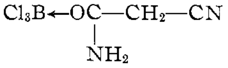
free ligand, at 2150 for $TiBr_4 \cdot L_A$, and 2160 cm^{-1} for $TiCl_4 \cdot L_A$, but the original band at 2220 cm^{-1} has vanished for both solutions of the complexes, thus giving an indication that no appreciable dissociation into the halide and the ligand was happening.

In order to check the possibility of ionization the conductances were measured and the values of molar conductances reported in Table III clearly indicate that ionization is not important in these complexes.

Conclusion

New coordination complexes of aminonitriles of general formula $R_2N(CH_2)_nC{\equiv}N$ with some group IV halides have been prepared. The complexes thus prepared are all one-to-one addition compounds.

The complexes in which the aminonitrile was $(C_2H_5)_2NCH_2C{\equiv}N$ were particularly studied. Their infrared spectra indicated a bathochrome effect of the CN stretching frequency. Since these compounds were found to be monomeric molecular addition compounds, this bathochrome effect could be attributed either to an inductance effect assuming that the ligand is a monodentate or to a coordination through the triple bond assuming that the ligand is a bidentate. The first of these two possibilities can reasonably be ruled out because in a recent work on complexes of cyanoacetamide[8] we found that in a complex of the composition



$$Cl_3B{\leftarrow}O\underset{\displaystyle NH_2}{\underset{|}{C}}{-}CH_2{-}CN$$

coordination of the oxygen of the carbonyl group had no influence on the position of the CN stretching frequency.

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(8) S. C. Jain and R. Rivest, *Can. J. Chem.*, in press.

CONTRIBUTION FROM THE MELLON INSTITUTE,
PITTSBURGH, PENNSYLVANIA

Organosulfur Derivatives of the Metal Carbonyls. IX. Some Transition Metal Derivatives Containing Both π-Cyclopentadienyl and Bis(trifluoromethyl)ethylene Dithiolate Ligands[1]

BY R. B. KING[2] AND M. B. BISNETTE

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Bis(trifluoromethyl)dithietene reacts with $C_5H_5Mo(CO)_2NO$ to give brown $[C_5H_5Mo(NO)S_2C_2(CF_3)_2]_2$. However, the analogous reaction between bis(trifluoromethyl)dithietene and $C_5H_5W(CO)_2NO$ gives green $C_5H_5W[S_2C_2(CF_3)_2]_2$ with the expected magnetic moment for one unpaired electron. The tungsten compound $C_5H_5W(CO)_3H$ reacts with bis(trifluoromethyl)dithietene to give primarily brown $[C_5H_5W(CO)S_2C_2(CF_3)_2]_2$ as well as minor amounts of $C_5H_5W[S_2C_2(CF_3)_2]_2$. The manganese compound $[C_5H_5MnCONO]_2$ reacts with bis(trifluoromethyl)dithietene to give brown volatile paramagnetic $C_5H_5MnNOS_2C_2(CF_3)_2$. Reaction between $C_5H_5Rh(CO)_2$ and bis(trifluoromethyl)dithietene gives red $C_5H_5RhS_2C_2(CF_3)_2$. The red iridium analog of this compound, $C_5H_5IrS_2C_2(CF_3)_2$, may be obtained from $C_5H_5IrC_8H_{12}$ and bis(trifluoromethyl)dithietene. Reductions of some of these π-cyclopentadienyl compounds to anions with alcoholic hydrazine are described. The anions obtained from these reductions, including the previously unreported red-violet $\{C_5H_5W[S_2C_2(CF_3)_2]_2\}^-$ and green $\{[(CF_3)_2C_2S_2]_2MnNO\}^{2-}$, as well as the known[3] planar species $\{M[S_2C_2(CF_3)_2]_2\}^z$ (M = Fe, $z = -1$; M = Co, $z = -2$; M = Ni, $z = -2$) may be isolated as crystalline tetraethylammonium salts. Oxidation of the related brown $[CH_3SFeCOC_5H_5]_2$ with $AgSbF_6$ to the intense blue-green radical cation salt $[CH_3SFeCOC_5H_5]_2[SbF_6]$ is described. The mass spectra of numerous π-cyclopentadienylmetal complexes containing $(CF_3)_2C_2S_2$ ligands are described and discussed.

Introduction

In 1963 the first reactions between cyclopentadienylmetal carbonyls and bis(trifluoromethyl)diethietene (I) were described.[4] These reactions yielded the compounds $[C_5H_5MS_2C_2(CF_3)_2]_n$ (M = V, Cr, or Mo, $n = 2$; M = Co or Ni, $n = 1$) for which unusual structures were proposed. One objective of this work was the preparation of $[C_5H_5MS_2C_2(CF_3)_2]_n$ compounds of metals other than the five listed above, since all 24 transition metals (*i.e.*, three in each column from titanium to copper, inclusive) appear to be suitable candidates for the formation of such compounds albeit of different structures. The structures of these $[C_5H_5MS_2C_2(CF_3)_2]_n$ compounds would be expected to depend drastically upon the electronic configuration and possibly the size of the metal atom. Thus their comparison would be very interesting. This paper describes in detail attempts to prepare $[C_5H_5MS_2C_2(CF_3)_2]_n$ derivatives of the six additional metals tungsten, manganese, iron, ruthenium, rhodium, and iridium. Of these additional six metals only rhodium and iridium have been found to yield compounds of the type $[C_5H_5MS_2C_2(CF_3)_2]_n$ (M = Rh or Ir, $n = 1$).

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(1) For part VIII of this series see R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4**, 1663 (1965).

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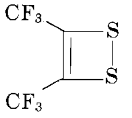
(3) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **3**, 814 (1964).

(4) R. B. King, *J. Am. Chem. Soc.*, **85**, 1587 (1963).

Tungsten and manganese did not yield $[C_5H_5MS_2C_2(CF_3)_2]_n$ compounds from the reactions tried but instead gave other products of interest such as the tungsten compound $C_5H_5W[S_2C_2(CF_3)_2]_2$ and the manganese nitrosyl derivative $C_5H_5MnNOS_2C_2(CF_3)_2$. The iron and ruthenium systems yielded complex mixtures which could not be fully characterized.[5]



I

Compounds of the type $M[S_2C_2(CF_3)_2]_n$ (n = 2, M = Co,[3] Ni,[6] or Pt;[3] n = 3, M = Cr,[7] Mo,[8] W,[7] or Fe[3]) have been prepared by reactions of metal carbonyls, their derivatives, and other related compounds with bis(trifluoromethyl)dithietene. All of these compounds are readily reduced to anions including the following: $\{M[S_2C_2(CF_3)_2]_n\}^z$ ($n = 2$, $z = -1$, M = Fe,[3] Co,[3] Ni,[6] Pd,[3] or Pt;[3] $n = 2$, $z = -2$, M = Co,[3] Ni,[6] Pd,[3] or Pt;[3] $n = 3$, $z = -1$, M = V,[9] Cr,[7] Mo,[7] or W;[7] $n = 3$, $z = -2$, M = V,[9] Cr,[7] Mo,[7] or W[7]). A frequently useful reducing agent is alcoholic hydrazine. A second objective of the work described in this paper was the exploration of the reduction of compounds containing π-cyclopentadienyl and organosulfur ligands with alcoholic hydrazine hoping to obtain anions containing both π-cyclopentadienyl and organosulfur ligands. The only such anion obtained was the red-violet $\{C_5H_5W[S_2C_2(CF_3)_2]_2\}^-$ anion. However, the novel green nitrosyl anion $\{[(CF_3)_2C_2S_2]_2MnNO\}^{2-}$ was also prepared. In other cases (*e.g.*, the $C_5H_5MS_2C_2(CF_3)_2$ compounds of cobalt and nickel) alcoholic hydrazine reduction led to disproportionation to the $\{M[S_2C_2(CF_3)_2]_2\}^{2-}$ anions. A related discovery, also discussed in this paper, is the oxidation of the brown neutral diamagnetic $[CH_3SFeCOC_5H_5]_2$ to the intense blue-green paramagnetic $[CH_3SFeCOC_5H_5]_2^+$ radical cation.

The simultaneous presence of at least carbon, hydrogen, fluorine, sulfur, and a metal in the $[C_5F_5MS_2C_2(CF_3)_2]_n$ and related compounds makes elemental analyses unusually difficult. Furthermore, the limited solubility of some of these compounds in organic solvents makes direct determination of their molecular weights in solution by vapor pressure osmometry or other methods difficult or even impossible. Therefore, the third objective of this work was the establishment of mass spectroscopy as a means for providing elemental composition, molecular weight, and other data pertinent to the characterization of nonionic compounds obtained from various cyclopentadienylmetal carbonyls and bis(trifluoromethyl)dithietene.

Experimental Section

Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany.[10] Infrared spectra were generally taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 21 spectrometer. In addition, the metal carbonyl and nitrosyl stretching frequencies in the relatively few new compounds containing these groups were taken in Halocarbon oil mulls and recorded on a Beckman IR-9 grating spectrometer with the scale expanded by a factor of 4. Proton and fluorine nmr spectra were taken in the indicated solvents and recorded on Varian A-60 and DP-60 spectrometers, respectively. Ultraviolet and visible spectra were taken in dichloromethane or 1:9 hydrazine–ethanol solutions and recorded on a Cary Model 14 spectrometer. Mass spectra were taken at 70-ev electron energies on an Associated Electrical Industries MS-9 spectrometer. Magnetic susceptiblity measurements were made on a Faraday balance originally constructed at the Mellon Institute by Professor L. Vaska. In order to eliminate any effects of ferromagnetic impurities, measurements were made at two to four different field strengths. 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 reaction, (b) handling all filtered solutions of metal complexes, and (c) admitting to evacuated flasks.

Reagents.—Bis(trifluoromethyl)dithietene was prepared by bubbling hexafluorobutyne-2 (from Peninsular Chemical Research Inc., Gainesville, Fla.) through boiling sulfur as described by Krespan and McKusick.[11] Material which had remained a mobile liquid gave the best results in the preparations described below. If the bis(trifluoromethyl)dithietene had become a viscous liquid or a solid, it was found advisable to redistil it at atmospheric pressure before use.

The required intermediates $C_5H_5W(CO)_3H$,[12] $[C_5H_5MnCONO]_2$,[13] $[C_5H_5Fe(CO)_2]_2$,[14] $C_5H_5Co(CO)_2$,[15] $C_5H_5CoC_8H_{12}$,[16] $C_5H_5Rh(CO)_2$,[17] and $C_5H_5IrC_8H_{12}$[18] were prepared by the cited procedures using the commercially available $W(CO)_6$ (Pressure Chemical Co., Pittsburgh, Pa.), $C_5H_5Mn(CO)_3$ (Ethyl Corporation, New York, N. Y.), $Fe(CO)_5$ (Antara), $(C_5H_5)_2Co$ (Arapahoe Chemical Corp., Boulder, Colo.), "$RhCl_3(H_2O)_3$" (Englehard Industries, Inc., Newark, N. J.), and "$IrCl_3(H_2O)_4$" (Englehard) as sources of the appropriate metals. The ruthenium compound $[C_5H_5Ru(CO)_2]_2$ was obtained from commercial hydrated ruthenium(III) chloride (Englehard) by carbonylation under pressure in methanol followed by treatment with sodium cyclopentadienide in tetrahydrofuran.[19]

The molybdenum and tungsten derivatives of the type $C_5H_5M(CO)_2NO$ (M = Mo or W) were prepared by the following modi-

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(5) The following factors have impeded study of the $[C_5H_5MS_2C_2(CF_3)_2]_n$ derivatives of the remaining thirteen transition metals: (a) lack of a suitable known π-cyclopentadienyl derivative—zirconium, hafnium, copper, silver, and gold; (b) difficulty in preparing sufficient of the $C_5H_5M(CO)_4$ compound required for the synthesis of the $[C_5H_5MS_2C_2(CF_3)_2]_n$ compound—niobium and tantalum; and (c) present high cost of the metal–technetium and osmium. Attempts to prepare a $[C_5H_5PdS_2C_2(CF_3)_2]_n$ compound from bis(trifluoromethyl)dithietene and $C_3H_5PdC_5H_5$ have appeared completely unpromising. Reaction between $C_5H_5Pt(CH_3)_3$ and bis(trifluoromethyl)dithietene gives a low yield of a volatile green substance which appears from its mass spectrum to be $[(CF_3)_2C_2S_2]_2Pt(CH_3)_2$. In this case the cyclopentadienyl ring is removed in preference to the methyl groups.

(6) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **2**, 1227 (1963).

(7) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **86**, 2799 (1964).

(8) R. B. King, *Inorg. Chem.*, **2**, 641 (1963).

(9) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *ibid.*, **4**, 55 (1965).

(10) Direct oxygen analyses could not be performed on the compounds described in this paper since they also contained fluorine. In other cases difficulties were experienced in obtaining satisfactory analytical data. Fortunately the characterization of all of the new compounds reported in this paper is strongly supported by physical and spectroscopic measurements.

(11) C. G. Krespan and B. C. McKusick, *J. Am. Chem. Soc.*, **83**, 3434 (1961).

(12) (a) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1955); (b) R. B. King, *Organometal. Syn.*, **1**, 156 (1965).

(13) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 791 (1964).

(14) R. B. King, *Organometal. Syn.*, **1**, 114 (1965).

(15) R. B. King, *ibid.*, **1**, 116 (1965).

(16) R. B. King, *ibid.*, **1**, 131 (1965). The chromatography step was omitted in the purification of the $C_5H_5CoC_8H_{12}$.

(17) E. O. Fischer and K. Bittler, *Z. Naturforsch.*, **16b**, 225 (1961).

(18) S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 4997 (1965).

(19) Publication of the details of this procedure will be deferred until it has been more fully worked out.

fication of a reaction first described by Piper and Wilkinson:[12a] A solution of ~100 moles of $NaM(CO)_3C_5H_5$ (M = Mo or W) in redistilled tetrahydrofuran (M = Mo) or 1,2-dimethoxyethane (M = W) was prepared from the corresponding metal hexacarbonyl and sodium cyclopentadienide.[20] This solution was treated successively with 21.4 g (100 mmoles) of N-methyl-N-nitroso-*p*-toluenesulfonamide ("Diazald" purchased from Aldrich Chemical Co., Milwaukee, Wis.) and 10.0 ml (10.5 g, 175 mmoles) of glacial acetic acid. After stirring for several hours at room temperature solvent was removed at ~25° (25 mm). The residue was sublimed for several hours at 80–100° (0.1 mm) to give orange crystals of the appropriate $C_5H_5M(CO)_2NO$ compound in about 60% yield. Sometimes in the preparation of $C_5H_5W(CO)_2NO$ a less volatile white crystalline material contaminated the orange sublimate in small quantity; this could be removed by resublimation for the minimum period of time necessary for volatilization only of the orange crystals.

Preparation of $[C_5H_5Mo(NO)S_2C_2(CF_3)_2]_2$.—A mixture of 1.0 g (4.05 mmoles) of $C_5H_5Mo(CO)_2NO$, 0.8 g (3.5 mmoles) of bis(trifluoromethyl)dithietene, and 50 ml of hexane was boiled under reflux for 40 hr with magnetic stirring. After cooling to toom temperature the brown precipitate was filtered, washed with pentane, and dried. This solid was recrystallized twice from a mixture of dichloromethane and hexane to give 0.46–0.84 g (31–58% yield) of brown $[C_5H_5Mo(NO)S_2C_2(CF_3)_2]_2$.

This compound could be sublimed at 150–180° (0.1 mm) to give a black sublimate indicated by analyses to be essentially unchanged $[C_5H_5Mo(NO)S_2C_2(CF_3)_2]_2$. However, since the mass spectrum suggested some tendency for $[C_5H_5Mo(NO)S_2C_2(CF_3)_2]_2$ vapor to decompose slightly into $(C_5H_5)_2Mo_2[S_2C_2(CF_3)_2]_3$ and possibly other species, unsublimed $[C_5H_5Mo(NO)S_2C_2(CF_3)_2]_2$ was used to provide the data needed for its characterization.

Anal. Calcd for $C_{18}H_{10}F_{12}N_2O_2S_4Mo_2$: C, 25.9; H, 1.2; N, 3.4; F, 27.3; S, 15.4; Mo, 23.0; mol wt, 834. Found (unsublimed sample): C, 26.1; H, 1.4; N, 2.6; F, 26.8; S, 15.1; Mo, 22.7; mol wt, 840 (Mechrolab vapor pressure osmometer in benzene solution). Found (sublimed sample): C, 26.1; H, 1.2; N, 2.7; F, 27.3; S, 15.7; Mo, 22.6.

Infrared Spectrum.—ν_{CH} band at 3060 (vw) cm^{-1}; ν_{NO} band at 1661 (s) cm^{-1};[21] $\nu_{C=C}$ band from the $(CF_3)_2C_2S_2$ ligand at 1535 (m) cm^{-1}; ν_{CF} bands at 1242 (s), 1236 (s), 1230 (s), 1144 (s), 1140 (s, sh), and 1120 (m) cm^{-1}; other bands at 1420 (w), 1360 (vw), 1065 (w), 1019 (w), 1005 (w), 891 (m), 853 (w), 832 (m), 826 (m), 713 (m), and 687 (w) cm^{-1}.

Nmr Spectrum. (A) Proton.—Singlet resonance at τ 4.11 in $CHCl_3$ solution due to the ten equivalent π-cyclopentadienyl protons.

(B) Fluorine.—Not observed in a saturated $CHCl_3$ solution.

Ultraviolet and Visible Spectra.—Maxima at 228 mμ (ϵ 29,000) and 375 mμ (ϵ 5900) in a dichloromethane solution (brown).

Preparation of $C_5H_5W[S_2C_2(CF_3)_2]_2$.—A mixture of 5.0 g (14.9 mmoles) of $C_5H_5W(CO)_2NO$, 2.5 ml (~4.0 g, 17.5 mmoles) of bis(trifluoromethyl)dithietene, and 50 ml of methylcyclohexane was boiled under reflux ~20 hr with magnetic stirring. The reaction mixture was cooled to room temperature and finally in a −78° bath. The resulting black solid was filtered and dried. Sublimation of this material at 170° (0.1 mm) for ~8 hr gave 3.90 g (37.3% yield) of dark green crystals of $C_5H_5W[S_2C_2(CF_3)_2]_2$, mp 224–225°.

Anal. Calcd for $C_{13}H_5F_{12}S_4W$: C, 22.2; H, 0.7; F, 32.6; S, 18.3; W, 26.2. Found: C, 22.1, 22.6; H, 0.8, 0.7; F, 32.2, 32.8; S, 18.2, 18.0; W, 26.0, 25.7.

Infrared Spectrum.—ν_{CH} band at 3070 (w) cm^{-1}; no ν_{CO} or ν_{NO} bands; $\nu_{C=C}$ bands from the $(CF_3)_2C_2S_2$ ligand at 1517 (w) and 1496 (w) cm^{-1}; ν_{CF} bands at 1212 (vs), 1175 (vs), and 1143 (vs) cm^{-1}; other bands at 1421 (w), 1065 (w), 1010 (w), 1007 (w), 906 (w), 894 (m), 870 (w), 850 (s), 717 (s), and 689 (m) cm^{-1}.

Magnetic Susceptibility.—$\chi_{\rm mole}^{23^\circ} = +980 \times 10^{-6}$ cm^3/mole corresponding to a magnetic moment of 1.68 BM after making the necessary correction of -230×10^{-6} cm^3/mole for the diamagnetism of the ligands.

Ultraviolet and Visible Spectra.—Maxima (mμ) at 232 (ϵ 22,000), 308 (ϵ 3500), 340 (ϵ 3000), 429 (ϵ 3400), 470 (ϵ 4600), and 621 (ϵ 4000) in dichloromethane solution (green).

Reaction between $C_5H_5W(CO)_3H$ and Bis(trifluoromethyl)dithietene.—A mixture of 2.33 g (7 mmoles) of $C_5H_5W(CO)_3H$, 1.6 g (7 mmoles) of bis(trifluoromethyl)dithietene, and 50 ml of hexane was stirred 22 hr at room temperature and then boiled 3 hr under reflux. After an additional 17 hr at room temperature, the mixture was heated back to the boiling point and filtered hot. The residue was washed with 100 ml of boiling hexane in five portions to remove the green $C_5H_5W[S_2C_2(CF_3)_2]_2$ also formed as a product in this reaction.[22] The brown solid residue was recrystallized repeatedly from mixtures of dichloromethane and hexane, washing the product with several portions of boiling hexane after each recrystallization to remove green $C_5H_5W[S_2C_2(CF_3)_2]_2$. After about two such recrystallizations no green could be detected in the boiling hexane solutions. Further recrystallizations beyond this point were not attempted. Elemental analyses and the mass spectrum indicated this solid to be primarily $[C_5H_5W(CO)S_2C_2(CF_3)_2]_2$. The yield of this brown solid was 1.79 g (51%).

Anal. Calcd for $C_{20}H_{10}O_2F_{12}S_4W_2$: C, 23.9; H, 1.0; F, 22.6; S, 12.7; W, 36.6. Found: C, 22.8; H, 1.1; F, 23.0; S, 15.3; W, 37.5.

Infrared Spectrum.—ν_{CH} bands at 3060 (vw) cm^{-1}; ν_{CO} bands at 2048 (m), 2011 (m), and 1983 (w) cm^{-1};[21] $\nu_{C=C}$ bands of the $(CF_3)_2C_2S_2$ ligand at 1540 (w) and 1530 (w) cm^{-1}; ν_{CF} bands at 1227 (s) and 1150 (m) cm^{-1}; other bands at 1420 (vw), 1003 (vw), 882 (w), 858–835 (w, br), 708 (w), and 690 (w) cm^{-1}.

Ultraviolet and Visible Spectra.—Maximum at 495 mμ (ϵ 4900) in dichloromethane solution (red-brown).

Magnetic Susceptibility.—$\chi_{\rm mole}^{23^\circ} = -282 \times 10^{-6}$ cm^3/mole.

Preparation of $C_5H_5Mn(NO)S_2C_2(CF_3)_2$.—A mixture of 1.5 g (4.2 mmoles) of $[C_5H_5MnCONO]_2$, 1.6 g (7 mmoles) of bis(trifluoromethyl)dithietene, and 50 ml of hexane was exposed 16 hr in a quartz tube to the irradiation from a 450-w ultraviolet lamp. A brown precipitate formed. After cooling in a −78° bath to ensure complete precipitation of the $C_5H_5Mn(NO)S_2C_2(CF_3)_2$, the brown crystals were filtered, washed with three 20-ml portions of pentane, and dried. After one recrystallization from a mixture of dichloromethane and hexane, 2.08 g (79% yield) of brown crystalline $C_5H_5Mn(NO)S_2C_2(CF_3)_2$ was obtained. The analytical sample, mp 142–144°, was obtained by sublimation of this material at 80–100° (0.1 mm).

Anal. Calcd for $C_9H_5F_6NOS_2Mn$: C, 28.7; H, 1.3; N, 3.7; F, 30.3; S, 17.0; Mn, 14.6. Found: C, 28.9; H, 1.3; N, 3.7; F, 29.8; S, 17.1; Mn, 15.2.

Infrared Spectrum.—ν_{CH} band at 3070 (w) cm^{-1}; ν_{NO} band at 1797 (vs) cm^{-1};[21] $\nu_{C=C}$ of the $(CF_3)_2C_2S_2$ ligand at 1486 (m) cm^{-1}; ν_{CF} at 1235 (vs), 1166 (vs), and 1135 (vs) cm^{-1}; other bands at 1417 (m), 1343 (w), 1005 (m), 929 (w), 897 (m), 833 (s), 787 (vw, br), 766 (vw, br), 746 (vw, br), 727 (vw), 715 (m), and 687 (m) cm^{-1}.

Magnetic Susceptibility.—$\chi_{\rm mole}^{23^\circ} = +1138 \times 10^{-6}$ cm^3/mole corresponding to a magnetic moment of 1.73 BM after making the necessary correction of -137×10^{-6} cm^3/mole for the diamagnetism of the ligands.

Ultraviolet and Visible Spectra.—Maxima (mμ) at 223 (ϵ 22,000), 255 (ϵ 16,000), 378 (ϵ 1300), 433 (ϵ 1600), and 524 (ϵ 1150) in dichloromethane solution (red-brown).

Preparation of $C_5H_5CoS_2C_2(CF_3)_2$.—The preparation of $C_5H_5CoS_2C_2(CF_3)_2$ from $C_5H_5Co(CO)_2$ and bis(trifluoromethyl)dithietene in boiling methylcyclohexane has already been described.[4]

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

(21) This region of the infrared spectrum was investigated in a Halocarbon oil mull and recorded on a Beckman IR-9 spectrometer.

(22) The $C_5H_5W[S_2C_2(CF_3)_2]_2$ was obtained from the hexane solutions by cooling to −78°. The green-brown crystals which separated were filtered, dried, and purified by several vacuum sublimations. The yield of pure product was only about 7%.

Two other methods for obtaining $C_5H_5CoS_2C_2(CF_3)_2$ are now described.

(A) Reaction between $C_5H_5Co(CO)_2$ and Bis(trifluoromethyl)dithietene at Room Temperature.—A mixture of 0.5 ml (0.7 g, 4 mmoles) of $C_5H_5Co(CO)_2$, 0.5 ml (0.8 g, 3.5 mmoles) of bis(trifluoromethyl)dithietene, and 50 ml of hexane was stirred 20 hr at room temperature. The resulting purple crystalline precipitate was filtered and recrystallized from a mixture of dichloromethane and hexane to give 0.82 g (67% yield) of purple $C_5H_5CoS_2C_2(CF_3)_2$, mp 147°. The infrared spectrum of this material was identical with that of an authentic sample of $C_5H_5CoS_2C_2(CF_3)_2$ prepared in boiling methylcyclohexane.[4]

(B) Reaction between $C_5H_5CoC_8H_{12}$ and Bis(trifluoromethyl)dithietene.—A mixture of 1.0 g (4.3 mmoles) of $C_5H_5CoC_8H_{12}$ (C_8H_{12} = 1,5-cyclooctadiene), 1.0 ml (1.6 g, 7 mmoles) of bis(trifluoromethyl)dithietene, and 50 ml of methylcyclohexane was refluxed 18 hr with magnetic stirring. After cooling to room temperature, the purple crystalline precipitate was filtered, dried, and recrystallized from a mixture of dichloromethane and hexane to give 0.96 g (64% yield) of purple $C_5H_5CoS_2C_2(CF_3)_2$, mp 153–154°.

Nmr Spectrum of $C_5H_5CoS_2C_2(CF_3)_2$. (A) Proton.—Sharp singlet resonance in chloroform solution at τ 4.49 due to the five equivalent π-cyclopentadienyl protons.

(B) Fluorine.—Sharp singlet resonance in chloroform solution at 55.5 ppm upfield relative to internal $CFCl_3$.[23]

Ultraviolet and Visible Spectra of $C_5H_5CoS_2C_2(CF_3)_2$.—Maxima (mμ) at 229 (ϵ 15,600), 283 (ϵ 31,000), 340 (ϵ 3700), 521 (ϵ 6500), and 715 (ϵ 620) in dichloromethane solution (red-violet).

Preparation of $C_5H_5RhS_2C_2(CF_3)_2$.—A mixture of 0.34 g (1.5 mmoles) of $C_5H_5Rh(CO)_2$, 0.45 g (2 mmoles) of bis(trifluoromethyl)dithietene, and 20 ml of methylcyclohexane was boiled under reflux 16 hr with magnetic stirring. The reaction mixture became dark red almost immediately. After the reaction period was over, the reaction mixture was allowed to cool to room temperature and kept at 10° for 5 days. The resulting red crystals were filtered, washed with three 20-ml portions of pentane, and dried. After one recrystallization from a mixture of dichloromethane and hexane, 0.35 g (59% yield) of red crystalline $C_5H_5RhS_2C_2(CF_3)_2$ was obtained. The analytical sample, mp 179–180°, was purified further by sublimation at 105° (0.2 mm).

Anal. Calcd for $C_9H_5F_6S_2Rh$: C, 27.4; H, 1.3; Rh, 26.1. Found: C, 27.1; H, 1.1; Rh, 26.5.

Infrared Spectrum.—ν_{CH} band at 3060 (w) cm^{-1}; $\nu_{C=C}$ band of the $(CF_3)_2C_2S_2$ ligand at 1512 (w) cm^{-1}; ν_{CF} bands at 1230 (vs), 1165 (vs), and 1133 (vs) cm^{-1}; other bands at 1416 (w), 1400 (m), 1344 (w), 1050 (w), 1008 (m), 988 (w), 911 (w), 884 (w), 838 (m), 816 (vw), 793 (vw, br), 768 (vw, br), 745 (vw, br), 718 (m), and 688 (m) cm^{-1}.

Nmr Spectrum. (A) Proton.—Doublet (J_{Rh-H} = 0.7 cps) in chloroform solution at τ 4.23 due to the five equivalent π-cyclopentadienyl protons.

(B) Fluorine.—Doublet in chloroform solution at +56.0 ppm upfield from internal $CFCl_3$.

Ultraviolet and Visible Spectra.—Maxima at 245 mμ (ϵ 61,000) and 468 mμ (ϵ 9100) in dichloromethane solution (orange).

Preparation of $C_5H_5IrS_2C_2(CF_3)_2$.—A mixture of 0.5 g (1.37 mmoles) of $C_5H_5IrC_8H_{12}$, 0.8 g (3.5 mmoles) of bis(trifluoromethyl)dithietene, and 50 ml of methylcyclohexane was boiled under reflux 45 hr with magnetic stirring. The reaction mixture was then allowed to cool to room temperature and finally overnight in a −78° bath. The red-brown crystals which separated were filtered, dried, and finally sublimed at 110° (0.1 mm) to give 0.165 g (25% yield) of red crystalline $C_5H_5IrS_2C_2(CF_3)_2$, mp 187–188°.

Anal. Calcd for $C_9H_5F_6S_2Ir$: C, 22.4; H, 1.0; F, 23.6; S, 13.2; Ir, 39.8. Found: C, 22.1; H, 0.9; F, 23.7; S, 13.6; Ir, 39.5.

Infrared Spectrum.—ν_{CH} band at 3050 (w) cm^{-1}; $\nu_{C=C}$ band of the $(CF_3)_2C_2S_2$ ligand at 1512 (s) cm^{-1}; ν_{CF} bands at 1238 (vvs), 1168 (vvs), and 1134 (vvs) cm^{-1}; other bands at 1410 (m), 1395 (m), 1344 (w), 1005 (s), 984 (m), 935 (vw), 909 (m), 891 (w), 857 (s), 852 (s), 846 (m), 719 (s), and 690 (m) cm^{-1}.

Nmr Spectrum. (A) Proton.—Singlet in chloroform solution at τ 4.16 due to the five equivalent π-cyclopentadienyl protons.

(B) Fluorine.—Singlet in chloroform solution at +55.4 ppm upfield from internal $CFCl_3$.

Ultraviolet and Visible Spectra.—Maxima (mμ) at 240 (ϵ 12,000), 277 (ϵ 9400), and 398 (ϵ 7000) in dichloromethane solution (yellow).

Preparation of $[(C_2H_5)_4N]\{C_5H_5W[S_2C_2(CF_3)_2]_2\}$.—A 0.81-g sample of $C_5H_5W[S_2C_2(CF_3)_2]_2$ (1.15 mmoles) was shaken ~10 min with a mixture of 1.4 ml of 95+% hydrazine and 25 ml of methanol. The reaction mixture became an intense red-purple immediately. The reaction mixture was filtered and the filtrate treated with a filtered solution of 1.0 g (4.76 mmoles) of tetraethylammonium bromide in ~50 ml of methanol. Cooling the mixture overnight at −15° precipitated dark red-violet crystals of the product. These were filtered, washed with a few milliliters of cold methanol, and recrystallized from a mixture of acetone and 95% ethanol to give 0.32 g (33.5% yield) of deep red-violet crystalline $[(C_2H_5)_4N]\{C_5H_5W[S_2C_2(CF_3)_2]_2\}$, mp 231–233° dec.

Anal. Calcd for $C_{21}H_{25}F_{12}NS_4W$: C, 30.3; H, 3.1; N, 1.7; F, 27.5; S, 15.4; W, 22.1. Found: C, 29.9; H, 2.9; N, 1.7; F, 27.6; S, 15.4; W, 22.3.

Infrared Spectrum.—ν_{CH} bands at 3080 (vw) and 2940 (vw) cm^{-1}; $\nu_{C=C}$ band of the $(CF_3)_2C_2S_2$ ligand at 1540 (m) cm^{-1}; ν_{CF} bands at 1230 (vs), 1157 (vs), and 1117 (vs) cm^{-1}; other bands at 1443 (m), 1435 (m), 1420 (vw), 1392 (w), 1295 (w), 1065 (vw), 1029 (vw), 1004 (w), 999 (w), 882 (m), 856 (w), 837 (w), 813 (w), 795 (vw), 788 (vw), 708 (m), and 688 (w) cm^{-1}.

Nmr Spectrum. (A) Proton.—Resonances at τ 5.20 (singlet), 6.73 (quartet, J = 7 cps), and 8.76 (triple triplet, J_1 = 7 cps, J_2 = 2 cps) in $(CD_3)_2CO$ solution of approximate relative intensities 5:8:12 due to the five π-cyclopentadienyl protons, the eight methylene protons of the $(C_2H_5)_4N^+$ ion, and the twelve methyl protons of the $(C_2H_5)_4N^+$ ion.

(B) Fluorine.—Singlet in acetone solution at +54.3 ppm upfield from internal $CFCl_3$.

Ultraviolet and Visible Spectra.—Maxima at 337 mμ (ϵ 2600) and 498 mμ (ϵ 7600) in 9:1 ethanol–hydrazine solution (red-violet).

Magnetic Susceptibility.—$\chi_{\text{mole}}^{23°} = -245 \times 10^{-6}$ cm^3/mole.

Preparation of $[(C_2H_5)_4N]_2\{[(CF_3)_2C_2S_2]_2MnNO\}$.—A 0.58-g sample of $C_5H_5Mn(NO)S_2C_2(CF_3)_2$ (1.54 mmoles) was allowed to stand 4 hr with a mixture of 1.4 ml of 95+% hydrazine and 50 ml of ethanol. The originally brown solution became an intense green. The filtered reaction mixture was treated with a filtered solution of 1.0 g (4.76 mmoles) of tetraethylammonium bromide in 25 ml of ethanol. After storing for 2 weeks at −15° the green crystals which separated were filtered and dried. After one recrystallization from a mixture of acetone and ethanol 0.14 g (23% yield based on available $(CF_3)_2C_2S_2$ groups) of dark green $[(C_2H_5)_4N]_2\{[(CF_3)_2C_2S_2]_2MnNO\}$, mp 165–171° dec, brown melt, was obtained.

Anal. Calcd for $C_{24}H_{40}F_{12}N_3OS_4Mn$: C, 36.2; H, 5.0; N, 5.3; F, 28.6; S, 16.1; Mn, 6.9. Found: C, 36.0; H, 5.0; N, 5.2; F, 29.2; S, 15.8; Mn, 5.4.

Infrared Spectrum.—ν_{CH} band at 2950 (w) cm^{-1}; ν_{NO} band at 1660 (s) cm^{-1}; $\nu_{C=C}$ band of the $(CF_3)_2C_2S_2$ ligand at 1518 (m) cm^{-1}; ν_{CF} bands at 1230 (vs), 1150 (vs), and 1105 (vs) cm^{-1}; other bands at 1475 (m), 1453 (w), 1430 (w), 1390 (m), 1362

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[23] The reported[4] value for the ^{19}F nmr chemical shift of the CF_3 groups in $C_5H_5CoS_2C_2(CF_3)_2$ is −710 cps relative to internal $(CFCl_2)_2$ at 56.4 Mc. Since the ^{19}F chemical shift of $(CFCl_2)_2$ is +67.8 ppm upfield from internal $CFCl_3$ (R. B. King, unpublished measurements), this reported[4] ^{19}F chemical shift of $C_5H_5CoS_2C_2(CF_3)_2$ corresponds to +55.2 ppm upfield from internal $CFCl_3$ in reasonable agreement with the presently measured value of +55.5 ppm.

(vw), 1022 (w), 998 (m), 892 (m), 832 (w), 780 (w), 712 (s), and 687 (m) cm^{-1}.

Ultraviolet and Visible Spectra.—Maximum at 725 mμ (ε 2040) and inflection point at ~303 mμ (ε 6100) in 9:1 ethanol–hydrazine solution (pale green).

Magnetic Susceptibility.—$\chi_{\text{mole}}^{23°} = +484 \times 10^{-6}$ cm^3/mole corresponding to a magnetic moment of 1.30 BM after making the necessary correction of -226×10^{-6} cm^3/mole for the diamagnetism of the ligands and of the tetraethylammonium ions.

Reduction of the Compounds $C_5H_5MS_2C_2(CF_3)_2$ (M = Co or Ni) with Hydrazine in Methanol Solution.—A 0.66-g sample of $C_5H_5CoS_2C_2(CF_3)_2$ (1.88 mmoles) was stirred 20 hr at room temperature with a mixture of 1.4 ml of 95+% hydrazine and 25 ml of methanol. The intense purple color of the $C_5H_5CoS_2C_2(CF_3)_2$ gradually became a much less intense dirty orange-brown. The filtered reaction mixture was treated with a filtered solution of 1.0 g (4.76 mmoles) of tetraethylammonium bromide in 15 ml of methanol and then kept at −10° for 20 hr. The pale red needles which separated were filtered, washed with diethyl ether, and dried. The crude product was recrystallized once from a mixture of acetone and 95% ethanol and a second time from boiling ethanol containing a few drops of hydrazine to give 0.153 g (21% yield based on available $(CF_3)_2C_2S_2$ groups) of pale red $[(C_2H_5)_4N]_2\{[(CF_3)_2C_2S_2]_2Co\}$, mp 257° dec (lit.[3] dec pt 245°).

This product was found to have a molar magnetic susceptibility ($\chi_{\text{mole}}^{23°}$) of $+1565 \times 10^{-6}$ cm^3 /mole corresponding to a magnetic moment of 2.16 BM (literature value for $\{[(CF_3)_2C_2S_2]_2Co\}^{2-}$ = 2.06 BM). The composition was also confirmed by analysis.

Anal. Calcd for $C_{24}H_{40}F_{12}N_2S_4Co$: C, 37.3; H, 5.2; N, 3.6; S, 16.6; F, 29.6. Found: C, 38.1; H, 5.0; N, 3.5; S, 16.6; F, 28.8.

A similar reduction of 0.50 g (1.43 mmoles) of the deep green $C_5H_5NiS_2C_2(CF_3)_2$ with 1 ml of hydrazine in 25 ml of methanol gave an immediate yellow-orange solution in an exothermic reaction. Precipitation with 1.0 g (4.76 mmoles) of tetraethylammonium bromide in methanol solution gave yellow crystals. After one recrystallization from a mixture of acetone and ethanol, 0.29 g (53% yield based on available $(CF_3)_2C_2S_2$ groups) of yellow-orange crystalline $[(C_2H_5)_4N]_2\{[(CF_3)_2C_2S_2]_2Ni\}$, mp 267–268° (lit.[6] mp 248–251° dec), was obtained. The product was found to be diamagnetic ($\chi_{\text{mole}}^{23°} = -250 \times 10^{-6}$ cm^3/mole) and to have the correct composition.

Anal. Calcd for $C_{24}H_{40}F_{12}N_2S_4Ni$: C, 37.4; H, 5.2; N, 3.6; S, 16.6; F, 29.6. Found: C, 38.3; H. 4.7; N, 3.4; S, 16.3; F, 28.7.

Isolation of $[(C_2H_5)_4N]\{[(CF_3)_2C_2S_2]_2Fe\}$ from $[C_5H_5Fe(CO)_2]_2$ and Bis(trifluoromethyl)dithietene.—A mixture of 1.5 g (4.24 mmoles) of $[C_5H_5Fe(CO)_2]_2$, 1.0 ml (1.6 g, 7 mmoles) of bis(trifluoromethyl)dithietene, and 50 ml of benzene[24] was exposed to intense ultraviolet irradiation for 40 hr. The resulting mixture was then filtered. The black benzene filtrate contained a complex mixture of paramagnetic species which has not yet been completely separated owing to its instability to sublimation and chromatography.[25]

The black residue was then extracted with 40 ml of dichloromethane in three portions which removed more of the brown-black soluble material. The dichloromethane-insoluble solid was extracted with 100 ml of ethanol in four portions. The filtered ethanol extracts were treated with a filtered solution of 1.5 g (7.14 mmoles) of tetraethylammonium bromide in 50 ml of ethanol. The black mixture was stored at −10° for 2 weeks. The resulting black crystals were filtered and dried to give 0.19 g (8.5% yield) of $[(C_2H_5)_4N]\{[(CF_3)_2C_2S_2]_2Fe\}$.

Anal. Calcd for $C_{16}H_{20}F_{12}NS_4Fe$: C, 30.1; H, 3.1; N, 2.2; S, 20.1; F, 35.7. Found: C, 30.2; H, 2.8; N, 2.1; S, 20.6; F, 34.7.

Preparation of $[CH_3SFe(CO)C_5H_5]_2[SbF_6]$.—A mixture of 0.98 g (2.5 mmoles) of $[CH_3SFe(CO)C_5H_5]_2$,[26] 0.86 g (2.5 mmoles) of silver hexafluoroantimonate(V) (purchased from Ozark-Mahoning Co., Tulsa, Okla.), and 50 ml of CP acetone was stirred for 16 hr at room temperature. The reaction mixture soon became intense blue-green. The gray precipitate of silver metal was then filtered off. Removal of acetone from the filtrate at 25° (25 mm) left dark green crystals. These were washed with dichloromethane and recrystallized once from a mixture of acetone and benzene at room temperature to give 0.745 g (47.5% yield) of blue-green $[CH_3SFe(CO)C_5H_5]_2[SbF_6]$.

Anal. Calcd for $C_{14}H_{16}F_6O_2S_2Fe_2Sb$: C, 26.7; H, 2.5; S, 10.2; F, 18.2; Fe, 17.8. Found: C, 26.9; H, 2.9; S, 10.2; F, 18.4; Fe, 17.6.

Infrared Spectrum.—ν_{CH} band at 3050 (vvw) cm^{-1}; ν_{CO} bands at 1980 (s) and 1945 (m) cm^{-1}; other bands at 1413 (w), 1306 (w), 1010 (vw), 1006 (vw), 1004 (vw), 843 (w), and 832 (w) cm^{-1}.

Ultraviolet and Visible Spectra.—Maxima (mμ) at 330 (ε 9000), 377 (ε 7000) and 607 (ε 3000) in a freshly prepared acetonitrile solution (green).

Magnetic Susceptibility.—$\chi_{\text{mole}}^{23°} = +2030 \times 10^{-6}$ cm^3/mole corresponding to a magnetic moment of 2.3 BM after making the necessary correction of -176×10^{-6} cm^3/mole for the diamagnetism of the ligands and the SbF_6^- anion.

Conductivity.—A molar conductance of 229 ± 11 ohm^{-1} cm^2 mole^{-1} was obtained for acetone solutions in the concentration range 0.0005 to 0.0025 *M*.

Mass Spectra.[27] (A) $[C_5H_5VS_2C_2(CF_3)_2]_2$.—The following ions with *m/e* >360 were observed: $(C_5H_5)_2V_2(C_4F_6S_2)_2^+$ (*m/e* 684, relative intensity 1000), $(C_5H_5)_2V_2(C_4F_6S_2)(C_4F_5S_2)^+$ (*m/e* 665, relative intensity 35), $C_5H_5V(C_4F_6S_2)_2^+$ (*m/e* 568, relative intensity 2), $C_5H_5V(C_4H_5S_2)_2^+$ (*m/e* 530, relative intensity 29), $(C_5H_5)_2V_2S_2(C_4F_6S_2)^+$ (*m/e* 522, relative intensity 17), $C_5H_5V(C_4F_5S_2)(C_4F_4S_2)^+$ (*m/e* 511, relative intensity 12), $C_5H_5V(C_4F_4S_2)_2^+$ (*m/e* 492, relative intensity 15), and $(C_5H_5)_2V_2S_4^+$ (*m/e* 360, relative intensity 100).

(B) $[C_5H_5MoS_2C_2(CF_3)_2]_2$.[28]—The following ions with *m/e* >450 were observed: $(C_5H_5)_2Mo_2(C_4F_6S_2)_2^+$ (*m/e* ~774, relative intensity 137), $(C_5H_5)_2Mo_2(C_4F_6S_2)(C_4F_5S_2)^+$ (*m/e* ~755, relative intensity 11), $(C_5H_5)_2Mo_2S_2(C_4F_6S_2)^+$ (*m/e* ~612, relative intensity 15), $(C_5H_5)_2Mo_2S_2(C_4F_5S_2)^+$ (*m/e* ~593, relative intensity 5), $C_5H_5Mo_2S_2(C_4F_6S_2)^+$ (*m/e* ~547, relative intensity 2), $C_5H_5Mo_2(C_4F_6S_2)^+$ (*m/e* ~483, relative intensity 13), (C_5H_5)-$Mo_2S_4^+$ (*m/e* ~450, relative intensity 285).

(C) $[C_5H_5Mo(NO)S_2C_2(CF_3)_2]_2$.[28]—The following ions with *m/e* >368 were observed: $(C_5H_5)_2Mo_2(C_4F_6S_2)_3^+$ (*m/e* ~1000, relative intensity 53),[29] $(C_5H_5)_2Mo_2(C_4F_6S_2)_2(C_4F_5S_2)^+$ (*m/e* ~981, relative intensity 12),[29] $(C_5H_5)_2Mo_2(C_4F_6S_2)(C_4F_5S_2)_2^+$ (*m/e* ~962, relative intensity ~1),[29] $(C_5H_5)_2Mo_2(NO)_2(C_4F_6S_2)_2^+$ (*m/e* ~834, relative intensity 21), $(C_5H_5)_2Mo_2(NO)(C_4F_6S_2)_2$ (*m/e* ~804, relative intensity 6), $(C_5H_5)_2Mo_2(C_4F_6S_2)_2^+$ (*m/e* ~774, relative intensity 19), $C_5H_5Mo(C_4F_6S_2)_2^+$ (*m/e* ~613, relative intensity 510), $C_5H_5Mo(C_4F_6S_2)(C_4F_5S_2)^+$ (*m/e* ~594, relative intensity 170), $(C_5H_5)_2Mo_2SC_4F_6S_2^+$ (*m/e* ~580, relative intensity 9), $(C_5H_5)_2Mo_2C_4F_6S_2^+$ (*m/e* ~548, relative intensity ~3), $(C_5H_5)_2Mo_2S_5^+$ (*m/e* ~482, relative intensity ~2), $(C_5H_5)_2Mo_2S_4^+$ (*m/e* ~450, relative intensity 30), $C_5H_5Mo(NO)C_4F_6S_2^+$ (*m/e* ~417,

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[24] Hexane was also used as a solvent for this reaction.

[25] The mass spectrum suggests that this solid contains a mixture of $C_5H_5FeS_2C_2(CF_3)_2$ and $[C_5H_5FeCO]_2S_2C_2(CF_3)_2$ (See Discussion section).

[26] R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3600 (1961); R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4**, 482 (1965).

[27] The *m/e* values given for the ions reported correspond to those containing ^{96}Mo, ^{184}W, ^{193}Ir, or ^{58}Ni. The expected multiline patterns were observed for ions containing these metals. Other elements present in the observed ions are either monoisotopic (F, V, Mn, Co, Rh) or have one isotope of over 98% natural abundance (C, H, S, N, O).

[28] This mass spectrum could not be precisely counted in the higher *m/e* regions. The mass numbers of the higher *m/e* ions were estimated by comparison of the spacings of the ions with the spacings of the ions in another mass spectrum which could be counted in the regions of interest. The validity of this comparison was checked by comparing the scan rates of the two spectra being compared in the lower *m/e* regions where both could be counted.

[29] These ions appear to arise from an impurity either present in the original sample or formed during its vaporization into the mass spectrometer. The possibility for selective vaporization of one component over another does not make the mass spectrum a reliable indicator of the composition of the sample.

relative intensity 190), $C_5H_5MoNC_4F_6S_2^+$ (m/e $\sim$401, relative intensity 60), $C_5H_5MoC_4F_6S_2^+$ (m/e $\sim$387, relative intensity 370), and $C_5H_5MoC_4F_5S_2^+$ (m/e $\sim$368, relative intensity 125).

(**D**) **$[C_5H_5W(CO)S_2C_2(CF_3)_2]_2$**.—The following ions with m/e >440 were observed: $(C_5H_5)_2W_2S_2(C_4F_6S_2)_2^+$ (m/e $\sim$1014, relative intensity 8),[29] $(C_5H_5)_2W_2(CO)_2(C_4F_6S_2)_2^+$ (m/e 1006, relative intensity 15), $(C_5H_5)_2W_2S_2(C_4F_6S_2)(C_4F_5S_2)^+$ (m/e $\sim$995, relative intensity 4),[29] $(C_5H_5)_2W_2(CO)(C_4F_6S_2)_2^+$ (m/e $\sim$978, relative intensity 2.5), $(C_5H_5)_2W_2(C_4F_6S_2)_2^+$ (m/e $\sim$950, relative intensity 22), $(C_5H_5)_2W_2(C_4F_6S_2)(C_4F_5S_2)^+$ (m/e $\sim$931, relative intensity 4), $(C_5H_5)_2W_2S_2O_2C_4F_6S_2^+$ or $(C_5H_5)_2W_2S_3C_4F_6S_2^+$ (m/e $\sim$820, relative intensity 22), $(C_5H_5)_2W_2S_2OC_4F_6S_2^+$ (m/e $\sim$804, relative intensity 14), $(C_5H_5)_2W_2S_2C_4F_6S_2^+$ (m/e $\sim$788, relative intensity 19), $(C_5H_5)_2W_2SC_4F_6S_2^+$ (m/e $\sim$756, relative intensity 6), $(C_5H_5)_2W_2OC_4F_6S_2^+$ (m/e 740, relative intensity 2), $C_5H_5W(C_4F_6S_2)_2^+$ (m/e 701, relative intensity 33), $C_5H_5W(C_4F_6S_2)(C_4F_5S_2)^+$ (m/e $\sim$682, relative intensity 78), $(C_5H_5)_2W_2S_5^+$ (m/e $\sim$658, relative intensity 13), $(C_5H_5)_2W_2S_4^+$ (m/e $\sim$626, relative intensity 64), $(C_5H_5)_2W_2S_3^+$ (m/e 594, relative intensity 50), $(C_5H_5)_2W_2S_2O^+$ (m/e $\sim$578, relative intensity 50), $C_5H_5WS_2C_4F_6S_2^+$ (m/e $\sim$539, relative intensity 56), $C_5H_5WSC_4F_6S_2^+$ (m/e $\sim$507, relative intensity 320), $C_5H_5WFC_4F_6S_2^+$ (m/e $\sim$494, relative intensity 150), $C_5H_5WC_4F_6S_2^+$ (m/e $\sim$475, relative intensity 19), and $WSC_4F_6S_2^+$ (m/e $\sim$442, relative intensity 32).

(**E**) **$C_5H_5W[S_2C_2(CF_3)_2]_2$**.—The following ions at m/e >440 were observed:[30] $C_5H_5W(C_4F_6S_2)_2^+$ (m/e $\sim$701, relative intensity $\sim$750), $C_5H_5W(C_4F_6S_2)(C_4F_5S_2)^+$ (m/e $\sim$682, relative intensity 148), $C_5H_5WS_2C_4F_6S_2^+$ (m/e $\sim$539, relative intensity 67), $C_5H_5WSC_4F_6S_2^+$ (m/e $\sim$507, relative intensity 46), $C_5H_5WFC_4F_6S_2^+$ (m/e $\sim$494, relative intensity 190), $C_5H_5WC_4F_6S_2^+$ (m/e $\sim$475 relative intensity 15), $WSFC_4F_6S_2^+$ (m/e $\sim$461, relative intensity 28), and $WSC_4F_6S_2^+$ (m/e $\sim$442, relative intensity 14).

(**F**) **$C_5H_5Mn(NO)S_2C_2(CF_3)_2$**.—The following ions at m/e >188 were observed: $(C_5H_5)_2Mn_2S_2C_4F_6S_2^+$ (m/e 530, relative intensity 6),[29] $C_5H_5Mn(NO)(C_4F_6S_2)^+$ (m/e 376, relative intensity 15), $C_5H_5MnC_4F_6S_2^+$ (m/e 346, relative intensity 34), $C_5H_5MnC_4F_5S_2^+$ (m/e 327, relative intensity 6), $C_4F_6S_2^+$ (m/e 226, relative intensity 74), $C_4F_5S_2^+$ (m/e 207, relative intensity 55), and $C_4F_4S_2^+$ (m/e 188, relative intensity 35).

(**G**) **$C_5H_5CoS_2C_2(CF_3)_2$**.—The following ions at m/e >120 were observed: $C_5H_5CoC_4F_6S_2^+$ (m/e 350, relative intensity 105), $C_5H_5CoC_4F_5S_2^+$ (m/e 331, relative intensity 19), $C_5H_5CoC_2F_3S^+$ (m/e 237, relative intensity 3), $C_4F_5S_2^+$ (m/e 207, relative intensity 32), $C_5H_5CoS_2^+$ and/or $C_4F_4S_2^+$ (m/e 188, relative intensity 160), $C_4F_6^+$ (m/e 162, relative intensity 19), $C_4F_5^+$ (m/e 145, relative intensity 52), and $C_5H_5Co^+$ (m/e 124, relative intensity 89).

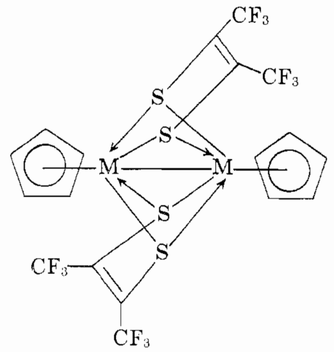
(**H**) **$C_5H_5RhS_2C_2(CF_3)_2$**.—The following ions at m/e >165 were observed: $C_5H_5RhC_4F_6S_2^+$ (m/e 394, relative intensity 350), $C_5H_5RhC_4F_5S_2^+$ (m/e 375, relative intensity 42), $C_5H_5RhS_2^+$ (m/e 232, relative intensity 490), and $C_5H_5Rh^+$ (m/e 168, relative intensity 220).

(**I**) **$C_5H_5IrS_2C_2(CF_3)_2$**.—The following ions at m/e >320 were observed: $C_5H_5IrC_4F_6S_2^+$ (m/e 484, relative intensity 250), $C_5H_5IrC_4F_5S_2^+$ (m/e 465, relative intensity 38), $C_5H_5IrC_3F_3S_2^+$ (m/e 415, relative intensity 4), $C_5H_5IrC_3F_3S^+$ (m/e 383, relative intensity 0.7), $C_5H_5IrC_2F_3S^+$ (m/e 371, relative intensity 8), and $C_5H_5IrS_2^+$ (m/e 322, relative intensity 290).

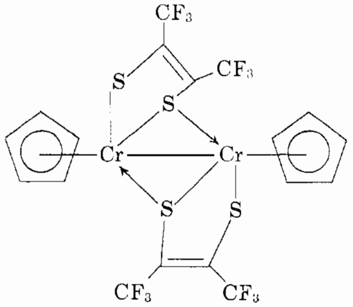
(**J**) **$C_5H_5NiS_2C_2(CF_3)_2$**.—The following ions at m/e >120 were observed: $C_5H_5NiC_4F_6S_2^+$ (m/e 349, relative intensity 71), $C_5H_5NiC_4F_5S_2^+$ (m/e 330, relative intensity 9), $C_4F_6S_2^+$ (m/e 226, relative intensity 12), $C_4F_5S_2^+$ (m/e 207, relative intensity 37), $C_4F_4S_2^+$ (m/e 188, relative intensity 9), $C_5H_5NiS_2^+$ (m/e 187, relative intensity 13), $C_4F_6^+$ (m/e 162, relative intensity 47), $C_4F_5^+$ (m/e 143, relative intensity 79), and $C_5H_5Ni^+$ (m/e 123, relative intensity 107).

Discussion

(A) Molybdenum and Tungsten Compounds.—Chromium and molybdenum compounds of the types $[C_5H_5MS_2C_2(CF_3)_2]_2$ (M = Cr or Mo) have been obtained from bis(trifluoromethyl)dithietene and $[C_5H_5Cr(CO)_3]_2Hg$ or $[C_5H_5Mo(CO)_3]_2$, respectively.[4] Structures with four bridging sulfur atoms (II) were originally proposed for these compounds.[4] Subsequent structural studies by X-ray diffraction have confirmed[31] structure II (M = Mo) with four sulfur bridges for the molybdenum compound $[C_5H_5MoS_2C_2(CF_3)_2]_2$, but have shown the chromium compound $[C_5H_5CrS_2C_2(CF_3)_2]_2$ to have a different structure (III) with only two sulfur bridges.[31]



II



III

The reaction between bis(trifluoromethyl)dithietene and $C_5H_5W(CO)_3H$ was investigated in an attempt to prepare an analogous tungsten compound, $[C_5H_5WS_2C_2(CF_3)_2]_2$. A diamagnetic brown air-stable solid was obtained with approximately this composition. However, this solid appears to be the dicarbonyl $[C_5H_5W(CO)S_2C_2(CF_3)_2]_2$ for the following reasons: (1) the presence of carbonyl stretching frequencies at 2048, 2011, and 1983 cm^{-1} and (2) the observation of ions in the mass spectrum corresponding to $(C_5H_5)_2W_2(CO)_2(C_4F_6S_2)_2^+$ and $(C_5H_5)_2W_2(CO)(C_4F_6S_2)_2^+$.

A possible structure for $[C_5H_5W(CO)S_2C_2(CF_3)_2]_2$ is IV. This structure is closely related to that for $[C_5H_5CrS_2C_2(CF_3)_2]_2$ (III). However, in structure IV each tungsten atom has the rare gas electronic configuration and is bonded to four atoms (one carbonyl carbon and three sulfur atoms) besides the π-cyclopentadienyl ring and the other tungsten atom. This differs from structure III, where each chromium atom has two electrons less than the rare gas configuration and is

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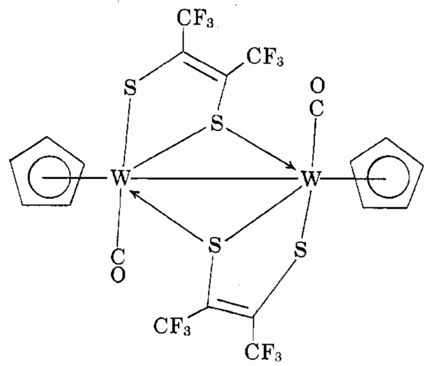
[30] The sample of $C_5H_5W[S_2C_2(CF_3)_2]_2$ also contained a small quantity of $[C_5H_5W(CO)S_2C_2(CF_3)_2]_2$. The known spectrum of the latter material was subtracted from the observed spectrum before reporting it here.

[31] H. W. Baird, private communication. These results were also presented publicly by Professor L. F. Dahl at several meetings.



IV

bonded to only the three sulfur atoms besides the π-cyclopentadienyl ring and the other chromium atom. This difference between the products $[C_5H_5CrS_2C_2(CF_3)_2]_2$ (III) and $[C_5H_5W(CO)S_2C_2(CF_3)_2]_2$ (IV) is consistent with the tendency for tungsten to form stronger metal–carbon bonds and to exhibit a higher coordination number.

Subsequent to the initial work[4] with cyclopentadienylmetal carbonyl derivatives and bis(trifluoromethyl)dithietene, Davison, Edelstein, Holm, and Maki[3] discovered that neutral complexes such as those obtained from certain metal carbonyls and bis(trifluoromethyl)dithietene could be reduced to anions. A frequently useful reducing agent was hydrazine in alcoholic solution. In an attempt to obtain anions containing both π-cyclopentadienyl and bis(trifluoromethyl)ethylene dithiolate ligands, the reduction of most available neutral compounds with ethanolic hydrazine was investigated. As expected from their strong colors, complexes containing the bis(trifluoromethyl)ethylene dithiolate ligands generally have characteristic electronic spectra[32] which vary significantly with the ionic charge and electronic configuration. Thus the course of reduction of neutral bis(trifluoromethyl)ethylene dithiolate complexes could be examined conveniently and unequivocally by a comparison of their ultraviolet and visible spectra in an ethanol solution containing hydrazine with their spectra in a pure dichloromethane solution. Most of the new compounds were examined in this manner.

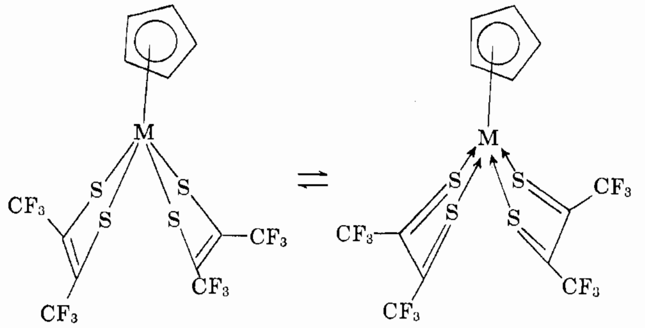
Using this technique the tungsten compound $[C_5H_5W(CO)S_2C_2(CF_3)_2]_2$ was found to give identical ultraviolet and visible spectra in ethanolic hydrazine as in dichloromethane. It thus appears that $[C_5H_5W(CO)S_2C_2(CF_3)_2]_2$ is not readily reduced to an anion.

One sample of $[C_5H_5W(CO)S_2C_2(CF_3)_2]_2$ exhibited the ions $(C_5H_5)_2W_2S_2(C_4F_6S_2)_2^+$ and $(C_5H_5)_3W_2S_2(C_4F_6S_2)(C_4F_6S_2)^+$ in the mass spectrum.[33] It is difficult to understand how these ions could arise from $[C_5H_5W(CO)S_2C_2(CF_3)_2]_2$ by a simple ionization and fragmentation process. A more likely possibility is that a second product in the reaction between $C_5H_5W(CO)_3H$ and bis(trifluoromethyl)dithietene is $[C_5H_5W(S)S_2C_2(CF_3)_2]_2$, which cannot be efficiently removed from $[C_5H_5W(CO)S_2C_2(CF_3)_2]_2$. The presence of some $[C_5H_5W(S)S_2C_2(CF_3)_2]_2$ in the $[C_5H_5W(CO)S_2C_2(CF_3)_2]_2$ may account for the tendency toward high sulfur analyses.

The reaction between $C_5H_5W(CO)_3H$ and bis(trifluoromethyl)dithietene was also found to give a green product which could be separated from brown $[C_5H_5W(CO)S_2C_2(CF_3)_2]_2$ by the solubility of the green compound in warm hexane. The same green compound was obtained in much better yield from $C_5H_5W(CO)_2NO$ and bis(trifluoromethyl)dithietene in boiling methylcyclohexane. This green compound was volatile and could be purified efficiently by vacuum sublimation. It gave intense green solutions in both nonpolar and polar organic solvents.

Analyses of this green material indicated the composition $C_5H_5W[S_2C_2(CF_3)_2]_2$. The mass spectrum exhibited a parent ion at about *m/e* 700, indicating the monomeric formula. In accord with its expected one unpaired electron, $C_5H_5W[S_2C_2(CF_3)_2]_2$ was found to be paramagnetic with a moment of 1.68 BM. The structure of $C_5H_5W[S_2C_2(CF_3)_2]_2$ may be represented as a resonance hybrid between the extreme structures Va and Vb (M = W).

Treatment of $C_5H_5W[S_2C_2(CF_3)_2]_2$ with hydrazine in alcohol solution gave a red-violet solution from which deep red-violet diamagnetic $[(C_2H_5)_4N]\{C_5H_5W[S_2C_2(CF_3)_2]_2\}$ could be obtained after addition of tetraethylammonium bromide. The proton nmr spectrum showed the presence of both a π-cyclopentadienyl ring and a tetraethylammonium group in the expected 1:1 ratio, confirming the elemental analyses. The $\{C_5H_5W[S_2C_2(CF_3)_2]_2\}^-$ anion appears to be entirely analogous to the likewise red-violet $\{C_5H_5W[S_2C_2(CN)_2]_2\}^-$ anion recently obtained by Locke andMcCleverty[34] from $C_5H_5W(CO)_3Cl$ and sodium maleonitrile dithiolate. Although the yield of solid $[(C_2H_5)_4N]\{C_5H_5W[S_2C_2(CF_3)_2]_2\}$ from $C_5H_5W[S_2C_2(CF_3)_2]_2$ was only 34%, the intensities of the ultraviolet and visible spectral bands in the solution obtained from $C_5H_5W[S_2C_2(CF_3)_2]_2$ and hydrazine in ethanol indicated the yield in the reduction step to be ~98%. Thus the losses in the preparation of $[(C_2H_5)_4N]\{C_5H_5W[S_2C_2(CF_3)_2]_2\}$ occur during the isolation of the salt rather than during the reduction.



Va Vb

In an attempt to prepare $C_5H_5Mo[S_2C_2(CF_3)_2]_2$, the molybdenum analog of V (M = W), the reaction

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[32] For the electronic spectra of some related metal dithiolate complexes see E. I. Stiefel, R. Eisenberg, R. C. Rosenberg, and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 2956 (1966).

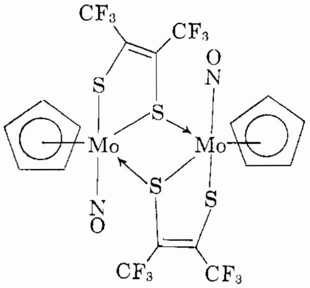
[33] The assignment of these ions to an impurity is also supported by observation of a mass spectrum of $[C_5H_5W(CO)S_2C_2(CF_3)_2]_2$ with these ions absent.

[34] J. Locke and J. A. McCleverty, *Inorg. Chem.*, **5**, 1157 (1966).

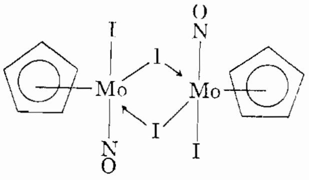
between $C_5H_5Mo(CO)_2NO$ and bis(trifluoromethyl)dithietene was investigated. The major product of this reaction was $[C_5H_5Mo(NO)S_2C_2(CF_3)_2]_2$, a brown-black sublimable solid characterized by elemental analyses, a strong metal nitrosyl stretching frequency at 1661 cm^{-1} in the infrared spectrum, and a parent ion $(C_5H_5)_2Mo_2(NO)_2(C_4F_6S_2)_2^+$ undergoing successive losses of the two nitrosyl groups in the mass spectrum.

A possible structure for $[C_5H_5Mo(NO)S_2C_2(CF_3)_2]_2$ is VI with two bridging sulfur atoms and terminal nitrosyl groups. This structure is closely related to the structure VII proposed[35] for $[C_5H_5Mo(NO)I_2]_2$, which is obtained by treatment of $C_5H_5Mo(CO)_2NO$ with iodine, an oxidizing agent like bis(trifluoromethyl)dithietene. In structure VI for $[C_5H_5Mo(NO)S_2C_2(CF_3)_2]_2$ one chelating $(CF_3)_2C_2S_2$ ligand replaces two iodide atoms in structure VII for $[C_5H_5Mo(NO)I_2]_2$. The position of the metal nitrosyl stretching frequency (1661 cm^{-1}) in $[C_5H_5Mo(NO)S_2C_2(CF_3)_2]_2$ is close to that found in $[C_5H_5Mo(NO)I_2]_2$ (1670 cm^{-1}) and also within the range (1660–1680 cm^{-1}) found for the related $C_5H_5Mo(NO)I_2L$ ($L = (C_6H_5)_3P$, C_5H_5N, or $(C_6H_5O)_3P$) compounds.[35]

Furthermore structure VI for $[C_5H_5Mo(NO)S_2C_2(CF_3)_2]_2$ is related to the structure IV proposed for $[C_5H_5W(CO)S_2C_2(CF_3)_2]_2$ by interchanging nitrosyl groups for carbonyl groups. Because a nitrosyl group donates three electrons whereas a carbonyl group donates only two electrons, a metal–metal bond is not needed in $[C_5H_5Mo(NO)S_2C_2(CF_3)_2]_2$ (VI) as it is in $[C_5H_5W(CO)S_2C_2(CF_3)_2]_2$ (IV) to give the metal atom the favored rare gas configuration.



VI

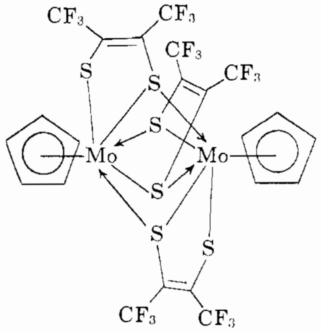


VII

Solutions of $[C_5H_5Mo(NO)S_2C_2(CF_3)_2]_2$ in organic solvents are brown. However, a solution of $[C_5H_5Mo(NO)S_2C_2(CF_3)_2]_2$ in ethanolic hydrazine is intense blue, suggesting reduction to an anion. The ultraviolet and visible spectra of this blue solution exhibited maxima at 306 and 584 mμ. This spectrum differs markedly from the spectrum of the likewise intense blue solution of $Mo[S_2C_2(CF_3)_2]_3$ in ethanolic hydrazine which exhibits maxima at 340 and 628 mμ. The blue anion formed upon reduction of $[C_5H_5Mo(NO)S_2C_2(CF_3)_2]_2$ thus does not appear to be $\{Mo[S_2C_2(CF_3)_2]_3\}^{2-}$ which could be formed in a disproportionation reaction. This blue anion could possibly be $\{C_5H_5Mo[S_2C_2(CF_3)_2]_2\}^-$, analogous to the red-violet anion $C_5H_5W[S_2C_2(CF_3)_2]_2^-$ described above. A related blue anion $\{C_5H_5Mo[S_2C_2(CN)_2]_2\}^-$ was reported by Locke and McCleverty.[34] More definite suggestions regard- the nature of this blue reduction product of $[C_5H_5Mo(NO)S_2C_2(CF_3)_2]_2$ will be deferred until more experimental data become available.

A characteristic feature of the mass spectrum of $[C_5H_5Mo(NO)S_2C_2(CF_3)_2]_2$ is the presence of the ions $C_5H_5Mo(C_4F_6S_2)_2^+$ and $C_5H_5Mo(C_4F_6S_2)(C_4F_5S_2)^+$ in large abundances. These ions can arise from a species $C_5H_5Mo[S_2C_2(CF_3)_2]_2$ (V, M = Mo) either present in the original $[C_5H_5Mo(NO)S_2C_2(CF_3)_2]_2$ or produced during its vaporization into the mass spectrometer. This compound would be analogous to the compound $C_5H_5W[S_2C_2(CF_3)_2]_2$ (V, M = W) described above. However, the ions $C_5H_5Mo(C_4F_6S_2)_2^+$ and $C_5H_5Mo(C_4F_6S_2)(C_4F_5S_2)^+$ can also arise from fragmentation of the ions from $[C_5H_5Mo(NO)S_2C_2(CF_3)_2]_2$.

Other ions of interest in the mass spectrum of $[C_5H_5Mo(NO)S_2C_2(CF_3)_2]_2$ are $(C_5H_5)_2Mo_2(C_4F_6S_2)_3^+$ and its fragmentation products $(C_5H_5)_2Mo_2(C_4F_6S_2)_2(C_4F_5S_2)^+$ and $(C_5H_5)_2Mo_2(C_4F_6S_2)(C_4F_5S_2)_2^+$ formed by two successive losses of fluorine (mass differences of 19). Since these ions occur at higher m/e than even the parent ion from $[C_5H_5Mo(NO)S_2C_2(CF_3)_2]_2$, these ions must arise from a separate species, probably $(C_5H_5)_2Mo_2[S_2C_2(CF_3)_2]_3$, either present as an impurity in the $[C_5H_5Mo(NO)S_2C_2(CF_3)_2]_2$ or produced during its vaporization. A possible structure for $(C_5H_5)_2Mo_2[S_2C_2(CF_3)_2]_3$ is VIII.



VIII

The green paramagnetic compound $C_5H_5W[S_2C_2(CF_3)_2]_2$ is closely related to the green paramagnetic compound $C_5H_5NiS_2C_2(CF_3)_2$. The immediate predecessor of nickel in the periodic table, cobalt, forms a very stable red-purple diamagnetic compound $C_5H_5CoS_2C_2(CF_3)_2$. This reasoning by analogy suggests that tantalum would form a very stable diamagnetic complex $C_5H_5Ta[S_2C_2(CF_3)_2]_2$, which probably could be prepared from cyclopentadienyltetracarbonyltantalum,[36] $C_5H_5Ta(CO)_4$, and bis(trifluoromethyl)dithietene. Difficulties in obtaining $C_5H_5Ta(CO)_4$ are presently preventing the study of this reaction.

The reaction between bis(trifluoromethyl)dithietene and $C_5H_5V(CO)_4$ has been reported to give green $[C_5H_5VS_2C_2(CF_3)_2]_2$. The mass spectrum of a sample of this material (5 years old) exhibited not only the expected ions arising from $[C_5H_5VS_2C_2(CF_3)_2]_2$ but also the ions

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(35) R. B. King, *Inorg. Chem.*, **6**, 30 (1967).

(36) R. P. M. Werner, A. H. Filbey, and S. A. Manastyrskyj, *ibid.*, **3**, 298 (1964).

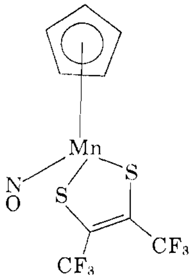
$C_5H_5V(C_4F_6S_2)_2^+$ and $C_5H_5V(C_4F_5S_2)_2^+$, which could arise from some $C_5H_5V[S_2C_2(CF_3)_2]_2$ either present as an impurity in the $[C_5H_5VS_2C_2(CF_3)_2]_2$ or produced during its vaporization.

(B) **Manganese Compounds.**—No compound of the type $[C_5H_5MnS_2C_2(CF_3)_2]_2$ is known. Attempts to prepare such a compound by subjecting mixtures of $C_5H_5Mn(CO)_3$ and bis(trifluoromethyl)dithietene to heat or ultraviolet irradiation have always failed due to the relative inertness of $C_5H_5Mn(CO)_3$ as compared with the cyclopentadienyl metal carbonyls (*e.g.*, $C_5H_5V(CO)_4$, $[C_5H_5Mo(CO)_3]_2$, $C_5H_5Co(CO)_2$, and $[C_5H_5NiCO]_2$) which do form $[C_5H_5MS_2C_2(CF_3)_2]_n$ derivatives with bis(trifluoromethyl)dithietene.[4]

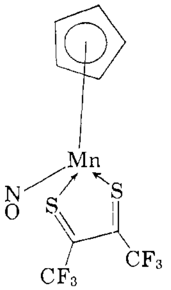
A search for a more reactive cyclopentadienyl derivative of manganese to react with bis(trifluoromethyl)dithietene led to an investigation of the reaction between $[C_5H_5MnCONO]_2$[13] and bis(trifluoromethyl)dithietene. Ultraviolet irradiation of these two materials in hexane solution gave a brown solid from which brown volatile $C_5H_5Mn(NO)S_2C_2(CF_3)_2$ could be isolated by crystallization followed by vacuum sublimation.

The monomeric nature of $C_5H_5Mn(NO)S_2C_2(CF_3)_2$ is confirmed by its mass spectrum, which exhibits a parent ion at *m/e* 376. In accord with its expected unpaired electron, $C_5H_5Mn(NO)S_2C_2(CF_3)_2$ is paramagnetic with a moment of 1.73 BM. The single nitrosyl group in $C_5H_5Mn(NO)S_2C_2(CF_3)_2$ exhibits a sharp stretching frequency at 1797 cm^{-1} in the infrared spectrum.

All of these data suggest $C_5H_5Mn(NO)S_2C_2(CF_3)_2$ to be a resonance hybrid of the extreme structures IXa and IXb. It is related to the likewise monomeric and paramagnetic derivatives $C_5H_5NiS_2C_2(CF_3)_2$ and $C_5H_5W[S_2C_2(CF_3)_2]_2$. However, the manganese compound is brown whereas the nickel and tungsten compounds are intense green.



IXa



IXb

Treatment of brown $C_5H_5MnNOS_2C_2(CF_3)_2$ with ethanolic hydrazine results gradually in the formation of a green solution exhibiting maxima at 316 and 720 mμ in the ultraviolet and visible spectra. Treatment of this solution with tetraethylammonium bromide followed by prolonged cooling at −15° results in the slow deposition of green crystals with the same electronic spectrum. Analyses indicate this green material to be the tetraethylammonium salt $[(C_2H_5)_4N]_2\{[(CF_3)_2C_2S_2]_2Mn(NO)\}$. The presence of the nitrosyl group is confirmed by the presence of a strong nitrosyl stretching frequency at 1660 cm^{-1}.

The $\{[(CF_3)_2C_2S_2]_2Mn(NO)\}^{2-}$ anion appears to be closely related to the nonionic dialkyldithiocarbamate complexes of the type $(R_2NCS_2)_2M(NO)$ (M = V,[37] Fe,[38] or Co[39]). All of these compounds appear to be five-coordinate derivatives with square-pyramidal coordination.[40,41]

Magnetic susceptibility measurements indicate the tetraethylammonium salt of the $\{[(CF_3)_2C_2S_2]_2Mn(NO)\}^{2-}$ anion to be paramagnetic with a magnetic moment of 1.30 BM. This is intermediate between the expected diamagnetism for a structure with no unpaired electrons (singlet state) and the expected magnetic moment of 2.83 BM for a structure with two unpaired electrons (triplet state). Further magnetic studies are needed to establish whether this anion represents an example of an equilibrium between a singlet and a triplet state. No direct comparison is possible between the $\{[(CF_3)_2C_2S_2]_2Mn(NO)\}^{2-}$ anion and the bis(dialkyldithiocarbamate)metal nitrosyls cited above, since none of the latter compounds contains manganese.

(C) **Iron and Ruthenium Compounds.**—The reactions between bis(trifluoromethyl)dithietene and the cyclopentadienylmetal carbonyls $[C_5H_5M(CO)_2]_2$ (M = Fe or Ru) are considerably more complex. Brown to black nonvolatile paramagnetic materials are obtained. The compositions of these materials approximate $C_5H_5M[S_2C_2(CF_3)_2]S_x$, but the presence of metal carbonyl stretching frequencies indicates carbonyl groups also to be present. The mass spectrum of the iron compound exhibits ions at *m/e* 347 and 328 due to $C_5H_5FeC_4F_6S_2^+$ and its expected degradation product $C_5H_5FeC_4F_5S_2^+$, respectively. Also present in the mass spectrum of the product from the reaction between $[C_5H_5Fe(CO)_2]_2$ and bis(trifluoromethyl)dithietene are ions at *m/e* 524, 496, 468, and 449 due to $(C_5H_5)_2Fe_2(CO)_2(C_4F_6S_2)^+$ and its expected degradation products $(C_5H_5)_2Fe_2(CO)(C_4F_6S_2)^+$, $(C_5H_5)_2Fe_2(C_4F_6S_2)^+$, and $(C_5H_5)_2Fe_2(C_4F_5S_2)^+$, respectively. The product from this reaction is thus probably a mixture of $C_5H_5FeS_2C_2(CF_3)_2$ and $[C_5H_5FeCO]_2S_2C_2(CF_3)_2$.

The mass spectrum of the brown product obtained from $[C_5H_5Ru(CO)_2]_2$ and bis(trifluoromethyl)dithietene is likewise complex. The ions observed are consistent with a ternary mixture of $[C_5H_5Ru]_2(CO)S_2C_2(CF_3)_2$, $[C_5H_5Ru]_3(S)_2S_2C_2(CF_3)_2$, and the ionic $[(C_5H_5)_2Ru]\{[(CF_3)_2C_2S_2]_3Ru\}$.

Difficulties in separating these complex mixtures obtained from the reactions between bis(trifluoromethyl)dithietene and the carbonyls $[C_5H_5M(CO)_2]_2$ (M = Fe or Ru) have prevented separation and characterization of the components suggested to be present.

Reference has been made both in this paper and other papers[3] to the *reduction* of neutral organosulfur deriva-

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(37) L. Malatesta, *Gazz. Chim. Ital.*, **71**, 615 (1941).

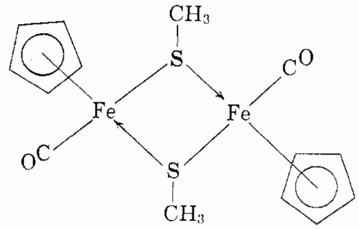
(38) L. Cambi and A. Cagnasso, *Atti Accad. Nazl. Lincei*, **13**, 254 (1931); **13**, 809 (1931).

(39) L. Cambi and A. Cagnasso, *ibid.*, **13**, 404 (1931).

(40) The square-pyramidal coordination of $[(CH_3)_2NCS_2]_2Co(NO)$ has been confirmed by X-ray crystallography.[41]

(41) P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *J. Chem. Soc.*, 668 (1962).

tives to anions. The brown iron complex $[CH_3SFeCOC_5H_5]_2$ (X) obtained from $[C_5H_5Fe(CO)_2]_2$ and dimethyl disulfide[26] undergoes *oxidation* to the intense blue-green paramagnetic $[CH_3SFeCOC_5H_5]_2^+$ cation. This oxidation, first achieved electrochemically,[42] has now been accomplished chemically with silver hexafluoroantimonate according to the equation



X

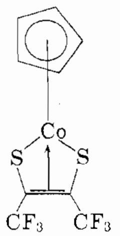
$$[CH_3SFeCOC_5H_5]_2 + AgSbF_6 \longrightarrow Ag + [CH_3SFeCOC_5H_5]_2[SbF_6]$$

The silver hexafluoroantimonate functions not only as an oxidizing agent but also as a source of the hexafluoroantimonate anion required for formation of a stable salt of the $[CH_3SFeCOC_5H_5]_2^+$ cation. A related blue-green salt, undoubtedly $[CH_3SFeCOC_5H_5]_2[PF_6]$, may be obtained from $[CH_3SFeCOC_5H_5]_2$ and silver hexafluorophosphate, but this hexafluorophosphate decomposes during attempted isolation and purification. The greater stability of SbF_6^- salts relative to analogous PF_6^- salts was noted with some studies of these salts of the dioxygenium (O_2^+) cation.[43]

Neutral $[CH_3SFeCOC_5H_5]_2$ exhibits a single metal carbonyl stretching frequency at 1930 cm^{-1} (KBr pellet). In the cation $[CH_3SFeCOC_5H_5]_2^+$ this frequency is raised to 1980 cm^{-1}. This is consistent with the positive charge of the cation[44] reducing the electronic density on the iron atoms which thus decreases the partial $p\pi$–$d\pi$ bonding with the metal carbonyl groups. This increases the carbon–oxygen bond order which thus increases its stretching frequency.

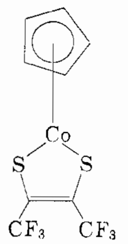
(D) Cobalt, Rhodium, and Iridium Compounds.—The cobalt compound $C_5H_5CoS_2C_2(CF_3)_2$ has been obtained from $C_5H_5Co(CO)_2$ and bis(trifluoromethyl)dithietene in boiling methylcyclohexane.[4] This reaction has been found to proceed readily under much milder conditions, *i.e.*, $C_5H_5Co(CO)_2$ and bis(trifluoromethyl)dithietene in hexane at room temperature. Furthermore, $C_5H_5CoC_8H_{12}$ rather than $C_5H_5Co(CO)_2$ can be used as a starting material for the preparation of $C_5H_5CoS_2C_2(CF_3)_2$. Thus, bis(trifluoromethyl)dithietene can remove olefinic as well as carbonyl ligands to give $(CF_3)_2C_2S_2$ complexes.

A previous paper[4] postulated structure XI (M = Co) for $C_5H_5CoS_2C_2(CF_3)_2$. The characteristic feature of this structure is a π bond between the double bond of the $(CF_3)_2C_2S_2$ ligand and the cobalt atom.

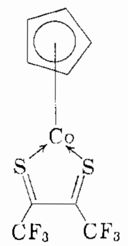


XI

In an attempt to obtain further evidence for this unusual structure XI (M = Co), certain reactions of $C_5H_5CoS_2C_2(CF_3)_2$ were investigated hoping to find a way to break the π bond between the carbon–carbon double bond and the cobalt atom without totally destroying the $C_5H_5CoS_2C_2(CF_3)_2$ system. In particular, Lewis bases such as pyridine and triphenylphosphine might react with $C_5H_5CoS_2C_2(CF_3)_2$ to give $C_5H_5Co(L)S_2C_2(CF_3)_2$ (L = the Lewis base). However, $C_5H_5CoS_2C_2(CF_3)_2$ appeared to be inert to pyridine and triphenylphosphine even on heating. This raises doubt regarding structure XI (M = Co) for $C_5H_5CoS_2C_2(CF_3)_2$, especially since another alternative, the resonance hybrid between the extremes XIIa and XIIb (M = Co), is a likely possibility.[44a]



XIIa



XIIb

The unusual nature of $C_5H_5CoS_2C_2(CF_3)_2$ prompted attempts to prepare the analogous rhodium and iridium compounds. The red rhodium compound $C_5F_5RhS_2C_2(CF_3)_2$ was readily obtained from $C_5H_5Rh(CO)_2$ and bis(trifluoromethyl)dithietene. Like its cobalt analog it was volatile and stable to air oxidation. The single sharp CF_3 resonance in the ^{19}F nmr spectrum of $C_5H_5RhS_2C_2(CF_3)_2$ confirms its diamagnetism.

Since the synthesis[45] of $C_5H_5Ir(CO)_2$ requires the difficultly accessible $Ir(CO)_3Cl$, the more readily available 1,5-cyclooctadiene complex[18] $C_5H_5IrC_8H_{12}$ was used for the synthesis of $C_5H_5IrS_2C_2(CF_3)_2$. The iridium compound $C_5H_5IrS_2C_2(CF_3)_2$ was volatile, diamagnetic, and air stable like its cobalt and rhodium analogs. The red color of $C_5H_5IrS_2C_2(CF_3)_2$ appeared to be appreciably less intense than that of its rhodium analog.

The reduction of these three complexes $C_5H_5MS_2C_2(CF_3)_2$ (M = Co, Rh, or Ir) and of the related nickel complex[4] $C_5H_5NiS_2C_2(CF_3)_2$ was investigated using hydrazine in ethanol solution. The cobalt compound $C_5H_5CoS_2C_2(CF_3)_2$ was found to give the pink $\{[(CF_3)_2C_2S_2]_2Co\}^{2-}$ anion previously obtained[3] from the

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[42] R. E. Dessy, F. E. Stary, R. B. King, and M. E. Waldrup, *J. Am. Chem. Soc.*, **88**, 471 (1966).

[43] I. J. Solomon, R. I. Brabets, R. K. Uenishi, J. N. Keith, and J. M. McDonough, *Inorg. Chem.*, **3**, 457 (1964).

[44] This positive charge is presumably delocalized over the two iron atoms and the two sulfur atoms.

[44a] Note Added in Proof.—A recently reported X-ray crystal structure determination of $C_5H_5CoS_2C_2(CF_3)_2$ supports the dithioketone structure XIIb for this complex: H. W. Baird and B. M. White, *J. Am. Chem. Soc.*, **88**, 4744 (1966).

[45] E. O. Fischer and K. S. Brenner, *Z. Naturforsch.*, **17b**, 774 (1962).

TABLE I

SOME FRAGMENTATION PROCESSES WHICH GIVE C_4F_6 FRAGMENTS IN THE MASS SPECTRA OF BIS(TRIFLUOROMETHYL)ETHYLENE DITHIOLATE COMPLEXES

Compound	Process			*m/e* parent	*m/e* daughter	Metastable ion Calcd	Metastable ion Found
(1) $[C_5H_5MoS_2C_2(CF_3)_2]_2$	$(C_5H_5)_2Mo_2(C_4F_6S_2)_2^+$	$\xrightarrow{-C_4F_6}$	$(C_5H_5)_2Mo_2S_2C_4F_6S_2^+$	774	612	484	484
	$(C_5H_5)_2Mo_2S_2C_4F_6S_2^+$	$\xrightarrow{-C_4F_6}$	$(C_5H_5)_2Mo_2S_4^+$	612	450	330.5	331
(2) $C_5H_5W[S_2C_2(CF_3)_2]_2$	$C_5H_5W(C_4F_6S_2)_2^+$	$\xrightarrow{-C_4F_6}$	$C_5H_5WS_2C_4F_6S_2^+$	701	539	414	414
(3) $C_5H_5CoS_2C_2(CF_3)_2$	$C_5H_5CoC_4F_6S_2^+$	$\xrightarrow{-C_4F_6}$	$C_5H_5CoS_2^+$	350	188	101	101
(4) $C_5H_5RhS_2C_2(CF_3)_2$	$C_5H_5RhC_4F_6S_2^+$	$\xrightarrow{-C_4F_6}$	$C_5H_5RhS_2^+$	394	232	136.5	136.5
(5) $C_5H_5IrS_2C_2(CF_3)_2$	$C_5H_5IrC_4F_6S_2^+$	$\xrightarrow{-C_4F_6}$	$C_5H_5IrS_2^+$	484	322	214	214

product of the reaction between $Co_2(CO)_8$ and bis(trifluoromethyl)dithietene after reduction with hydrazine. This anion was isolated and identified as the tetraethylammonium salt. The ultraviolet and visible spectra of the solution of $C_5H_5CoS_2C_2(CF_3)_2$ indicated that 50% of the cobalt had been converted to the $\{[(CF_3)_2C_2S_2]_2Co\}^{2-}$ anion, consistent with quantitative utilization of the $(CF_3)_2C_2S_2$ ligands in this disproportionation reaction.

Because of the greater rarity of the rhodium and iridium compounds of the type $C_5H_5MS_2C_2(CF_3)_2$, their reduction was investigated only by spectroscopic means without attempts to isolate solid reduction products. The rhodium compound $C_5H_5RhS_2C_2(CF_3)_2$ was destroyed upon treatment with ethanolic hydrazine as indicated by the disappearance of the maximum at 468 mμ. The iridium compound $C_5H_5IrS_2C_2(CF_3)_2$ was more stable to ethanolic hydrazine reduction since about 65% of the $C_5H_5IrS_2C_2(CF_3)_2$ was observed in the ultraviolet spectrum after about 15 min in ethanolic hydrazine at room temperature. However, the appearance of a new band at 317 mμ indicated that some reduction was taking place to give a new product. The greater resistance of the iridium compound $C_5H_5IrS_2C_2(CF_3)_2$ than its rhodium analog to hydrazine reduction is consistent with the generally greater stability of higher oxidation states of third row (5d) transition metals (*e.g.*, tungsten, rhenium, osmium, iridium, and platinum) than of the second row (4d) transition metals (*e.g.*, molybdenum, technetium, ruthenium, rhodium, and palladium).

Alcoholic hydrazine was found to react rapidly with green paramagnetic $C_5H_5NiS_2C_2(CF_3)_2$ to give a yellow solution from which the yellow tetraethylammonium salt of the known[3] $\{[(CF_3)_2C_2S_2]_2Ni\}^{2-}$ anion could be isolated. Ultraviolet spectra of the original yellow reduction mixture indicated that the ethanolic hydrazine had converted about 50% of the nickel in $C_5H_5NiS_2C_2(CF_3)_2$ to $\{[(CF_3)_2C_2S_2]_2Ni\}^{2-}$ in accord with quantitative utilization of the $(CF_3)_2C_2S_2$ groups.

The nickel and cobalt compounds $C_5H_5MS_2C_2(CF_3)_2$ both thus appear to disproportionate upon reduction with ethanolic hydrazine to give the anions $\{[(CF_3)_2C_2S_2]_2M\}^{2-}$. Moreover, the manganese compound $C_5H_5Mn(NO)S_2C_2(CF_3)_2$ also undergoes disproportionation upon reduction to give the anion $\{[(CF_3)_2C_2S_2]_2Mn(NO)\}^{2-}$. However, the tungsten compound $C_5H_5W[S_2C_2(CF_3)_2]_2$ gives the simple monoanion reduction product $\{C_5H_5W[S_2C_2(CF_3)_2]_2\}^-$. The disproportionation reaction at some stage of its unknown mechanism must involve replacement of a C_5H_5 ligand with a $(CF_3)_2C_2S_2$ ligand. Possibly the greater coordination number of the metal atom in $C_5H_5W[S_2C_2(CF_3)_2]_2$ as compared with the compounds $C_5H_5MS_2C_2(CF_3)_2$ (M = Co or Ni) prevents the necessary approach of the substituting $(CF_3)_2C_2S_2$ ligand to the metal atom to replace the π-C_5H_5 ring in $C_5H_5W[S_2C_2(CF_3)_2]_2$. Locke and McCleverty[34] in their work with complexes containing both π-cyclopentadienyl and maleonitrile dithiolate ligands have also noted some examples of easy loss of π-C_5H_5 ligands paralleling somewhat the cases of the reduction of the compounds $C_5H_5MS_2C_2(CF_3)_2$ discussed in this paper.

(E) Some General Comments on the Mass Spectra of Bis(trifluoromethyl)ethylene Dithiolate Complexes.—During the course of this work the mass spectra of several complexes of the $(CF_3)_2C_2S_2$ ligand have been measured. Ten of these spectra are reported in this paper. Specific features of many of these mass spectra have already been discussed.

In all of these mass spectra the tendency for the parent ion to lose a fluorine atom to form an ion with a mass difference of 19 was noted.[46] Somewhat more unusual was the degradation of the $MS_2C_2(CF_3)_2^+$ ion to the MS_2^+ ion with loss of the elements of hexafluorobutyne-2, $(CF_3)_2C_2$. This mode of degradation was supported in many cases by the observation of metastable ions with the expected mass numbers (Table I). Thus reactions occur in the mass spectrometer which are the reverse of preparing bis(trifluoromethyl)dithietene from hexafluorobutyne-2 and sulfur[11] or the nickel complex $[(C_6H_5)_2C_2S_2]_2Ni$ from nickel sulfide and diphenylacetylene.[47]

Acknowledgment.—We are indebted to the U. S. Air Force Office of Scientific Research for partial support of this work under Grants AF-AFOSR-580-64 and AF-AFOSR-580-66. We are also indebted to Mr. T. F. Korenowski for experimental assistance. We are indebted to Dr. D. G. Davies for providing valuable help with the ^{19}F nmr measurements.

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[46] If the parent ion contained carbonyl or nitrosyl groups, their loss to form ions without these groups was a favored degradation pathway. Thus the ion $C_5H_5Mn(NO)S_2C_2(CF_3)_2^+$ (*m/e* 376) tends to lose its nitrosyl group to form the ion $C_5H_5MnS_2C_2(CF_3)_2^+$ (*m/e* 346).

[47] G. N. Schrauzer and V. Mayweg, *Z. Naturforsch.*, **19b**, 192 (1964).