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Preliminary communication

TETRACARBONYLDIENEIRON COMPLEXES: PREPARATION AND PROTON ADDITION

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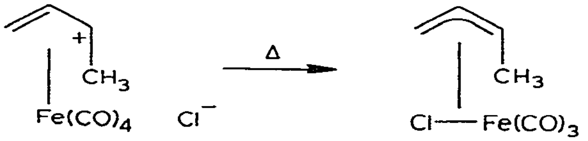
Summary

Three tetracarbonyldieneiron complexes have been characterized; the *s-cis* or *s-trans* nature of the diene ligand in these compounds is dependent upon steric factors and has been established in each case by protonation and deuteration studies which convert them to tetracarbonylallyliron cations in high yield.

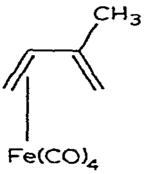
Although the chemistry of tricarbonyldieneiron compounds has been widely investigated, the corresponding tetracarbonyl complexes of dienes have not been thoroughly studied. The parent, tetracarbonylbutadieneiron, was reported by Murdoch and Weiss [1] to be a thermally unstable oil. Reaction of this complex with HCl was reported to yield tetracarbonyl *anti*-1-methyl-π-allyliron chloride; the unstable cation complex was then converted to the covalent chloride (Eqn. 1).



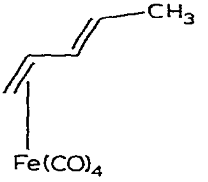
(1)

The assignments of stereochemistry to the organic ligands in these compounds rested on some earlier work by Impastato and Ihrman [2]; for reasons discussed below they are not considered certain.

In monitoring the progress of thermal reactions between several dienes and $Fe_2(CO)_9$ by infrared spectroscopy, we observed that the tetracarbonyl complexes were the predominant components of the reaction mixtures during the early stages of the reactions. Elution chromatography on florisil allowed us to isolate the air-sensitive tetracarbonyl derivatives of 2-methyl-1,3-butadiene and *trans*- and *cis*-1,3-pentadiene (I, II and III, respectively). In each case the NMR spectrum of the crude reaction mixture indicated that it contained a single tetracarbonyl complex together with a small amount of the corresponding tricarbonyldieneiron compound. For reasons discussed below, we have assigned the structures I—III to the tetracarbonyldiene complexes.



(I)



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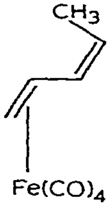
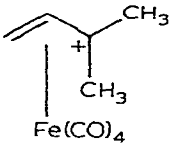


(III)

It was felt that the tetracarbonyldieneiron complexes might afford another synthetic route to tetracarbonylallyliron cations by direct electrophilic addition as with tetramethylalleneiron tetracarbonyl [3]. Proton addition to I might lead to any of the cations IV—VI, depending upon the site of coordination of the $Fe(CO)_4$ group and the conformation of the diene ligand.



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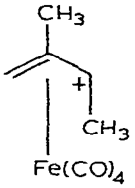

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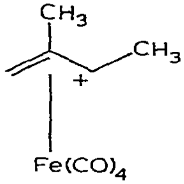

(VI)

The purified derivative from 2-methylbutadiene, I, was an orange-red oil which showed ν(C≡O) at 2090, 2020, 2005 and 1980. The NMR spectrum of I indicates that the $Fe(CO)_4$ moiety is attached to the least substituted double bond: the hydrogens of the vinyl group appear as pairs of doublets at τ 6.43, 7.46 and 7.95, whereas, the terminal methylene hydrogens appear as multiplets at much lower field (τ 5.32 and 5.53) in accord with expectations for hydrogens attached to an uncoordinated double bond*. At this point, however, the NMR data do not allow a definitive assignment of *s-trans* or *s-cis* geometry to the diene ligand.

Reaction of I with HBF_4 in acetic anhydride followed by precipitation in ether gave an 84% yield of the 1,1-dimethyl cation, IV, as the fluoborate salt [5]**. The proton addition reaction did not help in establishing the preferred conformation of the diene ligand, however, since IV is expected from either conformer. Reaction of I with CF_3COOD followed quickly by anion exchange and precipitation gave a fluoborate salt whose NMR spectrum showed (by integration) that a single deuterium atom had been incorporated into the *anti*

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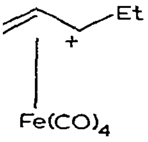
*The high field shifts of the protons bound to coordinated carbon atoms are expected from earlier work on tetracarbonylolefin complexes [4].

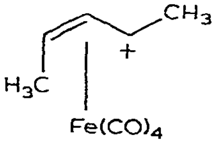
**A small amount of cation V is also seen in solutions of IV; this minor component is thought to arise by intramolecular rearrangement [6].

nethyl group of IV. These data clearly demonstrate that an *s-cis* conformation of he 2-methylbutadiene ligand is present in I.

With the 1,3-pentadiene complexes, also, any of a number of cation omplexes could result from proton addition depending upon the position of the Fe(CO)$_4$ group and the conformation of the diene. Either pentadiene complex ould give rise to any of the cations VII—IX.



(VII)



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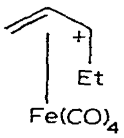

(IX)

lternatively, the *cis* compound could give the *anti,anti*-1,3-dimethyl cation nd the *trans* compound could yield the corresponding *syn,syn* isomer.

Reaction of *trans*-1,3-pentadiene with Fe$_2$(CO)$_9$ gives a single tetracarbonyl omplex, II, in which the Fe(CO)$_4$ group is again coordinated to the least-ubstituted double bond as evidenced by the NMR spectrum: the vinyl hydrogens ppear at τ 6.07 (1H) and 7.65 (2H) and the hydrogens at the noncoordinated ouble bond are seen as a multiplet centered at τ 4.52. Protonation of this ompound (HBF$_4$/AC$_2$O) gives the *syn*-1-ethyl cation [6] in 97% yield, thus owing that the *s-trans* conformation is preferred for the diene ligand.

A single tetracarbonyldiene complex, III, is also obtained from *cis*-1,3-entadiene and the Fe(CO)$_4$ moiety is attached to the vinyl position in this ompound as well. As reported earlier [6], III is converted exclusively to the *n*-1-ethyl cation. Reaction of II or III with CF$_3$COOD followed by anion xchange gives the *syn*-1-ethyl fluoborate salt with a single deuterium atom in e methylene group.

The inductive effect of the methyl group in each of the dienes might be pected to direct the Fe(CO)$_4$ moiety to the more highly-substituted double ond; however, the non-bonded interactions in the resulting complexes would be vere and it has been argued with simple olefins that their donor properties are rther offset by reduced back bonding when alkyl substituents are present [7]. he conformation of the diene in the tetracarbonyl derivatives appears to be etermined by steric factors; the deuteration studies indicate that the *s-cis* form preferred when a methyl group is bonded to the diene carbon adjacent to the tracarbonyl olefin unit.

With these considerations in mind, it seems likely that the preferred nformation of the diene ligand in tetracarbonylbutadieneiron is *s-trans*; this nformer should lead to the *syn*-1-methyl cation complex rather than the *anti* omer postulated earlier. Studies are in progress to establish this as well as the eans by which these tetracarbonyl complexes are converted to the *s-cis* tri-rbonyldieneiron compounds.

cknowledgement

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References

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