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Preliminary communication

ANTI TO *SYN* ISOMERIZATION IN π-ALLYLIRON CARBONYL COMPLEXES

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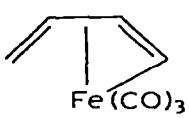
Summary

Tetracarbonylallyliron cations having *anti*-1 substituents are isomerized to the corresponding *syn* isomers upon heating; these results have led us to reinterpret some other isomerizations involving π-allyl ligands of iron in terms of *anti* to *syn* rearrangements.

Although *anti*—*syn* isomerism has been demonstrated in π-allyl ligands of several transition metals [1], it has not been observed in the corresponding iron compounds. We have recently studied the behavior of several tetracarbonylallyliron cations in which the allyl ligand bears an *anti*-1-methyl group and determined that these compounds are configurationally unstable. Thus *anti*-1-methyltetracarbonylallyliron fluoroborate [2] is converted to the corresponding *syn* isomer (compound I in Table 1) after 36 h at 60° in CF_3COOH or SO_2 and the *anti,syn*-1,3-dimethyl cation (II) [3] requires 16 hours for isomerization to the *syn,syn* isomer (III). With the *anti*-1-isopropyl-2-methyl cation. the conversion is difficult and requires about 6 days at 70° to produce IV.



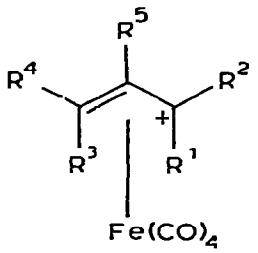
(VI)

Cation III (together with II) is also obtained in the disproportionation reaction of tricarbonyl-*cis*-1,3-pentadieneiron (VI). Earlier [4] this cation had been assigned the *anti,anti* stereochemistry, however, comparison of our NMR data from this cation with that of others necessitates its reassignment as the *syn,syn* isomer. In this series, *cis* hydrogens have *J* values averaging 7.0 Hz whereas the average *trans* value is 11.7*; the value of 12.0 Hz for $J_{1,5}$ (or $J_{3,5}$)

* D.K. Erwin, unpublished results.

TABLE 1

PROTON NMR DATA OF TETRACARBONYLALLYLIRON CATIONS IN CF_3COOH SOLUTION[a]



Compound	R^1	R^2	R^3	R^4	R^5
I	H	CH_3	H	H	H
	5.45(m)	7.84(d)	7.02(d of d)	5.91(d of d)	4.16(m)
II	CH_3	H	H	CH_3	H
	8.27(d)	4.56(m)	4.91(m)	7.16(d)	4.31(m)
III	H	CH_3	H	CH_3	H
	5.76(m)	7.89(d)	5.76(m)	7.89(d)	4.25(t)
IV	H	$(CH_3)_2CH$	H	H	CH_3
	5.89(m)	8.51(d), 8.56(d), 7.44(m)	7.16(d)	6.00(d)	7.51(s)
V	H	CH_3CH_2	H	H	H
	5.53(m)	7.58(m), 8.65(t)	7.04(d of d)	5.97(d of d)	4.27(m)

[a] Peak positions are in τ units relative to internal tetramethylsilane.

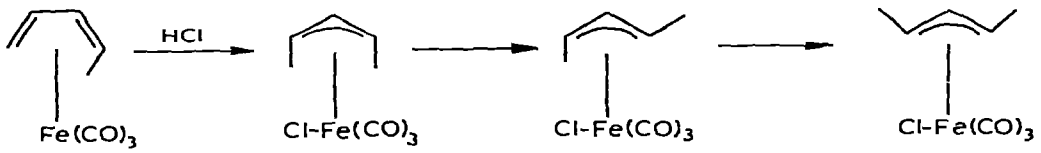
thus demands *syn,syn* stereochemistry for the methyl groups in III*. Quenching of the reaction shows that isomerization of the *cis* diene complex (VI) to the *trans* isomer is complete after a few minutes at room temperature in HBF_4/CF_3COOH.

The pathway originally formulated [5] for HCl addition to a tricarbonyldieneiron complex involved a rotation step in which the initial coordinatively unsaturated adduct would transfer a chlorine to the iron atom as the *anti*-1-methyl group shifted to the *syn* position. Consistent with this mechanism was the observation that HCl addition to tricarbonyl-*trans*-1,3-pentadieneiron afforded tricarbonyl-*syn,syn*-1,3-dimethylallyliron chloride**. More recently it has been shown that this type of mechanism is not operative for tricarbonyl-3-methyl-1-phenylbutadieneiron in reaction with HCl or DCl [6].

After our observations on the behavior of *cis* diene complex VI with HBF_4, it seemed that HCl addition to it might yield interesting results; indeed, the covalent chloride product is the same as that obtained from the *trans* diene complex although *cis—trans* isomerization is not observed (nor was it expected since the work on DCl addition [6] indicates that it is not readily reversible). We propose that the final stereochemistry of the allyl ligand in the HCl addition is established through a sequence of rapid *anti—syn* isomerizations

* These values are similar to the J_{cis} and J_{trans} values which have been reported for other π-allylmetal complexes [1].

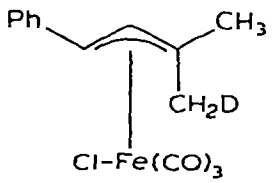
** For this compound we have found that $J_{1,2}$ is equal to 12.6 Hz; the magnitude of the coupling constant thus supports the original assignment of *syn,syn* stereochemistry to the methyl groups.



(1)

(eqn.1). The driving force for the easier double conversion in the HCl reaction can probably be attributed to the greater steric bulk of an axial [7] halogen over a carbon monoxide.

Whether the rearrangements reported here involve σ complexes, such as those suggested for related reactions [8], is not yet known. The fact that Whitesides and Arhart [6] found deuterium exclusively in the *anti*-methyl substituent in the product A may result from a higher activation energy needed for the formation of the requisite σ complex in which iron is coordinated to the disubstituted terminus. In this regard, Faller and his coworkers [9] have reported an increase in free energy of activation of 1-3 kcal/mol per substituent at the terminal position for *anti* to *syn* isomerizations with related π-allylpalladium complexes.



(A)

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