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Preliminary communication

RING CLOSURE OF CYCLOOCTATETRAENETRICARBONYLIRON COMPLEXES: CRYSTAL STRUCTURE OF A BICYCLO[4.2.0]-2,4,7-OCTATRIENETRICARBONYLIRON COMPOUND

MICHAEL COOKE, JUDITH A.K. HOWARD, CHARLES R. RUSS*, F. GORDON A. STONE, and PETER WOODWARD

Department of Inorganic Chemistry, The University, Bristol BS8 1TS (Great Britain)

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Summary

Mono- or di-substituted cyclooctatetraenetricarbonyliron complexes on heating yield isomeric bicyclo[4.2.0]-2,4,7-octatriene compounds; in contrast, the carbonylruthenium analogues afford polynuclear species.

Although cyclooctatetraene (I) exists in equilibrium with its tautomer bicyclo[4.2.0]-2,4,7-octatriene (II), the latter is very unstable converting to I with a half-life of 14 minutes at 0° [1, 2]. It is possible to stabilise II by coordination to a tricarbonyliron group, and complex III has been prepared [3] by refluxing *syn*-tricyclo[4.3.0.0^{2,5}]-3,7-octadienetetracarbonyliron in hexane. There have, however, been no reports that cyclooctatetraenetricarbonyliron forms III by transannular ring closure. The only other example of a metal complex containing the bicyclic octatriene ligand appears to be a tetramethyl derivative, one of the several products obtained from the reaction between 1,3,5,7-tetramethylcyclooctatetraene and enneacarbonyldiiron [4].

A recent synthesis [5] of several mono- and di-substituted cyclooctatetraenetricarbonyliron complexes provides an efficient route via thermolysis to their bicyclic octatriene tautomers.

The deep red crystalline compound (1,2,3,4-η^4)-3-trimethylsilylcyclooctatetraenetricarbonyliron (IVa) on heating (sealed tube, octane, 160°) changed to a yellow oil (ν(CO) in hexane 2044s, 1979s and 1972 s cm^{-1}). The mass spectrum showed that this complex contained an $Fe(CO)_3$ group and that the parent ion was at *m/e* 316**. The ^{1}H NMR spectrum showed a signal due to the trimethylsilyl group (τ 9.7 ppm) and four resonances (τ 3.55s, 4.7dd, 6.9m and 7.1m ppm) of relative intensity 1/2/2/2. The singlet of intensity 1 is characteristic [6] in

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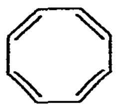
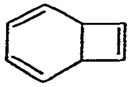
[*] On study leave from the University of Maine (Orono).

[**] All new compounds have been fully characterised by microanalysis and mass spectrometry.



(I)



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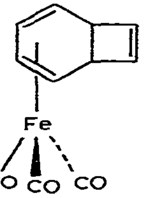
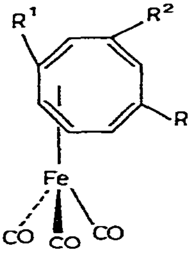
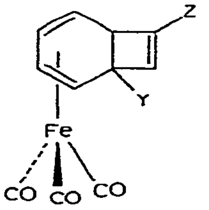


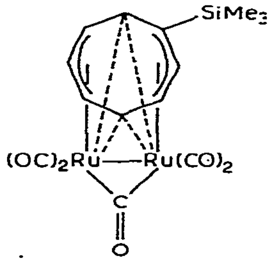
(III)



(IVa, R^1 = $SiMe_3$; R^2 = R^3 = H)
(IVb, R^1 = R^2 = H; R^3 = CPh_3)
(IVc, R^1 = $SiMe_3$; R^2 = CPh_3; R^3 = H)



(Va, Z = $SiMe_3$; Y = H)
(Vb, Z = CPh_3; Y = H)
(Vc, Z = CPh_3; Y = $SiMe_3$)



(VI)

chemical shift for a proton attached to a carbon atom of the double bond of a cyclobutene ring. The spectrum of III shows a singlet (2H) resonance at τ 3.78 ppm [3]. Accordingly, the yellow oil is assigned structure Va with the trimethylsilyl substituent attached to the C=C bond of the cyclobutene ring.

Similar rearrangements occur with cyclooctatetraenetricarbonyliron complexes having ring substituents which are not bonded to a carbon atom of the η^4-diene—iron system. Thus if IVb is heated (sealed tube, octane, 160°), it is converted into Vb (m.p. 174°C, ν(CO) (hexane), 2044s, 1979s and 1973s cm^{-1}, ^1H NMR: τ 2.8 (m, 15H), 4.0 (s, 1H), 4.7 (m, 1H), 5.1 (m, 1H), 6.74 (m, 2H), 6.98 (m, 1H) and 7.3 (m, 1H) ppm)

Studies were carried out on a disubstituted cyclooctatetraeneiron complex IVc in order to confirm unambiguously by X-ray crystallography the structure of these bicyclo[4.2.0]-2,4,7-octatrieneiron compounds and to ascertain the position of the substituents.

Crystals of Vc from hexane are triclinic ($P\bar{1}$) with two molecules in a unit cell of dimensions a = 10.968(4), b = 11.496(4), c = 12.213(5) Å, α = 95.63(3), β = 108.56(3), γ = 91.60(3)°. The structure was solved by heavy atom methods from data (3620) collected on a Syntex $P2_1$ four circle diffractometer to 2θ = 50° (Mo-K_α X-radiation), current R = 0.052.

The molecular structure (excluding H atoms) is shown in Fig. 1 and confirms the overall assignment Vc. The six-membered ring is folded into two planar segments (dihedral angle 142°) about the line C(3) . . . C(8); atoms C(3), C(2), C(1), C(8) comprise the formal diene segment, while atoms C(4) and C(7) form the bridgehead to the cyclobutene ring, C(4), C(5), C(6), C(7). The bond lengths indicate extensive delocalisation in the diene moiety (mean C—C 1.414 Å). The four carbon atoms lie at a mean distance of 2.085 Å from the iron atom, which

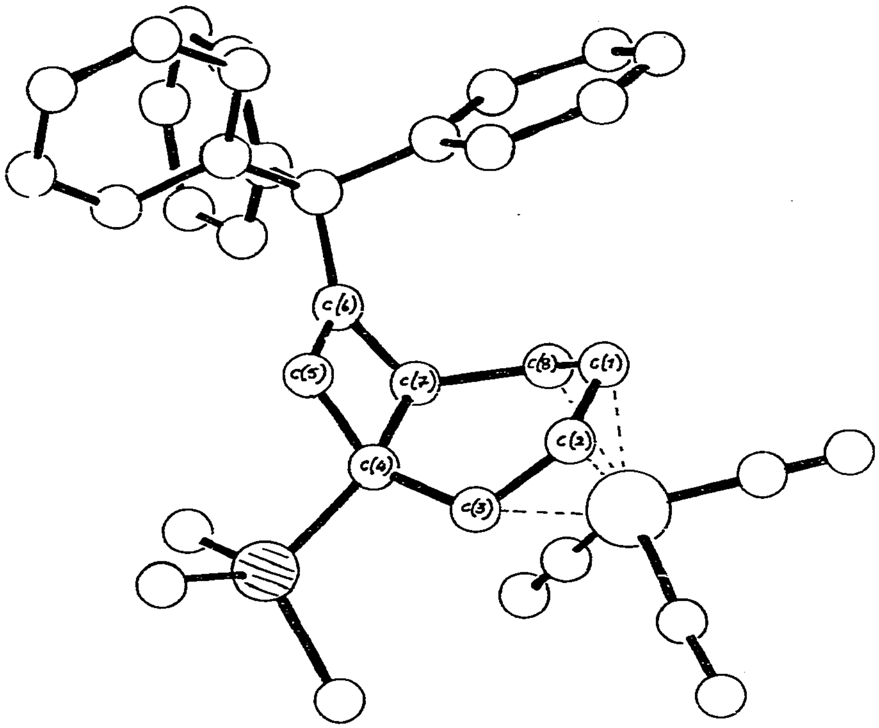


Fig. 1. Molecular structure of the complex $C_8H_6(SiMe_3)(CPh_3)Fe(CO)_3$.

carries the three carbonyl groups in an approximately orthogonal arrangement. The remaining C—C bonds in the two rings, apart from C(5)—C(6) which is a normal double bond at 1.345 Å, have a mean bond length, 1.546 Å, equal to that for single bonds, but the individual magnitudes show that the bridgehead bond C(4)—C(7) is significantly the longest at 1.586 Å.

The cyclobutene ring bends away from the iron atom, making an angle of 117° with the plane of C(3), C(4), C(7), C(8), as would be expected for a tetrahedral configuration at C(4) and C(7). Atom C(4) carries an $SiMe_3$ group in an *endo* configuration relative to the iron atom, while C(7) similarly carries a H atom and C(6) a triphenylmethyl group of which the pivotal C atom is coplanar with the cyclobutene ring. The geometries of the Ph_3C and Me_3Si groups are normal.

In contrast to the behaviour of IVa, the complex (1,2,3,4-η^4)-3-trimethylsilylcyclooctatetraenetricarbonylruthenium rapidly converts in refluxing octane to the binuclear ruthenium compound VI. No evidence for formation of the ruthenium analogue of IVa was obtained. On further heating (sealed tube, octane, 160°) compound VI affords pentalene complexes $(Me_3SiC_8H_5)Ru_3(CO)_8$ (two isomers), previously obtained [7] by reaction of $Me_3SiC_8H_7$ with $[Me_3SiRu(CO)_4]_2$.

The difference in behaviour between the ruthenium-cyclooctatetraene complexes and their iron analogues is further illustrated by the thermolysis of $[Ru(CO)_3(C_8H_7CPh_3)]$ which gives a polynuclear species without affording the ruthenium analogue of Vb.

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