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Preliminary communication

THE REACTION OF DIIRONENNEACARBONYL WITH 1,2-CYCLONONADIENE

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Summary

1,2-Cyclononadiene reacts with $Fe_2(CO)_9$ with dimerization of the allene ligand to give the bis(π-allylene)$Fe_2(CO)_6$ complex, which ^{13}C and ^{1}H NMR studies show to be fluxional.

Allenes react with iron carbonyls to give products displaying a variety of bonding schemes. Reaction of allene with $Fe_3(CO)_{12}$ results in dimerization to produce complex I, or, with excess allene, trimerization to produce three isomeric complexes of composition $C_9H_{12}Fe_2(CO)_6$ [1,2]. If $Fe_2(CO)_9$ is used, then in addition to I, a complex $C_3H_4Fe_2(CO)_7$ is obtained [3,4]. The reaction of 1-phenylallene with $Fe_3(CO)_{12}$ gives dimeric products having structures analogous to I [5], whereas tetramethylallene reacts with $Fe_2(CO)_9$ to give a mononuclear $(CH_3)_4C_3Fe(CO)_4$ complex which exhibits rapid tautomerism of the $Fe(CO)_4$ moiety between the two orthogonal π-orbitals of the allene system [6]. Recently, the reaction of several macrocyclic diallenes with $Fe_3(CO)_{12}$ has been reported to occur via an intramolecular cyclization to give bis(π-allylene) complexes of the type II [7].

We have found that the reaction of 1,2-cyclononadiene, the smallest stable cyclic allene, with $Fe_2(CO)_9$ at 35°C proceeded with dimerization of the allene ligand to give the bis(π-allylene)$Fe_2(CO)_6$ complex III (IR (CS_2): 2055, 2014, 1985, 1961 cm^{-1}; mass spectrum: M^+ 524).

Crystals of III, $C_{24}H_{28}Fe_2O_6$ (mol. wt. 524.2) are orthorhombic, space group *Pbca*, with a 17.78, b 26.52, c 10.03 Å, U 4729 $Å^3$, $Z = 8$, with a pronounced tendency for multiple twinning. 2926 reflexions with $\sin\theta/\lambda < 0.7$ $Å^{-1}$ were measured with an automated Stoe—Weissenberg

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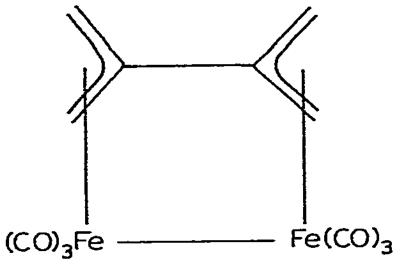
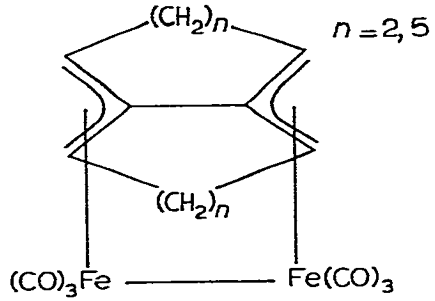


(I)



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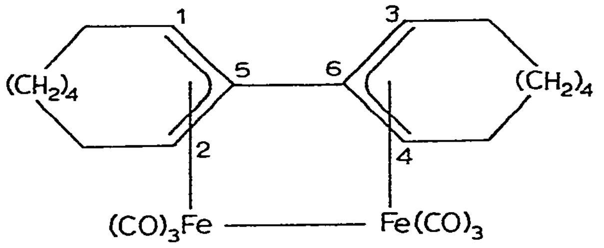


(III)

diffractometer using Mo-K_α radiation and a graphite monochromator. Analysis by conventional methods has yielded the essential details of the molecular structure, but a difference Fourier at R = 0.12 has shown the crystal to contain a minor twinned component, and refinement is therefore not yet complete.

The bis(π-allylene) unit is bound in an unsymmetrical fashion with a good C_2 molecular axis bisecting the Fe—Fe and C(5)—C(6) bonds. The distances Fe(1)—C(1) and Fe(2)—C(4) are shorter (av. 2.10 Å) than the Fe(1)—C(2) and Fe(2)—C(3) (2.19) by 4σ, and C(1)—C(5), C(4)—C(6) (av. 1.45(2) Å) are systematically shorter than C(2)—C(5) and C(3)—C(6) (1.39(2) Å). The four carbons comprising the *trans*-dienoid unit are much closer to planarity than are the four carbons comprising the *trans*-dimethylene-ethane moiety. Thus the torsion angle C(2)—C(5)—C(6)—C(3) is 12°, whereas the torsion angle C(1)—C(5)—C(6)—C(4) is 38°. The iron—iron bond (2.97 Å) is twisted by 12° relative to the C(5)—C(6) bond. Essentially the same molecular geometry has been found for complex I.

Unsymmetrical bonding of an allyl group in a pseudo-σ,π-olefin fashion is well established crystallographically, and is also apparent from ^{1}H NMR studies [8]. Room temperature ^{13}C and ^{1}H studies of complex III indicate, however, the equivalence of the outer allyl positions (1-4) and of positions (5,6) respectively. The ^{1}H NMR spectrum (CD_2Cl_2) consists of a triplet (J 9 Hz) at τ 6.74 due to H(1)-H(4) and a methylene multiplet at τ 7.6-8.7. The undecoupled ^{13}C spectrum (CD_2Cl_2, 0.05 M Cr(acac)$_3$) shows C(1)-C(4) as a doublet (J 140 Hz) at 66.6 ppm and C(5), C(6) as a singlet at 84.4 ppm. The methylene carbons are observed as two overlapping triplets at 28.7

(J 133 Hz) and 34.4 ppm (J 140 Hz). Two carbonyl resonances in the ratio of 1/2 are observed at 211.8 and 215.4 ppm. Localised carbonyl exchange between different sites on the same metal atom is thus not occurring.

Variable temperature studies showed that the molecule was fluxional. The proton decoupled limiting low temperature ^{13}C NMR spectrum (−85°C, Fig.1) showed the fast exchange singlet due to C(1)-C(4) as two pairs of lines of unequal intensity, while the signal due to C(5), C(6) remained unchanged. The methylene resonances increased in complexity, while the carbonyl resonance of intensity two reformed as two singlets of equal intensity. Analogous temperature-dependent behaviour of the proton resonances H(1)-H(4) was also observed.

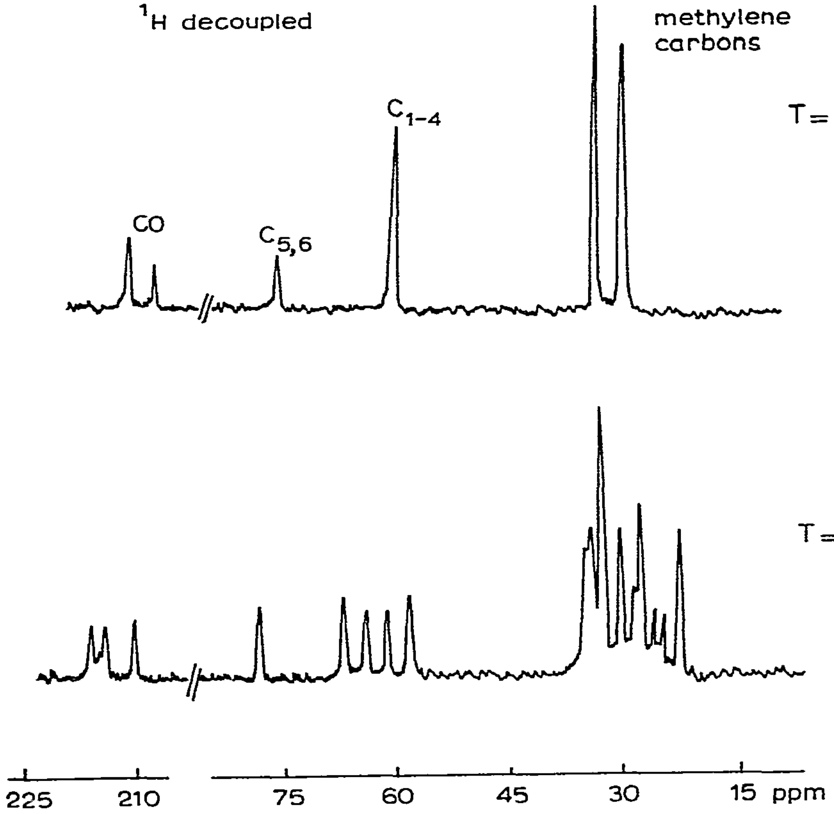
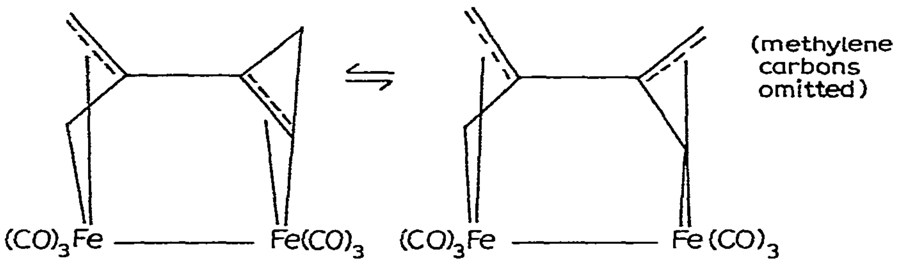


Fig.1. Variable temperature ^{13}C NMR spectra of III.

The C_2 symmetry of the crystallographic molecular ground state requires only two outer allylic signals. We believe that the presence of the two pairs of lines of inequivalent intensity indicates an equilibrium in solution between the two isomers shown below, involving a rapid *cis—trans* isomerization which renders the two sets of outer allyl positions equivalent at room temperature. Such a process is also consistent with the temperature dependent behaviour of the carbonyl resonances and the resonance due to C(5), C(6).

To our knowledge, this represents the first example of allyl fluxionality



of this type. The proposed explanation is not unreasonable, however, in view of the well-documented fluxional behaviour of complexes such as $(C_3H_5)_2Zn$ [9] and $(C_3H_5)Ti(NMe_2)_3$ [10], which possess σ-bonded ground state configurations, although an increase in temperature results in C(1)—C(3) interchange, presumably via a π-allyl intermediate.

Further work on this complex and other related complexes is continuing.

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