unsuccessful.

Table II

Voltammetric Data Obtained from π-Cyclopentadienyl- and π-Methylcyclopentadienylmanganese–Sulfur Complexes

Complex	$E_{1/2}$[a]	R[b]	i_d/c[c]	Couple
π-$C_5H_4CH_3Mn(NO)S_2C_2(CN)_2^-$	+0.09	+54	4.7[e]	$-1 \rightarrow 0$
π-$C_5H_4CH_3Mn(NO)S_2C_2(CN)_2^0$	+0.11	−59	4.2[e]	$0 \rightarrow -1$
π-$C_5H_4CH_3Mn(NO)S_2C_6Cl_4^0$	+0.91	+54	7.8	$0 \rightarrow +1$
	−0.32	−61	8.6	$0 \rightarrow -1$
π-$C_5H_4CH_3Mn(NO)S_2C_6H_3CH_3^0$	+0.54	+60	10.0	$0 \rightarrow +1$
	−0.52	−66	8.0	$0 \rightarrow -1$
π-$C_5H_4CH_3Mn(NO)S_2C{=}C(CN)_2^-$	+0.10	+58	5.8	$-1 \rightarrow 0$
π-$C_5H_4CH_3Mn(NO)S_2CN(CH_3)_2^0$	+0.38	+55	6.0	$0 \rightarrow +1$
π-$C_5H_4CH_3Mn(NO)S_2CN(C_2H_5)_2^0$	+0.32	+60	7.8	$0 \rightarrow +1$
π-$C_5H_5Mn(NO)S_2C_2(CN)_2^-$	0.00	*d*	*d*	$-1 \rightarrow 0$
π-$C_5H_5Mn(NO)S_2C_6Cl_4^0$	+0.90	+58	*d*	$0 \rightarrow +1$
	−0.34	−57	*d*	$0 \rightarrow -1$
π-$C_5H_5Mn(NO)S_2C_6H_3CH_3^0$	+0.56	+52	*d*	$0 \rightarrow +1$
	−0.51	−60	*d*	$0 \rightarrow -1$

[a] Half-wave potential (V). [b] Reversibility criterion: $E_{3/4} - E_{1/4}$ (mV); for reversible one-electron wave, $R = 56$ mV. [c] In μA/mmol. [d] Not measured. [e] Diffusion current is proportional to the surface area of the Pt electrode in the solution, and in this measurement an electrode, different from that used in the other measurements, was employed.

Voltammetric Studies.—All of the π-methylcyclopentadienyl complexes Ib–Vb were investigated by voltammetric techniques in dichloromethane solution, and the results are summarized in Table II. The majority of the voltammetric waves observed appear to correspond to reversible one-electron oxidation or reduction processes.[12] There appeared to be no significant differences between the measured half-wave potentials of the few simple π-cyclopentadienyl species examined and those of the ring-methyl-substituted derivatives.

The 1,2-dithiolenes Ib, IIb, and IIIb all exhibited a one-electron-transfer reaction corresponding to

$$\text{I}\ (z = 0) + e^- \rightleftharpoons \text{I}\ (z = -1)$$

$$\text{II}\ (z = 0) + e^- \rightleftharpoons \text{II}\ (z = -1)$$

and

$$\text{III}\ (z = 0) + e^- \rightleftharpoons \text{III}\ (z = -1)$$

The tetrachlorobenzene- and toluenedithiolenes also exhibited one-electron oxidation waves corresponding to the generation of monocations, $z = +1$. The fact that this wave was not observed in the dicyano-1,2-dithiolenes is probably due to the limitations in voltage scan (+2.00 to −2.00 V) and to the probable occurrence of this wave close to, or above, +2.00 V. Similar arguments can be advanced to account for the absence of the second anodic wave in the voltammogram of IVb ($z = -1$), which contained only one oxidation wave corresponding to the generation of IVb ($z = 0$).[13,14] The dithiocarbamates Vb ($R' = CH_3$ and C_2H_5, $z = 0$) could be oxidized in a reversible one-electron step to give the monocationic species, but there was no evidence for cathodic waves equivalent to the formation of Vb ($z = -1$).

The "rules" for the use of half-wave potential data obtained from dithiolene complexes in relation to the syntheses of oxidized or reduced species[15] have been applied with limited success to the new manganese–nitrosyl–sulfur complexes, as indicated in the synthetic section.

The half-wave potentials for the various couples in the 1,2-dithiolene series become increasingly negative as the electron-withdrawing properties of the sulfur ligand substituents decrease, as has been found in other dithiolene systems.[1,16] On the basis of our observations[1] that the $E_{1/2}$ values for one-electron-transfer reactions in tetrachlorobenzenedithiolene complexes are similar to or slightly more negative than the values for the corresponding processes in bis(perfluoromethyl)dithiolenes and that the chemistry of the two groups of compounds is often very similar, we would suggest that reduction of π-$C_5H_5Mn(NO)S_2C_2(CF_3)_2^0$ to the corresponding monoanion should occur smoothly using sodium amalgam or borohydride (rather than ethanolic hydrazine; *vide infra*[3]).

Infrared Studies.—The nitrosyl stretching frequencies of the new complexes are given in Table III, and the complete infrared spectra, measured in KBr disks and dichloromethane solution, are given in the Experimental Section.

The NO stretching frequencies appear to be governed by several factors. The most dramatic effect is that

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(12) The number of electrons involved in each electron transfer reaction was not determined directly (by coulometry). However, in view of the general chemistry of these complexes, this would appear to be one, and this is supported by the following data. For the reactions $W(S_2C_6Cl_4)_3^z$, $z = -1 \rightarrow 0$, $i_d/c = 5.7$ μA/mmol and $E_{3/4} - E_{1/4} = 57$ mV (both species have been isolated); for the reactions $V(S_2C_6Cl_4)_3^z$, $z = -1 \rightarrow -2$, $i_d/c = 6.5$ and $E_{3/4} - E_{1/4} = 68$ (both species have been isolated).[1] The i_d/c values in the foregoing series are entirely comparable with those presented in Table II and were obtained under identical conditions, except where noted.

(13) The occurrence of reversible electron-transfer reactions in IVb and Vb, where the metal and sulfur ligand form a four-membered chelate ring (1,1-dithiolene), is not unusual since similar, but irreversible, oxidation waves occur in the related nickel complexes[14] $Ni(S_2C{=}X)_2^{2-}$, where $X = C(CN)_2$, NCN, $CH(NO_2)$, etc. Chemical oxidation (using I_2) of these nickel complexes resulted in the formation of $Ni(S_3C{=}X)_2^{2-}$, which undergo reversible one-electron-transfer reactions, and the possibility that IVb ($z = -1$), on treatment with I_2, gave π-$C_5H_4CH_3Mn(NO)S_3C{=}C(CN)_2^0$ cannot be entirely dismissed. The parent monoanion does not apparently absorb sulfur, but it is hoped that further studies of the chemistry and electrochemistry of the species π-$C_5H_4RMn(NO)S_2C{=}X^z$ and related species will clarify this problem and possibly indicate whether the electron-transfer reactions have their origins primarily in the sulfur ligands or in the π-$C_5H_4RMn(NO)$ group.

(14) D. Coucouvanis and J. P. Fackler, *J. Am. Chem. Soc.*, **89**, 1346 (1967).

(15) A. Davison and R. H. Holm, *Inorg. Syn.* **10**, 8 (1967).

(16) D. C. Olson, V. P. Mayweg, and G. N. Schrauzer, *J. Am. Chem. Soc.*, **88**, 4876 (1966).

TABLE III

NITROSYL STRETCHING FREQUENCIES IN π-CYCLOPENTADIENYLMANGANESE–NITROSYL–SULFUR COMPLEXES

Complex	Cation	ν_{NO}, cm^{-1}	
		KBr	CH_2Cl_2
π-$C_5H_5Mn(NO)S_2C_2(CN)_2^-$	$(C_2H_5)_4N^+$	1705	1699
	$(C_6H_5)_4P^+$	1695	1700
π-$C_5H_4CH_3Mn(NO)S_2C_2(CN)_2^-$	$(C_2H_5)_4^+$	1703	1690
π-$C_5H_4CH_3Mn(NO)S_2C_6Cl_4^-$	...	1660	1670
π-$C_5H_4CH_3Mn(NO)S_2C_6H_3CH_3^-$	...[a]	...	1670[b]
π-$C_5H_5Mn(NO)S_2C{=}C(CN)_2^-$	$(C_2H_5)_4N^+$	1690	1698
π-$C_5H_4CH_3Mn(NO)S_2C{=}C(CN)_2^-$	...	1690	1690
π-$C_5H_4CH_3Mn(NO)S_2C_2(CN)_2^0$	...	1780	1795
π-$C_5H_5Mn(NO)S_2C_6Cl_4^0$	...	1790	1790
π-$C_5H_4CH_3Mn(NO)S_2C_6Cl_4^0$	...	1785	1780
π-$C_5H_5Mn(NO)S_2C_6H_3CH_3^0$	...	1770	1774
π-$C_5H_4CH_3Mn(NO)S_2C_6H_3CH_3^0$	...	1765	1770
π-$C_5H_4CH_3Mn(NO)S_2C{=}C(CN)_2^0$ [c]	...	...	1788[d]
π-$C_5H_5Mn(NO)S_2CN(CH_3)_2^0$ [e]	...	1712, 1697	1710
π-$C_5H_4CH_3Mn(NO)S_2CN(CH_3)_2^0$ [f]	...	1705, 1690	1695
π-$C_5H_5Mn(NO)S_2CN(C_2H_5)_2^0$ [g]	...	1710	1710
π-$C_5H_4CH_3Mn(NO)S_2CN(C_2H_5)_2^0$ [h]	...	1706	1708

[a] Compound not isolated. [b] Ethanol smear. [c] Black oil; compound not isolated. [d] $CHCl_3$ smear. [e] ν_{CN}: 1534 (KBr) and 1530 cm^{-1} (CH_2Cl_2). [f] ν_{CN}: 1530 (KBr) and 1533 cm^{-1} (CH_2Cl_2). [g] ν_{CN}: 1500 (KBr) and 1503 cm^{-1} (CH_2Cl_2). [h] ν_{CN}: 1495 (KBr) and 1495 cm^{-1} (CH_2Cl_2).

TABLE IV

MAGNETIC AND ESR SPECTRAL DATA OBTAINED FROM CYCLOPENTADIENYLMANGANESE–NITROSYL–SULFUR COMPLEXES

Complex	μ_{eff}[a]	$\langle g\rangle$[b]	$\langle a_{Mn}\rangle$[c]
π-$C_5H_5Mn(NO)S_2C_2(CN)_2^0$	*d*	2.015 ± 0.001[f]	56.9 ± 0.03[f]
π-$C_5H_5Mn(NO)S_2C_2(CN)_2^-$	Dia[g]	(2.014)[e]	(57)[e]
π-$C_5H_4CH_3Mn(NO)S_2C_2(CN)_2^0$	*d*	2.01 ± 0.001	59.0 ± 0.3
π-$C_5H_4CH_3Mn(NO)S_2C_6Cl_4^0$	1.80	2.016 ± 0.001	58.5 ± 0.3
π-$C_5H_4CH_3Mn(NO)S_2C_6Cl_4^-$	Dia[g]		
π-$C_5H_5Mn(NO)(S_2C_6H_3CH_3^0$	1.81	2.016 ± 0.001	59.0 ± 0.3
π-$C_5H_4CH_3Mn(NO)S_2C_6H_3CH_3^0$	1.74	2.013 ± 0.001	59.1 ± 0.3
π-$C_5H_5Mn(NO)S_2C{=}C(CN)_2^-$	Dia[g]	(2.020)[e]	(65)[e]
π-$C_5H_4CH_3Mn(NO)S_2C{=}C(CN)_2^0$	*d*	2.019 ± 0.001[f]	65.6 ± 0.3[f]

[a] Measured in the solid state at room temperature. [b] In acetone solution at room temperature. [c] Six-line spectra due to Mn^{53}, $I = {}^5/_2$. [d] Insufficient material for measurement, or not determined. [e] Weak resonances in $CDCl_3$ solution. [f] Sample generated by treatment of monoanion in solution with iodine. [g] $(C_2H_5)_4N^+$ salt.

due to changes in the over-all charge on the complex, as is evident in the 1,2- and 1,1-dithiolenes, where ν_{NO} shifts by *ca.* 100 cm^{-1} when z is increased or decreased by one unit. Smaller effects arise from changes in the cyclopentadienyl ring and sulfur ligand substituents and from the medium in which the spectra are recorded: the last mentioned is common in metal nitrosyls.[17] The effect of substitution of a hydrogen atom on the C_5H_5 ring by a CH_3 group on ν_{NO} is variable, the shifts being from 2 to 15 cm^{-1}, and it is notable that on substitution, the frequency is always lowered, possibly owing to the inductive effect of the CH_3 group. In the 1,2-dithiolene series, ν_{NO} decreases as the electron-withdrawing ability of the sulfur ligands decreases, providing that the over-all charge remains constant. In the spectra of V ($z = 0$) the effect of changing R$'$ on ν_{NO} is random, but ν_{C-N}, the stretching frequency associated with the S_2CNR_2 group,[18,19] is higher in the dimethyl derivatives than in the diethyl compounds, as previously observed.[20] The NO stretching frequencies in the monoanionic species Ib ($z = -1$) and IVb ($z = -1$) are close to each other in value, indicating that the 1,1-dithiolate $S_2C{=}C(CN)_2$ can function as a π acceptor almost equivalent to the 1,2-dithiolate $S_2C_2(CN)_2$.[21] A comparison of the NO stretching frequencies in the π-$CH_3C_5H_4$ species shows that those for the monoanionic 1,2- and 1,1-dithiolenes are very close to those of the neutral but isoelectronic dialkyldithiocarbamates which we believe underlines the poor π-acceptor ability of the $S_2CNR'_2$ ligands relative to the dithiolates.

Magnetic and Esr Spectral Studies.—The neutral 1,2- and 1,1-dithiolene complexes are paramagnetic and have magnetic moments consistent with one unpaired electron. These species gave rise to esr spectra (Table IV) in solution which consisted of six-line multiplets caused by interaction with Mn^{53}, $I = {}^5/_2$; the g factor in the 1,2-dithiolenes averaged 2.014 and a_{Mn} was 58.3 gauss; no nitrogen hyperfine splitting was detected. The marked difference between the esr parameters of I ($z = 0$), II ($z = 0$), and

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(17) B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, **7**, 277 (1966).

(18) The C–N bond is believed to have partial double-bond character arising as a result of the inductive effect of the NR$'_2$ group.[19]

(19) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Suomen Kemistilehti*, 75 (1956).

(20) F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, **3**, 1398 (1964).

(21) Similar observations have been made in the systems $Mn(CO)_4(S-S)^-$: N. G. Connelly, J. Locke, and J. A. McCleverty, *Inorg. Chim. Acta*, **2**, 411 (1968)..

TABLE V

VOLTAMMETRIC DATA OBTAINED FROM π-CYCLOPENTADIENYLDICYANODITHIOLENES AND RELATED METAL COMPLEXES

Complex	$E_{1/2}$[a]	R[b]	I[c]	Proposed couple	Ref
$(\pi\text{-}C_5H_5)_2TiS_2C_2(CN)_2$	-0.73	-80	20	$0 \rightarrow -1$	This work
$(\pi\text{-}C_5H_5)_2TiS_2C_6H_3CH_3$	-1.7[d]				25
$\pi\text{-}C_5H_5TiS_4C_4(CN)_4^-$	-0.73	-68	36	$-1 \rightarrow -2$?	This work
	$+0.98$	$+125$	14	$-1 \rightarrow 0$	This work
$\pi\text{-}C_5H_5MoS_4C_4(CN)_4^-$	-1.42	-70	17	$-1 \rightarrow -2$	This work
	$+0.78$	$+70$	14	$-1 \rightarrow 0$	This work
$\pi\text{-}C_5H_5WS_4C_4(CN)_4^-$	-1.70	-60	17	$-1 \rightarrow -2$	This work
	$+0.78$	$+70$	14	$-1 \rightarrow 0$	This work
$\pi\text{-}C_5H_5CoS_2C_2(CN)_2^0$	-0.45	-59	*e*	$0 \rightarrow -1$	This work
$\pi\text{-}C_5H_5CoS_2C_2(CF_3)_2^0$	-1.1[d]				24

[a] Half-wave potential (V) in CH_2Cl_2 *vs.* sce. [b] Reversibility criterion: $E_{3/4} - E_{1/4}$ (mV); for one-electron reversible wave, $R = 56$ mV. [c] $I = i_d/c$ (μA/mmol).[26] [d] Data obtained in dimethoxyethane using an Ag|$AgClO_4$ reference cell and a dropping mercury electrode. [e] i_d/c is difficult to estimate since the complex is only partially soluble in CH_2Cl_2.

III ($z = 0$) and IVb ($z = 0$) seems to suggest a considerable difference in the electronic structure of the two groups of complexes (1,2- and 1,1-dithiolenes). McDonald, Phillips, and Mower[22] previously correlated the differences between the esr spectral parameters of $Fe(NO)S_4C_4(CN)_4^{2-}$[23] and $Fe(NO)(S_2C{=}C(CN)_2)_2^{2-}$ with the size of the metal–ligand chelate ring (five *vs.* four members). In view of these observations we suggest that the esr data presented herein, which, together with the appropriate NO stretching frequency, constitute the principal evidence for an oxidized neutral species such as IVb ($z = 0$), are more consistent with the formulation IVb ($z = 0$) rather than with $\pi\text{-}C_5H_4CH_3\text{-}Mn(NO)S_3C{=}C(CN)_2^0$.

The monoanionic 1,2- and 1,1-dithiolenes and the dithiocarbamates are diamagnetic in the solid state (see Table IV). The failure to observe sharp proton magnetic resonance spectra from some of the analytically pure monoanions dissolved in $CDCl_3$ may be associated with the observation of weak six-line esr signals from these solutions. (The bulk susceptibility of these complexes in the solid state does not reveal significant amounts of paramagnetic impurities.) These esr signals may be removed by adding hydrazine hydrate to the solutions, and at the same time the pmr signals are sharpened and increased in intensity. These data are consistent with the view that the paramagnetic impurities present in the $CDCl_3$ solutions containing the monoanions are the corresponding neutral complexes.

Other π-Cyclopentadienyldicyano-1,2-dithiolene Complexes.—In part I of this series,[7] we described the preparation and characterization of some π-cyclopentadienyldicyano-1,2-dithiolene complexes. We have now examined these species by voltammetry in dichloromethane solution and the results are summarized in Table V. The data therein are compared with some relevant information obtained by Dessy and his coworkers[24,25] in their electrochemical studies of the related bis-perfluoromethyl and toluenedithiolene compounds.

The voltammogram of $(\pi\text{-}C_5H_5)_2TiS_2C_2(CN)_2$ exhibits a reduction wave which may correspond to the formation of a monoanion,[26] since such a species has been detected by esr spectroscopy[25] in electrochemically reduced solutions of $(\pi\text{-}C_5H_5)_2TiS_2C_6H_3CH_3$. Attempts to reduce the dicyanodithiolene complex using chemical reagents were unsuccessful.

The $E_{1/2}$ values for the reduction of $\pi\text{-}C_5H_5MS_4C_4(CN)_4^-$ (M = Ti, Mo, and W) to the corresponding dianions are such that this process cannot be effected by conventional wet chemical methods, and this also applies to the oxidation of the complexes to neutral species. The existence of $\pi\text{-}C_5H_5TiS_4C_4(CN)_4^{2-}$ may be in some doubt, since the diffusion current of the reduction wave in the voltammogram of the monoanion is more than twice that of the corresponding oxidation wave.[26]

The monodithiolene $\pi\text{-}C_5H_5CoS_2C_2(CN)_2^0$ exhibited a reversible reduction wave, and treatment of this purple compound with BH_4^- afforded a brown solution which displayed an eight-line esr spectrum whose parameters[27] are similar to the electrochemically produced $\pi\text{-}C_5H_5CoS_2C_2(CF_3)_2^-$.[24,28] We conclude that the borohydride-reduced species is the expected monoanion, although attempts to isolate this species were unsuccessful.

In conclusion, it may be noted that electron-transfer reactions occur in monodithiolene species with apparently the same facility as they do in bis- and tris-substituted systems, although the number of members of any one electron-transfer series in the monodithiolenes is generally much smaller than that in the other two series.

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(22) C. C. McDonald, W. D. Phillips, and H. F. Mower, *J. Am. Chem. Soc.*, **87**, 3319 (1965).

(23) J. A. McCleverty, N. M. Atherton, J. Locke, E. J. Wharton, and C. J. Winscom, *ibid.*, **89**, 6082 (1967).

(24) R. E. Dessy, F. E. Stary, R. B. King, and M. Waldrop, *ibid.*, **88**, 471 (1966).

(25) R. Dessy, R. B. King, and M. Waldrop, *ibid.*, **88**, 5112 (1966).

(26) The number of electrons involved in each electron-transfer reaction in these π-cyclopentadienyl complexes has not been directly determined. However, it seems likely that in most cases this is 1, and this suggestion is supported by the following i_d/c data which were collected under identical conditions:[23] $Fe(NO)S_4C_4(CF_3)_4^z$, $z = -1 \rightarrow 0$, $i_d/c = 18$, $z = -1 \rightarrow -2$, $i_d/c = 16$; $Fe(NO)S_4C_4(C_6H_5)_4^z$, $z = -1 \rightarrow 0$, $i_d/c = 20$, $z = -1 \rightarrow -2$, $i_d/c = 20$. Each of these waves was reversible on Pt, and each of the charged species was isolated and characterized.

(27) $\pi\text{-}C_5H_5CoS_2C_2(CN)_2^-$: $\langle g \rangle = ca.\ 2.5$; $\langle a_{Co} \rangle = ca.\ 40$ G; $\pi\text{-}C_5H_5\text{-}CoS_2C_2(CF_3)_2^-$:[24] $\langle g \rangle = 2.454$; $\langle a_{Co} \rangle = 41$ G; eight-line spectra due to interaction with Co^{59}, $I = {}^7/_2$.

(28) Attempts to prepare $\pi\text{-}C_5H_5CoS_2C_2(CF_3)_2^-$ by reduction of the neutral compound with ethanolic hydrazine resulted in the generation of $CoS_4C_4(CF_3)_4^{2-}$;[8] treatment of $\pi\text{-}C_5H_5CoS_2C_2(CN)_2^0$ with $S_2C_2(CN)_2^{2-}$, which is itself a mild reducing agent, resulted in the formation of $CoS_4C_4\text{-}(CN)_4^{2-}$.[7]

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Spectroscopic Studies of Metal–Metal Bonding. I. Absorption and Laser Raman Spectra and Vibrational Analyses of $Cl_3MCo(CO)_4$ (M = Sn, Ge, Si)[1]

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The complete absorption spectra (33–55,000 cm^{-1}) are reported for the three analogous metal–metal or metal–metalloid bound molecules $Cl_3SnCo(CO)_4$, $Cl_3GeCo(CO)_4$, and $Cl_3SiCo(CO)_4$, and the laser Raman spectra, including band polarization, have been measured for $\Delta\omega$ = 0–4000 cm^{-1}. The symmetry types of the vibrational bands are assigned for the 48 observed of the 60 allowed fundamentals, the overtone and combination bands observed are tentatively assigned, including the ν_{CO} type of overtones and combinations in the 4000–4250-cm^{-1} region, and the electronic ultraviolet transitions giving rise to the colors are reported. Vibrational normal-coordinate analyses for the molecules are reported which yield close agreement between calculated and validly assigned spectra and which are based on both reasonable spectroscopic assumptions and valence force field. The different k_{Co-M} values found (k_{Co-Sn} = 1.23 mdyn/Å, k_{Co-Ge} = 1.05 mdyn/Å, k_{Co-Si} = 1.32 mdyn/Å) do not appear to be significantly reflected in the 5-μ (ν_{CO}) spectra. The vibrational eigenvectors indicate that approximate methods of calculating k_{MM} from one assigned "ν_{MM}" are not reliable.

Introduction

The nature of metal–metal and metal–metalloid bonding is being studied by a number of techniques on a variety of systems which range from vapor-phase *n*-mers to metals and alloys. In the recent few years the syntheses of a number of relatively stable discrete metal–metal bonded molecules have led to the expenditure of considerable effort at the study of these bonds. To date, the studies have been primarily in survey form,[3] with the exception of structural studies and a few mass spectral studies. The potential of vibrational analysis leading to determination of the strengths of the bonds of interest is well recognized, but its fulfillment has been approached in only few cases.[4] The reasons for this are evident; the molecules and consequently the numbers of vibrations and sizes of force fields are large, and the larger they are the greater the disparity which must be overcome between the number of unknown force field elements and known experimental data.

Since finding a sufficiently complete valence force field which is both in complete agreement with the observed spectra and which can claim to be a substantially valid measure of bond strengths is a problem which normally demands somewhat more than spectral information for one molecule, we have selected a very favorable series of molecules, $Cl_3MCo(CO)_4$ (M = Sn, Ge, Si), to consider.

Its members can be prepared in high purity, structural information is available, spectra in important regions can be measured in the vapor as well as liquid phase, the spectral assignments of fundamentals are theoretically unambiguous because of the selection rules and polarization behavior of the Raman bands, and a relatively large fraction of the vibrational bands is allowed. There is strong spectral evidence that a large portion of the force field is constant through the series, there is a systematic change in the extent of mixing between the modes involving and not involving the constant portion as the series is descended, and the moieties of each molecule have very close parallels in other vibrationally analyzed molecules.[5,6]

We report the infrared and laser Raman spectra of the three molecules $Cl_3MCo(CO)_4$ (M = Sn, Ge, Si), their vibrational analyses, and the conclusions we have reached from these analyses concerning their bonding and the treatment of metal–metal bonded compounds.

Experimental Section

The compounds $Cl_3SiCo(CO)_4$,[7] $Cl_3GeCo(CO)_4$,[8] and $Cl_3SnCo(CO)_4$[9] were prepared by referenced reported routes from reagents carefully prepurified in all cases by repeated vacuum

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[3] (a) N. A. D. Carey and H. C. Clark, *Inorg. Chem.*, **7**, 95 (1968), and N. A. D. Carey and H. C. Clark, *Chem. Commun.*, 292, 1967; (b) R. A. Mackay and R. F. Schneider, *Inorg. Chem.*, **7**, 455 (1968).

[4] C O. Quicksall and T. G. Spiro, *ibid.*, **7**, 2365 (1968).

[5] H. Stammreich, K. Kawai, and Y. Tavares, *J. Chem. Phys.*, **32**, 1482 (1960).

[6] (a) K. Venkateswarlu, V. Somasunduram, and M. G. Pillai Krishna, *Z. Physik. Chem.*, **212**, 145 (1959); (b) G. W. Chantry and L. A. Woodward, *Trans. Faraday Soc.*, **56**, 1110 (1960); (c) C. W. F. T. Pistorius, *J. Chem. Phys.*, **28**, 514 (1958).

[7] A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 1134 (1965).

[8] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **4**, 771 (1965).

[9] D. J. Patmore and W. A. G. Graham, *ibid.*, **6**, 981 (1967).