olefin compared to a heat of vaporization of 11.1 kcal./mole for the product.

$$42B_2H_6 + (CH_3)_2NC_3H_5 \xrightarrow[\text{ethyl ether}]{25°} \underset{\text{white solid}}{(CH_3)_2C_3H_5N:BH_3} \xrightarrow[\text{no solvent}]{120°} \text{uncontrolled reaction}$$

An attempt to carry out the same reaction by the addition of boron trifluoride ethyl etherate to a solution of sodium borohydride and the amine in tetraethylene glycol dimethyl ether resulted in the formation of a dark polymer and no material more volatile than the solvent.

Acknowledgment.—We wish to thank the National Science Foundation Undergraduate Research Program for partial support of this work and Callery Chemical Company for the chemical and spectral analyses and for samples of sodium borohydride and trimethylamine-borane.

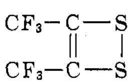
CONTRIBUTION FROM THE EXPLOSIVES DEPARTMENT,
EXPERIMENTAL STATION LABORATORY,
E. I. DU PONT DE NEMOURS AND COMPANY,
WILMINGTON, DELAWARE

Organosulfur Derivatives of the Metal Carbonyls. III. The Reaction between Molybdenum Hexacarbonyl and Bis-(trifluoromethyl)-dithietene[1]

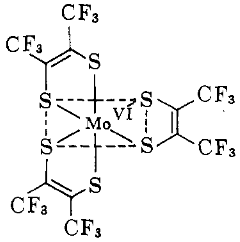
BY R. B. KING[2]

Received October 25, 1962

Recently the novel heterocyclic sulfur compound bis-(trifluoromethyl)-dithietene (I) was reported as being formed in good yield in the reaction between hexafluorobutyne-2 and sulfur under appropriate conditions.[3] In an attempt to prepare unusual organometallic compounds the reactions between bis-(trifluoromethyl)-dithietene and a variety of metal carbonyl derivatives were investigated. This note describes a novel compound obtained in the reaction between bis-(trifluoromethyl)-dithietene and molybdenum hexacarbonyl.



I



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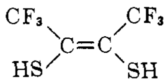

III

Experimental

Molybdenum hexacarbonyl was purchased from Climax Molybdenum Company. Bis-(trifluoromethyl)-dithietene was prepared by the method of Krespan and McKusick.[3] The infrared spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer Infracord machine.

The Reaction between Molybdenum Hexacarbonyl and Bis-(trifluoromethyl)-dithietene.—A mixture of 2.4 g. (9.1 mmoles) of molybdenum hexacarbonyl, 2 ml. (~3.2 g., ~14 mmoles) of bis-(trifluoromethyl)-dithietene, and 50 ml. of methylcyclohexane was refluxed 18 hr. under nitrogen with magnetic stirring, the reaction mixture turning black. After cooling to room temperature and then in a −78° bath, the black crystals were filtered and product was isolated from them by sublimation at 185–190° (0.2 mm.) for 24 hr. to give 1.96 g. (55% yield) of glistening purple crystals of $Mo(C_4F_6S_2)_3$, m.p. > 245°.

Anal. Calcd. for $C_{12}F_{18}S_6Mo$: C, 18.6; H, 0.0; F, 44.2; S, 24.8; Mo, 12.4; mol. wt., 774. Found: C, 18.8; H, 0.0; F, 43.5; S, 24.9; Mo, 12.9; mol. wt., 685 (isopiestic in tetrahydrofuran).

Infrared Spectrum.—C=C band at 1451 (w) cm.$^{-1}$; C–F bands at 1258 (s), 1214 (vs), 1176 (s), and 1148 (s) cm.$^{-1}$; other bands at 859 (w), 730 (m), 699 (m), and 692 (vw, sh) cm.$^{-1}$.

F^{19} N.m.r. Spectrum.—Single sharp peak at −316 cycles relative to internal $(CFCl_2)_2$.

Properties of $Mo(C_4F_6S_2)_3$.—This new molybdenum complex is a glistening purple solid sparingly soluble in organic solvents, giving intense blue-violet solutions. It was necessary to use the excellent solvent tetrahydrofuran in order to obtain solutions of sufficient concentration for n.m.r. and molecular weight studies. Both the solutions and the solid compounds seem to be extremely stable to air oxidation. The compound is also very stable to thermal decomposition as indicated by its isolation in 55% yield after a sublimation at 185–190° (0.1 mm.).

Discussion

The infrared spectrum and the analytical data of $Mo(C_4F_6S_2)_3$ indicate complete absence of carbonyl groups in the product. The F^{19} n.m.r. spectrum of a solution of the complex in tetrahydrofuran shows only a single sharp CF_3 peak, indicating the compound to be diamagnetic and all $C_4F_6S_2$ residues to be equivalent. On this basis, structure II is proposed for the complex, which may be regarded as a hexavalent molybdenum derivative of the as yet unknown dithiol III. It bears a formal analogy to molybdenum hexafluoride. Instead of six fluorine atoms, three chelating bidentate residues derived from bis-(trifluoromethyl)-dithietene surround the hexavalent molybdenum atom.

The formation of the hexavalent molybdenum derivative $Mo(C_4F_6S_2)_3$ from the zerovalent molybdenum derivative $Mo(CO)_6$ may be regarded as an oxidation–reduction reaction with the zerovalent molybdenum atom being oxidized to the hexavalent oxidation state by three equivalents of bis-(trifluoromethyl)-dithietene which are in turn reduced to the dianion formed by the loss of two protons from the dithiol III. The isolation of $Mo(C_4F_6S_2)_3$ from this reaction is believed to be the first example of the preparation of an organosulfur derivative of molybdenum by the reaction between molybdenum hexacarbonyl and an organosulfur derivative. On the other hand, numerous organosulfur derivatives of iron have been prepared by the reactions be-

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[1] Part II: R. B. King, *Inorg. Chem.*, **2**, 326 (1963).

[2] Mellon Institute, Pittsburgh 13, Pennsylvania.

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

tween various iron carbonyl derivatives and various organosulfur compounds.[1,4]

The reaction between tungsten hexacarbonyl and bis-(trifluoromethyl)-dithietene was found to yield an analogous purple solid volatile at 185° (0.1 mm.). Even when the reaction was conducted in the higher boiling ethylcyclohexane, conversion of tungsten hexacarbonyl to the purple compound was less than 2%, undoubtedly due to the much lower reactivity of $W(CO)_6$ as compared with $Mo(CO)_6$. Although only very limited analytical data were obtained on the tungsten compound due to the lack of material, the similarity between its infrared spectrum and that of $Mo(C_4F_6S_2)_3$ indicates the tungsten compound to be the analogous $W(C_4F_6S_2)_3$.

(4) W. Hieber and P. Spacu, *Z. anorg. allgem. Chem.*, **233**, 353 (1937); W. Hieber and C. Scharfenberg, *Ber.*, **73**, 1012 (1940); W. Hieber and W. Beck, *Z. anorg. allgem. Chem.*, **305**, 265 (1960); S. F. A. Kettle and L. E. Oregl, *J. Chem. Soc.*, 3890 (1960); R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3600 (1961); H. D. Kaesz, R. B. King, T. A. Manuel, L. D. Nichols, and F. G. A. Stone, *ibid.*, **82**, 4749 (1960).

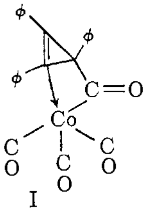
CONTRIBUTION FROM THE MELLON INSTITUTE,
PITTSBURGH 13, PENNSYLVANIA

Organometallic Chemistry of the Transition Metals. IV. The Reaction between Triiron Dodecacarbonyl and 1,3,3-Trimethylcyclopropene[1]

BY R. B. KING

Received November 28, 1962

The reaction between 1,2,3-triphenylcyclopropenyl bromide and sodium tetracarbonylcobaltate (−I) has been found to give a product of composition $(C_6H_5)_3C_3COCo(CO)_3$ to which structure I was assigned.[2] The isolation of this compound and of the closely related $(C_6H_5)_3C_3COFe(CO)_2NO$[2] suggested that compounds of interest might be obtained by heating cyclopropene derivatives with metal carbonyls. This note describes the reaction between triiron dodecacarbonyl and 1,3,3-trimethylcyclopropene[3] to give a novel compound of composition $C_6H_{10}COFe(CO)_3$.



I

Experimental

Infrared spectra were run in potassium bromide pellets on a Perkin-Elmer Model 21 double beam machine with sodium chloride optics. In addition, spectra of the metal carbony region were run in Halocarbon oil mulls on a Perkin-Elmer Model 112 single beam machine with calcium fluoride optics. Proton n.m.r. spectra were run on a Varian A-60 machine in carbon disulfide solution. 1,3,3-Trimethylcyclopropene was prepared by the decomposition of mesityl oxide *p*-toluenesulfonylhydrazone with sodium methoxide in refluxing diethylene glycol dimethyl ether.[3] The purity of the 1,3,3-trimethylcyclopropene used in this work was checked by elemental analysis and n.m.r. spectroscopy.

Reaction between Triiron Dodecacarbonyl and 1,3,3-Trimethylcyclopropene.—A mixture of 5.4 g. (10.7 mmoles) of triiron dodecacarbonyl, 3.5 ml. (2.4 g., 29 mmoles) of 1,3,3-trimethylcyclopropene, and 200 ml. of thiophene-free benzene was refluxed at the boiling point under nitrogen with magnetic stirring. A Dry Ice–acetone-cooled condenser was placed on top of the water-cooled condenser during the reflux period to prevent losses of the volatile 1,3,3-trimethylcyclopropene.

After 6 hr. the reaction mixture was allowed to cool to room temperature and then filtered by gravity. Solvent was removed from the filtrate at ~30 mm. The resulting dark yellow liquid residue was treated with 30 ml. of pentane and the mixture filtered by gravity. The filtrate was cooled 1 hr. in a −78° bath. The resulting yellow crystals were filtered and sucked dry. They were purified further by sublimation at 50° (0.1 mm.), collecting the product on a probe cooled with running water. Bright yellow crystals, m.p. 69°, of $C_6H_{10}COFe(CO)_3$ thus were obtained. In some experiments the product was somewhat greenish due to the presence of traces of unreacted triiron dodecacarbonyl; however, the greenish products had the same melting points and infrared spectra as the bright yellow products, indicating this contamination to be minor. The maximum yield obtained was 0.36 g. (5%).

Anal. Calcd. for $C_{10}H_{10}FeO_4$: C, 48.0; H, 4.0; Fe, 22.4; O, 25.6; mol. wt., 250. Found: C, 48.4, 48.2; H, 4.2, 4.2; Fe, 22.1, 22.1; O, 24.9, 25.3; mol. wt., 255.

Infrared Spectrum.—(Perkin-Elmer Model 21, KBr pellet, except where indicated): C–H bands at 2960 (vw), 2935 (vw), and 2890 (vw) cm.$^{-1}$; metal carbonyl bands (Perkin-Elmer Model 112, Halocarbon oil mull) at 1994 (vs) and 2053 (vs) cm.$^{-1}$; ketonic carbonyl bands at 1752 (sh) and 1728 (s) cm.$^{-1}$; other bands at 1544 (vw), 1495 (vw), 1488 (m), 1432 (w), 1385 (w), 1372 (m), 1332 (w), 1290 (vw), 1224 (w), 1068 (m), 1040 (vw), 1023 (w), 973 (vw), 947 (vw), 814 (w), 780 (m), and 691 (m) cm.$^{-1}$.

Proton N.m.r. Spectra. (a) 1,3,3-Trimethylcyclopropene.—Resonances at τ = 3.30 (singlet), 7.97 (doublet, $J \sim 1$ cycle), and 8.92 (singlet) of approximate relative intensities 1:3:6 due to the single olefinic proton, the three protons of the single methyl group bonded to the carbon atom involved in the double bond, and the six protons of the two *gem*-methyl groups, respectively.

(b) $C_6H_{10}COFe(CO)_3$.—Sharp peaks at τ = 4.39, 8.10, 8.20, and 8.82 of relative intensities 1:3:3:3, respectively.

Properties of $C_6H_{10}COFe(CO)_3$.—$C_6H_{10}COFe(CO)_3$ is a yellow air-stable crystalline solid soluble in organic solvents. It possesses a characteristic sweet odor and is extremely volatile, subliming slowly even in vials at room temperature and atmospheric pressure.

Discussion

Besides indicating diamagnetism, the proton n.m.r. spectrum of $C_6H_{10}COFe(CO)_3$, like that of 1,3,3-trimethylcyclopropene, exhibits a resonance due to a single olefinic proton and resonances due to three methyl groups, indicating that no proton migrations have occurred in the reaction between 1,3,3-trimethylcyclopropene and triiron dodecacarbonyl to produce $C_6H_{10}COFe(CO)_3$. The presence of a strong band at 1728 cm.$^{-1}$ in the infrared spectrum appears to arise from a ketonic carbonyl group and eliminates the possibility

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(1) For part III of this series see R. B. King, *Inorg. Chem.*, **2**, 528 (1963).

(2) C. E. Coffey, *J. Am. Chem. Soc.*, **84**, 118 (1962).

(3) G. L. Closs and L. E. Closs, *ibid.*, **83**, 2015 (1961).