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

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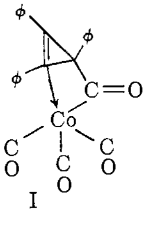
The reaction between 1,2,3-triphenylcyclopropenyl bromide and sodium tetracarbonylcobaltate (−I) has been found to give a product of composition $(C_6H_5)_3C_3COCo(CO)_3$ to which structure I was assigned.[2] The isolation of this compound and of the closely related $(C_6H_5)_3C_3COFe(CO)_2NO$[2] suggested 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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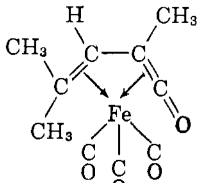
(1) For part III of this series see R. B. King, *Inorg. Chem.*, **2**, 528 (1963).

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

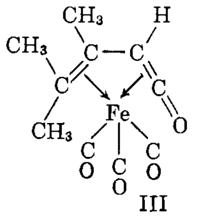
(3) G. L. Closs and L. E. Closs, *ibid.*, **83**, 2015 (1961).

that the new iron complex is π-1,3,3-trimethylcyclopropene-iron tetracarbonyl, analogous to π-acrylonitrile-iron tetracarbonyl.[4]

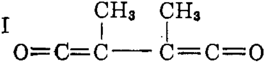
The infrared and n.m.r. data given above indicate that the new iron complex consists of an iron tricarbonyl group π-bonded to a $C_6H_{10}CO$ residue which acts as a four-electron donor and which contains a single olefinic hydrogen atom and three methyl groups. The two structures which satisfy these conditions are II and III, which differ only in the relative locations of a methyl group and a hydrogen atom.



II



III



$O{=}C{=}C(CH_3)-C(CH_3){=}C{=}O$

IV

In either of these structures an iron tricarbonyl group is π-bonded to a vinylketene derivative in a manner similar to the iron tricarbonyl complexes of various dienes.[5] Such diene complexes of vinylketene derivatives are related to diene complexes of butadiene derivatives by the replacement with an oxygen atom of the two substituents on one of the end carbon atoms of the four-carbon chain which is bonded to the iron atom.

It would be of interest to decide between structures II and III for $C_6H_{10}COFe(CO)_3$. However, the infrared and n.m.r. data do not permit an unequivocal decision between these two structures. Either a degradation of $C_6H_{10}COFe(CO)_3$ to a known compound by unambiguous methods or synthesis of $C_6H_{10}COFe(CO)_3$ from a vinylketene derivative of known structure would therefore seem to be necessary. Due to the relatively low yield of $C_6H_{10}COFe(CO)_3$, insufficient material was available for degradation studies. The instability of vinylketene derivatives and the obscurity of the vinylacetic acid derivatives which would be precursors to the desired ketenes made synthesis of $C_6H_{10}COFe(CO)_3$ from a ketene derivative of known structure unattractive. Therefore, no data were obtained which would permit an unequivocal decision between structures II and III for $C_6H_{10}COFe(CO)_3$.

Since vinylketene derivatives appear to form diene-iron tricarbonyl complexes, it seemed possible that a bis-ketene with two conjugated carbon–carbon double bonds would form similar complexes. Such bis-ketene derivatives are unknown. However, dialkylcyclobutenedione derivatives[5] might be expected to form small amounts of such bis-ketene derivatives on thermal cleavage of the four-membered ring. Nevertheless, attempts to make an iron tricarbonyl diene complex of the bis-ketene IV by the reaction between triiron dodecacarbonyl or iron pentacarbonyl and dimethylcyclobutenedione[6] were unsuccessful. Here, as in the preparation of other iron tricarbonyl complexes of unsaturated ketenes, the difficulty appears to be finding a suitable method of synthesis rather than instability of the final iron carbonyl complex since $C_6H_{10}COFe(CO)_3$ appears to be approximately as stable as other diene-iron tricarbonyl complexes.

Finally, it is of interest that both in the formation of I from 1,2,3-triphenylcyclopropenyl bromide and $NaCo(CO)_4$[2] and in the formation of $C_6H_{10}COFe(CO)_3$ from 1,3,3-trimethylcyclopropene and triiron dodecacarbonyl described above, one of the carbonyl groups of the metal carbonyl derivative is converted to a ketonic carbonyl group. The fact that products of different types are obtained in these two reactions is not surprising due to the differences in the nature of both the metal carbonyl derivatives and the cyclopropene derivative.

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[4] S. F. A. Kettle and L. E. Orgel, *Chem. Ind.* (London), 49 (1960); A. R. Luxmoore and M. R. Truter, *Proc. Chem. Soc.*, 466 (1961).

[5] B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 642 (1958); R. B. King, T. A. Manuel, and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **16**, 233 (1961).

[6] A. T. Blomquist and E. A. La Lancette, *J. Am. Chem. Soc.*, **83**, 1387 (1961); A. T. Blomquist and R. A. Vierling, *Tetrahedron Letters*, 655 (1961).

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
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The Kinetics of the Formation of the Monoazide Complex of Iron(III)[1]

BY D. SEEWALD[2] AND N. SUTIN

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The red color of aqueous solutions containing ferric ions and hydrazoic acid has been known for many years. According to Ricca,[3] Wallace and Dukes,[4] and Bunn, Dainton, and Duckworth,[5] the species responsible for the red color, at least at low azide concentrations, is FeN_3^{2+}. They have presented evidence that these equilibria exist in the red solutions

$$Fe^{3+} + HN_3 \rightleftharpoons FeN_3^{2+} + H^+ \qquad K_1$$

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+ \qquad K_h$$

$$HN_3 \rightleftharpoons H^+ + N_3^- \qquad K_a$$

where the coördinated water molecules are not shown. The values of K_1, K_h, and K_a are 5.91×10^{-1}, $1.65 \times$

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] Summer student from Brooklyn College, Brooklyn, New York.

[3] B. Ricca, *Gazz. chim. ital.*, **75**, 71 (1945).

[4] R. M. Wallace and E. K. Dukes, *J. Phys. Chem.*, **65**, 2094 (1961).

[5] D. Bunn, F. S. Dainton, and S. Duckworth, *Trans. Faraday Soc.*, **57**, 1131 (1961).