

becoming red but at a much slower rate than in the analogous reaction with $(CF_2)_2S_4$.

After 21 hr. the refluxing was discontinued and the reaction mixture allowed to cool to room temperature and filtered by gravity. Solvent was removed from the deep red filtrate at ~ 30 mm. leaving a deep red liquid. This liquid was dissolved in ~ 50 ml. of pentane and the solution chromatographed on a 2×60 cm. alumina column. The single orange band was eluted with pentane and the red eluate evaporated to dryness at ~ 50 mm. A red crystalline solid remained which weighed 1.67 g. (8% yield based on $Fe_3(CO)_{12}$).

For further purification the product was sublimed at 60° (0.1 mm.) to give 1.46 g. (7% yield) of red crystals of $C_2F_4S_2Fe_2(CO)_6$, m.p. $64-66^\circ$.

The infrared and F^{19} n.m.r. spectra both indicated the product to be the same as that obtained from $(CF_2)_2S_4$ and $Fe_3(CO)_{12}$. Analytical data were also in agreement with the $C_2F_4S_2Fe_2(CO)_6$ formula. The slightly lower melting point is presumably attributable to trace amounts of impurities.

Anal. Calcd. for $C_2F_4O_6S_2Fe_2$: C, 22.8; H, 0.0; F, 18.1. Found: C, 22.7; H, 0.3; F, 17.6.

Acknowledgment.—The author is indebted to Dr. C. G. Krespan of the Central Research Department for helpful advice and to Dr. W. R. Brasen for generous samples of the cyclic sulfides VIII and IX.

[CONTRIBUTION FROM E. I. DU PONT DE NEMOURS AND CO., EXPLOSIVES DEPARTMENT, EXPERIMENTAL STATION LABORATORY, WILMINGTON 98, DEL.]

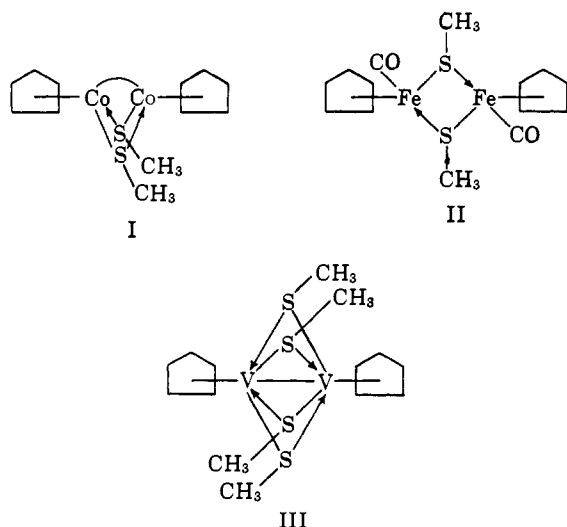
Organosulfur Derivatives of the Metal Carbonyls. V. The Reactions between Certain Organic Sulfur Compounds and Various Cyclopentadienyl Metal Carbonyl Derivatives¹

By R. B. KING²

RECEIVED DECEMBER 10, 1962

Dimethyl disulfide was found to react with $[C_5H_5Cr(CO)_3]_2$ and $[C_5H_5Mo(CO)_3]_2$ to give the new compounds $(C_5H_5)_2Cr_2(CH_3S)_3$ and $[C_5H_5Mo(CH_3S)_2]_2$, respectively. Reactions between bis-(trifluoromethyl)-dithietene and various cyclopentadienyl metal carbonyl derivatives gave the compounds $[C_5H_5MC_4F_6S_2]_2$ ($M = V, Cr$ and Mo), and the compounds $C_5H_5MC_4F_6S_2$ ($M = Co$ and Ni). The structures of some of these compounds are discussed.

Recently novel compounds obtained from reactions between dimethyl disulfide and several cyclopentadienyl carbonyl complexes of transition metals were described.^{3,4} The reaction between cyclopentadienylcobalt dicarbonyl and dimethyl disulfide gave a black solid of composition $[C_5H_5CoCH_3S]_2$, structure I³; the reaction between cyclopentadienyliron dicarbonyl dimer and dimethyl disulfide gave a brown-black solid of composition $[C_5H_5FeCOCH_3S]_2$, structure II; and the reaction between cyclopentadienylvanadium tetracarbonyl and dimethyl disulfide gave a dark brown solid of composition $[C_5H_5V(CH_3S)_2]_2$, apparently structure III.⁴ The vanadium compound III is especially unusual in that it appears to have four bridging CH_3S -groups and to be the first example of a complex containing four bridging groups. In view of the unusual



structure of the vanadium compound III it seemed of interest to investigate the reactions between dimethyl

disulfide and cyclopentadienyl carbonyl derivatives of metals near vanadium in the periodic table such as chromium and molybdenum.

In an attempt to prepare the molybdenum analog, the reaction between $[C_5H_5Mo(CO)_3]_2$ and dimethyl disulfide was investigated. Heating the two reactants for several hours in refluxing methylcyclohexane gave a deep brown reaction mixture from which a brown solid sublimable at 160° (0.1 mm.) could be isolated. Analyses indicated this material to be $[C_5H_5Mo(CH_3S)_2]_2$, corresponding to the vanadium derivative $[C_5H_5V(CH_3S)_2]_2$.⁴ The proton n.m.r. spectrum of the molybdenum compound indicated it to be diamagnetic and showed a resonance at 5.57 p.p.m. attributable to the protons of the π -bonded cyclopentadienyl groups and a second resonance at 1.26 p.p.m. attributable to the protons of the methyl groups. The diamagnetism of the compound, also confirmed by magnetic balance measurements, indicates that the molybdenum complex is dimeric like the analogous vanadium compound, since a monomer would have an odd number of electrons and would thus be paramagnetic. Unfortunately, $[C_5H_5Mo(CH_3S)_2]_2$ like many of the other compounds described in this paper proved to be too insoluble in organic solvents for successful determination of the molecular weight.^{4a}

It was found that when dimethyl disulfide was heated with either $[C_5H_5Cr(CO)_3]_2Hg^5$ or $[C_5H_5Cr(CO)_3]_2^5$ in refluxing methylcyclohexane, an intense purple solution was produced from which a dark purple solid

(4a) NOTE ADDED IN PROOF.—After this paper was accepted, Treichel, Morris and Stone^{4b} reported the reaction between cyclopentadienylmolybdenum tricarbonyl hydride and dimethyl disulfide at room temperature to give a brown crystalline material $[C_5H_5Mo(CO)_2SCH_3]_2$. It thus appears that cyclopentadienylmolybdenum carbonyl derivatives and disulfides can form compounds of either the types $[C_5H_5Mo(CO)_2SR]_2$ or $[C_5H_5Mo(SR)]_2$ depending on the reaction conditions. In this connection, it is of interest that cyclopentadienyltungsten tricarbonyl hydride when heated with dimethyl disulfide even to temperatures as high as 135° for several hours still forms significant quantities of $[C_5H_5W(CO)_2SCH_3]_2$,^{4b,4c} indicating that displacement of all of the carbonyl groups of the tungsten compound is much more difficult than the analogous reaction of the molybdenum compound.

(4b) P. M. Treichel, J. H. Morris and F. G. A. Stone, *J. Chem. Soc.*, 720 (1963).

(4c) R. B. King, unpublished results.

(5) R. B. King and F. G. A. Stone, *Inorg. Syn.*, 7, in press.

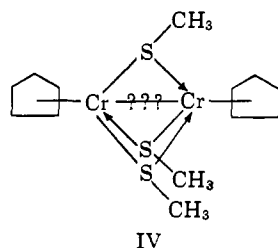
(1) For part IV, see R. B. King, *J. Am. Chem. Soc.*, **85**, 1584 (1963).

(2) Mellon Institute, 4400 Fifth Avenue, Pittsburgh 13, Penna.

(3) R. B. King, P. M. Treichel and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3600 (1961).

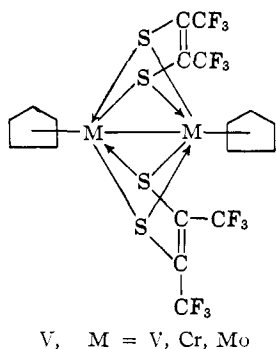
(4) R. H. Holm, R. B. King and F. G. A. Stone, *Inorg. Chem.*, **2**, 219 (1963).

sublimable at $\sim 120^\circ$ (0.1 mm.) could be isolated. Analyses indicated this material to have the composition $(C_5H_5)_2Cr_2(CH_3S)_3$; $[C_5H_5Cr(CO)_3]_2$ gave a much better yield of better quality product than $[C_5H_5Cr(CO)_3]_2Hg$. Difficulties in synthesizing $[C_5H_5Cr(CO)_3]_2$ made it impossible to obtain the product $(C_5H_5)_2Cr_2(CH_3S)_3$ in quantities sufficient for a detailed characterization and therefore the potentially interesting magnetic properties are still unknown. $(C_5H_5)_2Cr_2(CH_3S)_3$ was unstable and could not be kept without decomposition even in a sealed vial flushed with nitrogen. $(C_5H_5)_2Cr_2(CH_3S)_3$ is believed to have structure IV, but work on its magnetic properties is needed to establish the presence of a chromium–chromium bond.^{5a}



Recently novel metal complexes have been synthesized by the reactions between bis-(trifluoromethyl)-dithietene and certain metal carbonyls. Molybdenum hexacarbonyl gave the complex $Mo(C_4F_6S_2)_3$ ⁶ which may be regarded as a chelate derivative of hexavalent molybdenum. Iron pentacarbonyl reacted to form the complex $C_4F_6S_2Fe_2(CO)_6$.¹ It therefore seemed of interest to investigate the reactions between bis-(trifluoromethyl)-dithietene and various cyclopentadienyl metal carbonyls.

The reactions between bis-(trifluoromethyl)-dithietene and $C_5H_5V(CO)_4$, $[C_5H_5Cr(CO)_3]_2Hg$ or $[C_5H_5Mo(CO)_3]_2$ gave products of the general formula $[C_5H_5MC_4F_6S_2]_2$ ($M = V, Cr, Mo$). These compounds are intensely colored air-stable solids, the vanadium compound being olive-green and the chromium and molybdenum compounds various shades of purple-brown. Unfortunately, the solubilities of these materials in organic solvents were insufficient for molecular weight determinations. The F^{19} n.m.r. spectrum of the molybdenum complex besides indicating the compound to be diamagnetic exhibited a single resonance at -385 cycles relative to internal $(CFCl_2)_2$ indicating that all four CF_3 groups are equivalent. The diamagnetism of the compound, which was also confirmed by magnetic balance measurements, suggests the doubled formula $[C_5H_5MoC_4F_6S_2]_2$ since monomeric C_5H_5Mo-



(5a) NOTE ADDED IN PROOF.—An alternative possibility suggested by recent work by R. G. Hayter (private communication) on somewhat analogous phosphorus-bridged derivatives of metal carbonyls would be for this chromium compound to be $(C_5H_5)_2Cr_2(CH_3S)_3H$ with a chromium–hydrogen bond. This structure unlike structure IV could give both chromium atoms the same electronic configuration. The data available on this rare and unstable compound do not permit a decision regarding this possible structure.

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

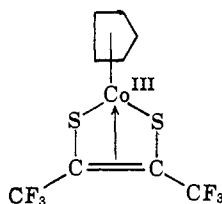
$C_4F_6S_2$ would be paramagnetic. In view of these data the most reasonable structure for $[C_5H_5MoC_4F_6S_2]_2$ is V ($M = Mo$). Structure V is completely analogous to the structure of the compounds $[C_5H_5M(CH_3S)_2]_2$ ($III, M = V, Mo$) obtained from dimethyl disulfide and the appropriate cyclopentadienyl carbonyls. Both types of compounds contain four bridging sulfur atoms and differ only in the nature of the organic groups bonded to the sulfur atoms. The most reasonable structures for the vanadium and chromium compounds are also V ($M = V, Cr$) since the physical properties including the volatilities are very similar to those of the molybdenum compound. The chromium compound was too insoluble in organic solvents, even tetrahydrofuran, for its n.m.r. spectrum to be taken.

It is of interest that $[C_5H_5VC_4F_6S_2]_2$ at 25° was found to be paramagnetic with a moment of 0.6 B.M. per vanadium atom as compared with the previously observed magnetic moment of 0.9 B.M. per vanadium atom for the analogous $[C_5H_5V(CH_3S)_2]_2$.⁴ If the compound has structure V ($M = V$) completely analogous to that of the diamagnetic molybdenum complex $[C_5H_5MoC_4F_6S_2]_2$ with a single vanadium–vanadium bond, it would be expected to have a magnetic moment per vanadium atom of 1.7 B.M. corresponding to one unpaired electron per vanadium atom. The substantially lower observed magnetic moment of 0.6 B.M. suggests that not only must there be a vanadium–vanadium bond in $[C_5H_5VC_4F_6S_2]_2$ comparable to the molybdenum–molybdenum bond in $[C_5H_5MoC_4F_6S_2]_2$ but also there must be partial pairing between the remaining unpaired electrons on each vanadium atom giving the vanadium–vanadium bond partial double bond character. The lower magnetic moment of $[C_5H_5VC_4F_6S_2]_2$ as compared with $[C_5H_5V(CH_3S)_2]_2$ suggests that the vanadium–vanadium double bond character in the former complex must be greater.

The reaction between cyclopentadienylcobalt dicarbonyl and bis-(trifluoromethyl)-dithietene was also investigated and gave a very intense purple reaction mixture from which a purple crystalline compound was isolated. Analyses of this compound indicated the composition $C_5H_5CoC_4F_6S_2$, similar to that of the vanadium, chromium, and molybdenum compounds described above.

This cobalt compound was soluble in organic solvents to a limited extent giving intense purple solutions. Molecular weight determinations were carried out both in dichloromethane by the isopiestic method and in benzene with the Mechrolab vapor pressure osmometer. Both determinations gave values in excellent agreement with the monomeric formula $C_5H_5CoC_4F_6S_2$. Further indication for the monomeric formula $C_5H_5CoC_4F_6S_2$ is the fact that the cobalt compound can be sublimed unchanged at 80° (0.1 mm.) whereas the dimeric compounds $[C_5H_5MC_4F_6S_2]_2$ ($M = V, Cr$ and Mo) require temperatures of at least 150° for sublimation at 0.1 mm.

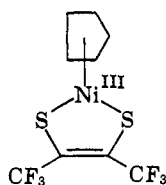
Insight into the nature of bonding in $C_5H_5CoC_4F_6S_2$ is provided by its infrared and F^{19} n.m.r. spectra. The F^{19} n.m.r. spectrum, besides showing the compound to be diamagnetic, exhibits a single resonance at -710 cycles relative to internal $(CFCl_2)_2$ indicating the compound to contain a single type of CF_3 group. The compounds $[C_5H_5MC_4F_6S_2]_2$ ($M = V, Cr, Mo$) exhibit a band of medium intensity in the $C=C$ region in the range $1530-1630\text{ cm}^{-1}$, whereas $C_5H_5CoC_4F_6S_2$ does not exhibit this band but instead a much weaker band at 1480 cm^{-1} . This suggests that the double bond of the bis-(trifluoromethyl)-dithietene system might be π -bonded to the metal atom. In view of these data, structure VI is suggested for $C_5H_5CoC_4F_6S_2$. This



VI

compound may be regarded as analogous to the well known hexacoordinate cobalt(III) complexes if one considers the cyclopentadienyl residue present as the stable $C_5H_5^-$ anion and the $C_4F_6S_2$ residue present as the dianion derived from the hypothetical mercaptan $CF_3C(SH)=C(SH)CF_3$ by the loss of two protons. The cyclopentadienyl anion would then donate three electron pairs, the dimercaptide anion two electron pairs, and the carbon-carbon double bond one electron pair to the cobalt atom giving the cobalt(III) atom a total of six electron pairs as in other stable cobalt(III) complexes.

The reaction between $[C_5H_5NiCO]_2$ and bis-(trifluoromethyl)-dithietene was also investigated. Upon mixing the reactants in hexane solution at room temperature the red color of the nickel complex gradually became a dark green and a black solid precipitated. From this reaction mixture black crystals of composition $C_5H_5NiC_4F_6S_2$ were isolated. Attempted sublimation of this material at 0.1 mm. caused only decomposition. This compound was found to be paramagnetic with a magnetic moment of 1.67 B.M. per nickel atom, suggesting the presence of one unpaired electron. The most reasonable structure for this complex seems to be VII. The nickel atom in $C_5H_5NiC_4F_6S_2$, like the cobalt atom in $C_5H_5CoC_4F_6S_2$, may be regarded as formally trivalent if one again considers the cyclopentadienyl residue present as the stable $C_5H_5^-$ anion and the $C_4F_6S_2$ residue present as the dianion derived from the hypothetical mercaptan $CF_3C(SH)=C(SH)CF_3$. The presence of a band at 1520 cm^{-1} of medium intensity in the infrared spectrum suggests that the carbon-carbon double bond of the $C_4F_6S_2$ residue is not π -bonded to the metal atom as is the case in $C_5H_5CoC_4F_6S_2$.



VII

The reactions of bis-(trifluoromethyl)-dithietene with dicobalt octacarbonyl and with nickel tetracarbonyl were also investigated. In the case of the reaction with $Co_2(CO)_8$ a black solid volatile at 110° (0.1 mm.) was obtained in erratic yields. The infrared spectrum indicated the presence of two carbonyl bands at 2110 and 2080 cm^{-1} . Analyses indicated the composition $C_4F_6S_2CoCO$. The solubility of the compound in dichloromethane was too low for a satisfactory F^{19} n.m.r. spectrum to be obtained. On treatment of the compound with tetrahydrofuran gas was evolved. F^{19} n.m.r. of the resulting black solution showed three resonances and probably represents a mixture of the compound and its decomposition products. Insufficient material was obtained for adequate characterization.

The reaction between nickel tetracarbonyl and bis-(trifluoromethyl)-dithietene gave a black reaction mixture at room temperature from which a brown-black material was obtained in very low yields after sub-

limation at 150° (0.2 mm.). Nickel analysis indicated the composition $C_4F_6S_2Ni$, but insufficient material was obtained for a detailed study.

Experimental

Infrared spectra were taken in KBr pellets and recorded on a Perkin-Elmer Infracord machine. Proton n.m.r. spectra were taken on a Varian Associates model A-60 machine. Chemical shifts are given in p.p.m. downfield from tetramethylsilane. F^{19} n.m.r. spectra were taken at 56.4 Mc. on a Varian Associates model 4300 B machine in dichloromethane or tetrahydrofuran solution. Chemical shifts are given in cycles relative to internal $(CFCl_2)_2$. Melting and decomposition points were determined in sealed capillaries and are uncorrected.

Bis-(trifluoromethyl)-dithietene was prepared from hexafluorobutene-2 and sulfur by the method of Krespan and McKusick.⁷ The cyclopentadienyl metal carbonyl derivatives were prepared by methods to be published by the author in collaboration with Prof. F. G. A. Stone in Volume VII of "Inorganic Syntheses."⁸ Dimethyl disulfide was obtained from Crown-Zellerbach.

Reaction between Cyclopentadienylmolybdenum Tricarbonyl Dimer and Dimethyl Disulfide.—A mixture of 3.0 g. (6.1 mmoles) of $[C_5H_5Mo(CO)_3]_2$, 10 ml. of dimethyl disulfide and 120 ml. of methylcyclohexane was refluxed 16 hr. under nitrogen with magnetic stirring. The reaction mixture was allowed to cool to room temperature and then cooled 4 hr. in a -78° bath. The resulting brown crystals were filtered and purified further by two sublimations at $170-185^\circ$ (0.1 mm.) to give 1.7 g. (54% yield) of deep brown crystals of $[C_5H_5Mo(CH_3S)_2]_2$; infrared spectrum: $3100(\text{vw})$, $2920(\text{m})$, $1415(\text{m})$, $1282(\text{m})$, $1098(\text{m})$, $996(\text{m})$, $935(\text{w})$, $812(\text{m})$ and $785(\text{s})\text{ cm}^{-1}$; proton n.m.r. spectrum: cyclopentadienyl resonance at 5.57 p.p.m., methyl resonance at 1.26 p.p.m. Both peaks were too broad to show fine structure. The magnetic susceptibility of $[C_5H_5Mo(CH_3S)_2]_2$ was checked on the Gouy balance. A magnetic susceptibility of $\chi_{\text{mol}}^{25} = -238 \times 10^{-6}\text{ cm}^3\text{ mole}^{-1}$ was found, confirming the diamagnetism of the compound.

Anal. Calcd. for $C_{14}H_{22}S_4Mo_2$: C, 32.9; H, 4.3; S, 25.1; Mo, 37.6. Found (two independent preparations): C, 32.6, 32.4; H, 4.1, 4.4; S, 24.9, 25.0; Mo, 38.0, 38.0.

Reaction between Cyclopentadienylchromium Tricarbonyl Dimer and Dimethyl Disulfide.—A mixture of 1.0 g. (2.5 mmoles) of $[C_5H_5Cr(CO)_3]_2$, 5 ml. of dimethyl disulfide and 50 ml. of methylcyclohexane was refluxed 20 hr. under nitrogen with magnetic stirring. The reaction mixture became a deep violet. After cooling to room temperature and finally in a -78° bath, the purple solid was filtered and purified by two sublimations at 160° (0.1 mm.) to give 300 mg. (32% yield) of purple crystalline $(C_5H_5)_2Cr_2(SCH_3)_4$; infrared spectrum: $3130(\text{vw})$, $2980(\text{m})$, $2900(\text{w})$, $1430(\text{w})$, $1012(\text{m})$, and $809(\text{s})\text{ cm}^{-1}$. The compound decomposed on storage for several months even in a sealed vial under nitrogen.

The more readily obtainable $[C_5H_5Cr(CO)_3]_2Hg$ gives the same compound when heated with dimethyl disulfide, but the yield and quality of product are both lower.

Anal. Calcd. for $C_{13}H_{19}S_3Cr_2$: C, 41.6; H, 5.1; S, 25.6; Cr, 27.7. Found (two independent preparations): C, 42.2, 40.3; N, 4.6, 4.9; S, 25.6, 25.6; Cr, 28.7, 28.4.

Preparation of the Compounds $[C_5H_5MC_4F_6S_2]_2$ (M = V, Cr and Mo).—A mixture of 1.2 g. (5.26 mmoles) of cyclopentadienylvanadium tetracarbonyl, 1.0 ml. ($\sim 1.6\text{ g.}$, $\sim 7\text{ mmoles}$) of bis-(trifluoromethyl)-dithietene and 50 ml. of methylcyclohexane was refluxed 16 hr. under nitrogen. The dark orange reaction mixture soon became black in color. After cooling to room temperature and then finally in a -78° bath for several hours, the green-black solid which had separated was filtered. Sublimation at 160° (0.25 mm.) through a plug of glass wool gave 900 mg. (50% yield) of green crystals of $[C_5H_5VC_4F_6S_2]_2$; infrared spectrum: C—H band at $3150(\text{vw})\text{ cm}^{-1}$, C=C at $1590(\text{m})$ and $1430(\text{vw})\text{ cm}^{-1}$; C—F bands at $1245(\text{s})$, $1175(\text{s})$ and $1140(\text{s})\text{ cm}^{-1}$; cyclopentadienyl bands at $1020(\text{w})$ and $823(\text{s})\text{ cm}^{-1}$; other $C_4F_6S_2$ bands at $893(\text{m})$, $717(\text{m})$ and $688(\text{m})\text{ cm}^{-1}$.

Anal. Calcd. for $C_{18}H_{10}F_{12}S_4V_2$: C, 31.6; H, 1.5; F, 33.3; S, 18.7; V, 14.9. Found (two independent preparations): C, 31.8, 31.6; H, 1.7, 1.7; F, 34.3, 34.3; S, 18.9, 18.7; V, 16.3, 15.1.

The chromium compound was prepared in an analogous manner using $[C_5H_5Cr(CO)_3]_2Hg$ in place of $C_5H_5V(CO)_4$. After a single sublimation at $\sim 180^\circ$ (0.2 mm.), a 38% yield of purple-brown crystalline $[C_5H_5CrC_4F_6S_2]_2$ was obtained; infrared spectrum: C—H band at $3150(\text{vw})\text{ cm}^{-1}$; C=C bands at $1530(\text{m})$ and $1435(\text{w})\text{ cm}^{-1}$; C—F bands at $1242(\text{vs})$, $1180(\text{s})$, $1170(\text{sh})$, $1142(\text{s})$ and $1126(\text{s})\text{ cm}^{-1}$; cyclopentadienyl bands at $1023(\text{w})$, $1019(\text{sh})$, $1008(\text{w})$ and $831(\text{s})\text{ cm}^{-1}$; other $C_4F_6S_2$ bands at $897(\text{m})$, $718(\text{m})$ and $686(\text{w})\text{ cm}^{-1}$; F^{19} n.m.r. spectrum:

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

too insoluble even in tetrahydrofuran (pale violet solution) for a satisfactory spectrum to be obtained although some evidence for the presence of a broad peak around -420 to -460 cycles relative to internal (CFC1₂)₂ was obtained.

Anal. Calcd. for C₁₅H₁₀F₁₂S₄Cr₂: C, 31.5; H, 1.5; F, 33.2; S, 18.7; Cr, 15.1. Found (two independent preparations): C, 31.7, 32.0; H, 1.7, 2.0; F, 33.6; S, 19.3; Cr, 14.9.

The molybdenum compound was prepared in an analogous manner using [C₅H₅Mo(CO)₂]₂ in place of C₅H₅V(CO)₄. After a single sublimation at $\sim 175^\circ$ (0.25 mm.), a 48% yield of purple-brown crystalline [C₅H₅MoC₄F₆S₂]₂ was obtained; infrared spectrum: C—H bands at 3130(vw) cm.⁻¹; C=C bands at 1650(w), 1630(m) and 1420(vw) cm.⁻¹; C—F bands at 1245(s), 1169(s), and 1135(s) cm.⁻¹; cyclopentadienyl bands at 1009(w) and 813(m) cm.⁻¹; other C₄F₆S₂ bands at 861(w), 840(w), 701(m) and 685(m) cm.⁻¹; F¹⁹ n.m.r. spectrum: resonance at -385 cycles relative to internal (CFC1₂)₂ in dichloromethane solution (deep purple).

Anal. Calcd. for C₁₅H₁₀F₁₂S₄Mo₂: C, 27.9; H, 1.3; F, 29.5; S, 16.5; Mo, 24.8. Found: C, 28.1; H, 1.7; F, 29.7; S, 16.8; Mo, 25.6.

Reaction between Cyclopentadienylcobalt Dicarboxyl and Bis-(trifluoromethyl)-dithietene.—A mixture of 1.0 ml. (~ 1.4 g., ~ 8 mmoles) of cyclopentadienylcobalt dicarbonyl, 0.5 ml. (~ 0.8 g., ~ 3.5 mmoles) of bis-(trifluoromethyl)-dithietene and 50 ml. of methylcyclohexane was refluxed 5.5 hr. under nitrogen with magnetic stirring. The reaction mixture became a dark purple. After cooling to room temperature and then in a -78° bath for several hours, the black crystals were filtered. They were purified by recrystallization from a mixture of dichloromethane and hexane to give a total of 930 mg. (76% yield) of dark violet crystals of C₅H₅CoC₄F₆S₂, m.p. 150° , isolated in two crops; infrared spectrum: C—H band at 3140(vw) cm.⁻¹; C=C bands at 1480(w), and 1417(w) cm.⁻¹; C—F bands at 1262(sh), 1240(s), 1176(s) and 1145(s) cm.⁻¹; cyclopentadienyl bands at 1015(w), 1007(w) and 849(m) cm.⁻¹; other C₄F₆S₂ bands at 930(w), 727(w) and 695(w) cm.⁻¹; F¹⁹ n.m.r. spectrum: resonance at -710 cycles relative to internal (CFC1₂)₂ in dichloromethane solution (very deep purple). The compound C₅H₅CoC₄F₆S₂ is the only new compound described in this paper that exhibits a definite melting point on heating in a closed capillary.

The compound C₅H₅CoC₄F₆S₂ may also be purified by sublimation at 80° (0.1 mm.). A significant amount of decomposition occurs during this process.

Anal. Calcd. for C₅H₅F₆S₂Co: C, 30.9; H, 1.4; F, 32.6; S, 18.3; Co, 16.8; mol. wt., 350. Found (sublimed sample): C, 31.2; H, 1.7; Co, 16.9. Found (recrystallized sample): C, 31.5; H, 1.5; F, 32.5; S, 18.4; Co, 16.6; mol wt., 360 (isopiestic in dichloromethane), 354 (Mechrolab vapor pressure osmometer in benzene).

Reaction between Cyclopentadienylnickel Carbonyl Dimer and Bis-(trifluoromethyl)-dithietene.—A mixture of 1.5 g. (~ 5 mmoles) of [C₅H₅NiCO]₂, 1.0 ml. (~ 1.6 g., ~ 7 mmoles) of bis-(trifluoromethyl)-dithietene and 50 ml. of hexane was stirred for 16 hr. at room temperature under nitrogen. The reaction mixture became dark green and much black solid separated. After cooling to -78° , the black crystals were filtered. They were purified by two recrystallizations from dichloromethane-hexane mixtures. After one recrystallization the yield was 1.2 g. (48%); infrared spectrum: C—H band at 3150(w) cm.⁻¹; C=C bands at 1520(m), 1440(w) and 1405(m) cm.⁻¹; C—F bands at 1248(s), 1170(s) and

1132(s) cm.⁻¹; cyclopentadienyl bands at 1020(m), 993(w), 848(m), 830(m), and 816(s) cm.⁻¹; other C₄F₆S₂ bands at 921(m), 724(m) and 695(m) cm.⁻¹; F¹⁹ n.m.r. spectrum: no resonance could be observed even in what appeared to be a fairly concentrated tetrahydrofuran solution (deep green) as would be expected due to the paramagnetism of this compound.

Anal. Calcd. for C₅H₅F₆S₂Ni: C, 30.9; H, 1.4; F, 32.6; S, 18.3; Ni, 16.8. Found: C, 31.1; H, 1.8; F, 31.4; S, 18.7; Ni, 16.8.

Reaction between Dicobalt Octacarbonyl and Bis-(trifluoromethyl)-dithietene.—A mixture of 2.0 g. (5.9 mmoles) of dicobalt octacarbonyl, 0.5 ml. (~ 0.8 g., ~ 3.5 mmoles) of bis-(trifluoromethyl)-dithietene and 50 ml. of methylcyclohexane was refluxed 3 hr. 15 min. under nitrogen with magnetic stirring, the reaction mixture becoming black. The reaction mixture was allowed to cool to room temperature and finally in a -78° bath and the black precipitate filtered. In some experiments the precipitate was pyrophoric. The product was isolated from the precipitate by sublimation at 170° (0.5 mm.) and purified by re-sublimation at 100 – 135° (0.25 mm.). A highly erratic yield of black crystals of empirical formula C₄F₆S₂CoCO was obtained; infrared spectrum: carbonyl bands at 2110(s) and 2080(s) cm.⁻¹; C=C bands at 1560(m) and 1530(m) cm.⁻¹; C—F bands at 1245(vs), 1185(s), and 1160(s) cm.⁻¹; other C₄F₆S₂ bands at 1012(w), 900(m), 890(m), 716(m), 693(w) and 689(w) cm.⁻¹.

Anal. Calcd. for C₄F₆OS₂Co: C, 19.2; H, 0.0; F, 36.4; S, 20.4; Co, 18.8. Found: C, 19.3; H, 0.6; F, 36.2; S, 20.8; Co, 17.8.

Reaction between Nickel Tetracarbonyl and Bis-(trifluoromethyl)-dithietene.—A mixture of 1.0 ml. (~ 1.6 g., ~ 7 mmoles) of bis-(trifluoromethyl)-dithietene and 50 ml. of hexane was prepared under nitrogen and treated with 2.0 ml. (~ 2.6 g., ~ 15 mmoles) of nickel tetracarbonyl, the reaction mixture turning black. The reaction mixture was refluxed 2 hr. under nitrogen with magnetic stirring, becoming a dark brown-black in color, much solvent being lost. The reaction mixture was allowed to cool to room temperature, diluted to 50 ml. with pentane, and cooled in a -78° bath. The resulting black solid was filtered and sublimed at 150° (0.2 mm.) for 24 hr., 50 mg. (2.5% yield) of brown-black crystals being obtained; infrared spectrum: C=C band at 1590(m) cm.⁻¹; C—F bands at 1240(s) and 1170(s) cm.⁻¹; other bands at 1010(w), 897(m), 720(m) and 692(m) cm.⁻¹.

Anal. Calcd. for C₄F₆S₂Ni: Ni, 20.6. Found: Ni, 20.8.

Magnetic Susceptibility Measurements.⁸

1. [C₅H₅MoC₄F₆S₂]₂: $\chi^{25^\circ} = -124 \times 10^{-6}$ cm.³/molybdenum atom

2. [C₅H₅VC₄F₆S₂]₂: $\chi^{25^\circ} = 0.00 \times 10^{-6}$ cm.³/vanadium atom (sample I); $\chi^{25^\circ} = +140 \times 10^{-6}$ cm.³/vanadium atom (sample II), corresponding to a magnetic moment of 0.58 B. M. for sample I and 0.62 B. M. for sample II after making the necessary correction for the diamagnetism of the cyclopentadienyl ring and the C₄F₆S₂ residue.⁹

3. C₅H₅NiC₄F₆S₂: $\chi_{mole}^{25^\circ} = +1030 \times 10^{-6}$ cm.³/mole corresponding to a magnetic moment of 1.67 B.M. after making the necessary correction for the diamagnetism of the ligands.⁹

(8) The author is indebted to Dr. L. Vaska of the Mellon Institute for carrying out these magnetic measurements.

(9) The total diamagnetism of the cyclopentadienyl ring and of the C₄F₆S₂ residue was estimated at -140×10^{-6} cm.³/metal atom.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY 4, CALIF.]

On the Purported Tetraphenylboric Acid

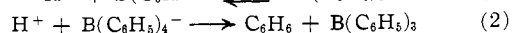
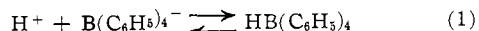
BY JOHN N. COOPER AND RICHARD E. POWELL

RECEIVED DECEMBER 18, 1962

The kinetics of the reaction of H⁺ with B(C₆H₅)₄⁻ shows no evidence for a molecular species HB(C₆H₅)₄. A decomposition mechanism involving attack of the proton on one of the aromatic rings is consistent with the observed acidity dependence, deuterium isotope effect, salt effect and activation parameters.

In his original work on the salts of tetraphenylborate anion, Wittig¹ stated that the corresponding acid is formed on addition of mineral acids to cold aqueous solutions of the salts, and that it can be back-titrated with base (reaction 1), although he also reported that in warm solutions decomposition takes place according to reaction 2. We were interested in preparing the

(1) G. Wittig, G. Keicher, A. Rückert and P. Raff, *Ann.*, **563**, 110 (1949).



substance HB(C₆H₅)₄, with the idea of investigating the physical properties of this apparently 5-coordinated boron compound.

Preliminary experiments showed, first, that the addition of mineral acid to cold sodium tetraphenylborate produced no acidic solid (although reaction 2