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Preliminary communication

TRICARBONYL[8-ACETYL 2-4:6-7-η-BICYCLO[3.2.1]OCTADIENYLIUM]-IRON, A NOVEL REARRANGEMENT IN THE ACYLATION OF η-$C_8H_8Fe(CO)_3$

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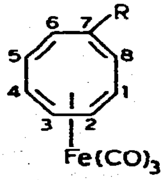
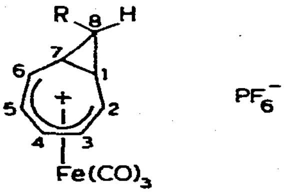
Summary

X-ray diffraction studies have established the molecular structure of the title compound as involving an unexpected [3.2.1]cyclooctadienylium ligand; the implications of this in terms of chemical reactivity are described.

Studies on the cationic complex obtained from the protonation of $C_8H_8Fe(CO)_3$ (Ia) [1, 2] revealed that the bicyclo[5.1.0]cyclooctadienylium ligand produced was bound to the $Fe(CO)_3$ moiety via a pentadienyl fragment (IIa). We have described [3] the reaction of Ia with acetyl chloride under Friedel—Crafts conditions to produce the adduct $[C_8H_8COCH_3Fe(CO)_3]^+$ together with small amounts of the substituted complex Ib. Because of the relationship between protonation and acylation, the bicyclo[5.1.0]structure IIb was proposed for the acyl cation. We have subsequently shown that the reaction of the cation with a range of nucleophiles X^- produces complexes IV—VI in which the mode of coordination of the organic fragment was different from that expected for the addition of X^- to the cation IIb. The basic C_8 unit in complexes IV—VI has been

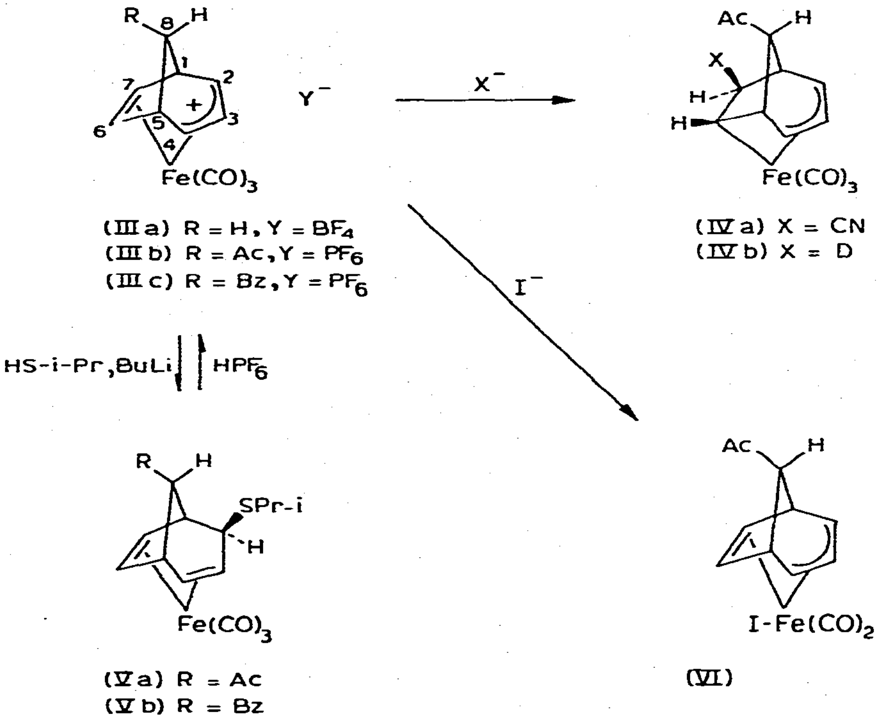


(Ia) R = H
(Ib) R = Ac



(IIa) R = H
(IIb) R = Ac

shown to have a bicyclo[3.2.1] arrangement in solution. Revelation of this alternative structure for the $C_8H_8COCH_3$ ligand prompted a reexamination of the acetyl salt. X-ray diffraction studies have confirmed the [3.2.1] solid state structure for the acetyl cation IIIb.



(IIIa) R = H, Y = BF_4
(IIIb) R = Ac, Y = PF_6
(IIIc) R = Bz, Y = PF_6

(IVa) X = CN
(IVb) X = D

(Va) R = Ac
(Vb) R = Bz

(VI)

Crystals of IIIb are monoclinic, space group $P2_1/c$, $Z = 4$, $a = 8.052(4)$, $b = 14.419(4)$, $c = 14.980(4)$ Å, $\beta = 114.43(6)°$, $U = 1583.5$ Å^3, $D_c = 1.812$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 10.6$ cm^{-1}, 3398 reflections were collected from 2 crystals with an automated Stoe two circle diffractometer, using monochromated Mo-K_α radiation. The data were reduced to a common scale, and averaged to give 1207 reflections with $F > 4\sigma(F)$; no correction was made for absorption. The structure was solved using multi-solution Σ_2 sign expansion in the space group $P2_1/c$ and refined by blocked least-squares $R = 0.047$, $R_w = \Sigma w^{1/2}\Delta/\Sigma w^{1/2}|F_0| = 0.046$. The PF_6^- anions are disordered. Essential crystallographic data are given under Fig. 1.

The C(8) acetyl group is *endo* to the C(6)—C(7) coordinated double bond. This is the only stereoisomer detected in the reaction. Initial electrophilic attack at C(6) or C(7) of Ia in a manner similar to the protonation of Ia [2b] would lead to the bicyclo[5.1.0] intermediate IIb. A rapid (1,4)-suprafacial shift of the C(1)—C(8) or C(7)—C(8) bonds to C(4) would then produce the bicyclo[3.2.1] isomer. This leads to a relief of ring strain in the [5.1.0] structure where the 7-membered ring is necessarily held almost planar by the dienyl fragment [4]. A related rearrangement has been observed in tricarbonyl(2—7-η-bicyclo[6.1.0]-

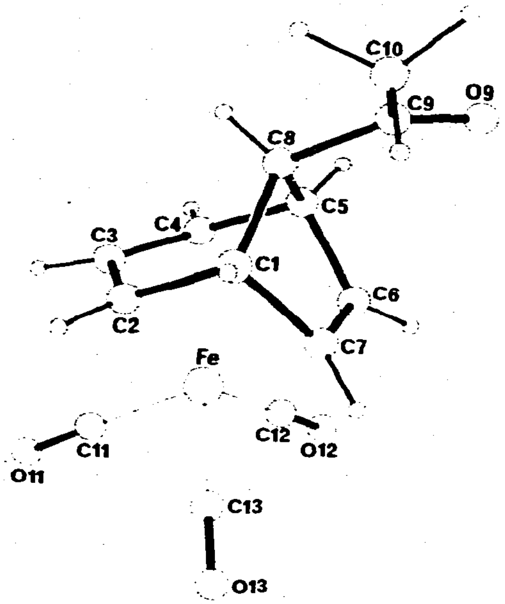


Fig. 1. Molecular structure of IIIb. Mean distance Fe—C(2), Fe—C(3), Fe—C(4), Fe—C(6), Fe—C(7) = 2.181 Å. C(2)—C(3) = C(3)—C(4) = 1.390 Å (mean). C(6)—C(7) = 1.349 Å. Other C—C bonds 1.503—1.530 Å. The acetyl group is twisted towards the atom C(5). The $Fe(CO)_3$ group is distorted from C_{3v} symmetry. Fe—C(CO) = 1.807 Å (mean), C—O(CO) = 1.132 Å. Fe—C—O mean angle 177.7°.

nonatriene)molybdenum [5]. Theoretical considerations by Hoffmann [6] predict the C(1)—C(8) and C(7)—C(8) bonds of the cyclopropane ring in IIb will be weakened by the presence of empty π^* acceptor orbitals α to the apical carbon C(8), with a corresponding strengthening of the C(1)—C(7) bond. In the present example the π^* orbitals are provided by the acetyl carbonyl group.

We have studied the reaction of IIIb and IIIc (prepared in a similar manner [3]) with a number of nucleophiles giving products containing the $Fe(CO)_3$ group coordinated in both σ-allyl (IV) and π-fashion (V). These reactions provide an effective entry into functionalised [3.2.1] compounds previously only available by multi-stage syntheses without substitution at C(8) [7]. The [1—4-η] diene complexes (Va, Vb) are assigned *M-exo* stereochemistry at C(2) by analogy with other ring systems [8] and on steric grounds. An X-ray structure determination of Vb is being undertaken to confirm this assignment. Similarly, an absolute stereochemical assignment at C(7) in complexes IVa, IVb cannot be made on the basis of coupling constants alone, although previous results [9] would suggest *M-exo* stereochemistry.

The structures of the cations IIIb and IIIc in solution have been investigated by ^{1}H NMR. Spin decoupling experiments in the presence of lanthanide shift reagents have confirmed the bicyclo[3.2.1] structure for Va and Vb. Protonation of these thio-ethers with HPF_6 yields the respective parent cations IIIb and IIIc. These cations have essentially identical ^{1}H NMR spectra in acetone-d_6 (IIIb: τ 4.74(t)(H^3), 5.06(t)($H^{2,4}$), 5.58(m)($H^{6,7}$), 6.34(m)($H^{1,5}$), 7.42(s)(H^8), 7.88(s)(Ac) ppm; IIIc: τ 4.62(t)(H^3), 4.96(t)($H^{2,4}$), 5.50(m)($H^{6,7}$), 6.19(m)($H^{1,5}$), 6.49(s)(H^8), 2.01(dd)(2H)(Bz, *o*-H), 2.46(m)(3H)(Bz,*m*,*p*-H) ppm. *J*(IIIb,IIIc):

$J_{2,3} = J_{3,4} = 6, J_{1,4} = J_{4,5} = 6, J_{5,6} = J_{1,7} = 2$ Hz). There is a close similarity between these data and the proton NMR of IIIa [7a], but little correlation with the ^{1}H NMR of IIa [1, 2]. We therefore propose that IIIb and IIIc have the same structure in solution and in the solid state. We have no evidence for any isomerisation to the bicyclo[5.1.0] isomer.

We are studying further aspects of these reactions and the mechanism of rearrangement.

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