Site of Ring Opening of an Asymmetric Cyclopropene with Iron Carbonyls: the *X*-Ray Crystal Structure of a Vinylketen–Iron Tricarbonyl Complex

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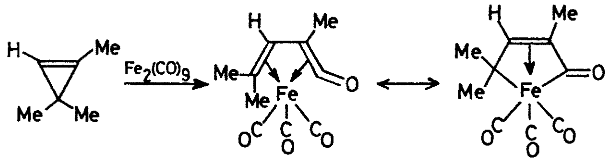
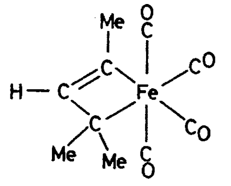
Summary The structure of the vinylketen–iron tricarbonyl derivative $C_6H_{10}COFe(CO)_3$ obtained from 1,3,3-trimethylcyclopropene and $Fe_3(CO)_{12}$ or preferably $Fe_2(CO)_9$ has been shown by *X*-ray crystallography to be 2,4-dimethylpenta-1,3-dien-1-one(tricarbonyl)iron.

IN 1963 one of us[1] reported the reaction of 1,3,3-trimethylcyclopropene (I) with $Fe_3(CO)_{12}$ to give a low yield (<5%) of a yellow crystalline solid of stoicheiometry $C_6H_{10}COFe(CO)_3$ for which a vinylketen–iron tricarbonyl structure was proposed. The asymmetry of 1,3,3-trimethylcyclopropene (I) generated an ambiguity concerning the site of ring opening and hence the location of the methyl groups in the resulting iron carbonyl complex. This communication reports an *X*-ray diffraction structure determination of this complex.

Greatly improved yields (*ca.* 60%) of $C_6H_{10}COFe(CO)_3$ (m.p.[1] 69 °C) can be obtained by reaction of 1,3,3-trimethylcyclopropene (I) with excess of $Fe_2(CO)_9$ in boiling diethyl ether for 4 h using water-cooled and −78 °C reflux condensers in series to minimize losses of the relatively volatile cyclopropene. After removal of the diethyl ether from the filtered solution, the $C_6H_{10}COFe(CO)_3$ can be isolated by low temperature crystallization from hexane and purified further by vacuum sublimation. The i.r. and ^1H n.m.r. spectra of the $C_6H_{10}COFe(CO)_3$ prepared by this method were identical to those previously reported.[1]



(I) (IIa) (IIb)



(III)

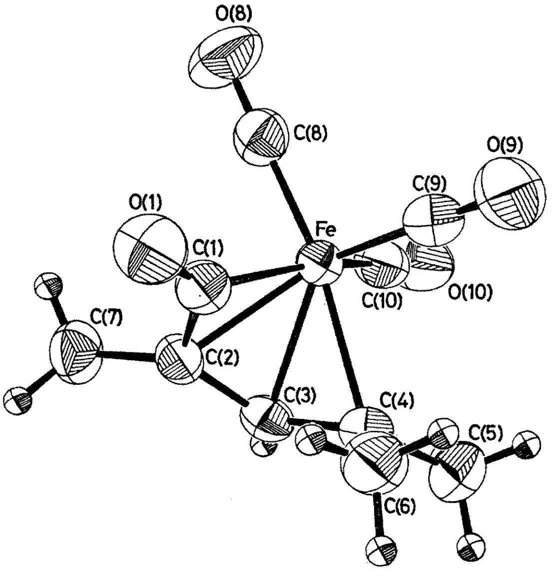


FIGURE. ORTEP drawing of the structure of $C_6H_{10}COFe(CO)_3$ (II).

The complex $C_6H_{10}COFe(CO)_3$ forms monoclinic crystals by sublimation: space group $P2_1/n$; $a = 9{\cdot}252(5)$, $b = 18{\cdot}27(1)$, $c = 6{\cdot}522(5)$ Å, $\beta = 95{\cdot}26(5)°$, $Z = 4$. Least squares anisotropic refinement using the 1342 observed reflections ($R = 0{\cdot}0269$, $R_w = 0{\cdot}0256$) indicates the structure depicted in the Figure.† This structure contains the vinylketen unit and can be represented by a resonance hybrid between the diene complex (IIa) and the 2σ–π 1-ferracyclopent-3-en-5-one structure (IIb). The large contribution of the canonical form (IIb) is indicated by the C(2)–C(1)–O(1) angle of 137° which is intermediate between ideals of 180° for the sp hybridized C(1) carbon in structure (IIa) and 120° for the sp^2 hybridized C(1) carbon in structure (IIb). The four metal–carbon bond distances of the 1—4-η-vinylketen system to the iron, Fe–C(1), Fe–C(2), Fe–C(3), and Fe–C(4), are 1·918(3), 2·107(3), 2·092(3), and 2·201(3) Å which represent a much larger variation than the comparable iron–carbon bond distances in other 1—4-η-1,3-diene iron tricarbonyl complexes.[2] This suggests that the carbonyl carbon atom of the vinylketen ligand participates more strongly in the metal–ligand back bonding than the other three carbons of this η^4-system. The 1—4-η-vinylketen ligand in (II) is unique since one end [C(1)] can participate strongly in ligand-to-metal back bonding because of the electron-withdrawing oxygen atom. This asymmetry in the ligand-to-metal back bonding properties of the vinylketen ligand is not reflected in any anomalies in the carbon–carbon distances C(1)–C(2), C(2)–C(3), and C(3)–C(4) which are 1·439(5), 1·397(4), and 1·414(4) Å corresponding to a typical Δ_2 parameter (difference between the 'inner' C–C distance and the average values of the 'outer' C–C distances)[2] of 0·029 Å for 1—4-η-dieneiron tricarbonyl derivatives. Atoms C(1), C(2), C(3), and C(4) are reasonably planar with C(3) having the largest deviation from planarity (0·07 Å). Atoms C(5), C(6), C(7), and O(1) lie 0·42, 1·14, 0·04, and 0·49 Å respectively from the best plane through C(1), C(2), C(3), and C(4). A related vinylketen ligand was recently[3] identified crystallographically in a product obtained by carbonylation of an η^3-vinylcarbene iron tricarbonyl derivative.

The positions of the methyl groups in $C_6H_{10}COFe(CO)_3$ (II) as determined by *X*-ray crystallography also indicate that the most sterically hindered of the two single bonds in the 1,3,3-trimethylcyclopropene (I) is the one cleaved by the iron carbonyl to form this complex. However, attack of an $Fe(CO)_4$ group at this site, possibly through formation of an intermediate ferracyclobutene (ferretene)[4] (III), may be favoured by increased electron density at the carbon atom of the cyclopropene double bond bearing the electron-releasing methyl group. This suggests that in this case electronic rather than steric factors influence the site of cyclopropene ring opening by iron carbonyls.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The increased availability of $C_8H_{10}COFe(CO)_3$ (II), owing to improvements in its method of preparation outlined above, has allowed a preliminary survey of its chemistry. The carbonyl group of the complexed vinylketen appears to be relatively unreactive as indicated by experiments with hydrazine, $NaBH_4$, and $LiAlH_4$. Reaction of (II) with tetracyanoethylene in boiling benzene for 2 h results in cleavage of the $Fe(CO)_3$ group to give a low yield of a white 1:1 adduct of the free trimethylvinylketen and tetracyanoethylene, m.p. 96—97 °C. A similar reaction of (II) with maleic anhydride in boiling xylene for 2 h gives a light yellow 1:1 adduct, m.p. 170 °C, still containing the $Fe(CO)_3$ group.

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[1] R. B. King, *Inorg. Chem.*, 1963, **2**, 642.

[2] F. A. Cotton, V. W. Day, B. A. Frenz, K. I. Hardcastle, and J. M. Troup, *J. Amer. Chem. Soc.*, 1977, **95**, 4522.

[3] T. Mitsudo, T. Sasaki, Y. Watanabe, Y. Takegami, S. Nishigaki, and K. Nakatsu, *J.C.S., Chem. Comm.*, 1978, 252.

[4] R. M. Moriarty, K.-N. Chen, C.-L. Yeh, J. L. Flippen, and J. Karle, *J. Amer. Chem. Soc.*, 1972, **94**, 8944.