Journal of Organometallic Chemistry, 82 (1974) 257—260

THE PREPARATION AND STUDY OF COMPLEXES OF THE TYPE [(DIENYL)(DIOLEFIN)Fe(CO)]BF_4 AND (DIOLEFIN)(DIOLEFIN)-Fe(CO)

J. ASHLEY-SMITH, D.V. HOWE, B.F.G. JOHNSON, J. LEWIS and I.E. RYDER

University Chemical Laboratory, Lensfield Road, Cambridge CB2, 1 EW (Great Britain)

(Received July 1st, 1974)

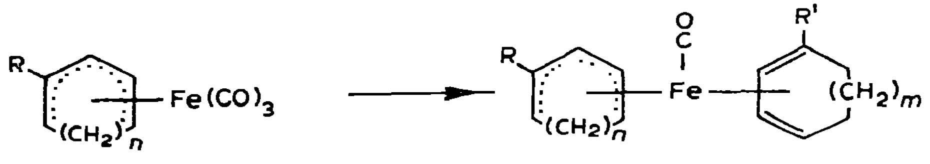
Summary

Mixed diolefin complexes of iron of the types (diolefin)(diolefin)Fe(CO) and [(dienyl)(diolefin)Fe(CO)]BF_4 have been prepared and their reactivity towards nucleophilic and electrophilic reagents examined.

There has been considerable interest in recent years in the preparation and reactivity of d^8 metal olefin complexes because of their significance in organic synthesis. In particular there have been extensive studies on the formation and properties of diolefintricarbonyl complexes of iron, whilst there have been few reports on the reactions of complexes containing two diolefinic ligands. The present work stems from interest in the effect of auxiliary ligands on the reactivity of coordinated olefins and the study of competitive reactions between different diene groups. Recently the direct preparation of several bis(diolefin)-iron monocarbonyl complexes from iron pentacarbonyl has been reported [1]. However, this preparative route leads only to complexes in which the two olefins are identical. Mixed olefin complexes have been obtained previously but only for the case where one olefin is cyclooctatetraene [2].

This communication deals with the isolation of a number of mixed diolefin complexes of iron of the types (diolefin)(diolefin)Fe(CO) and [(dienyl)-(diolefin)Fe(CO)]BF_4.

Irradiation of dienyl(tricarbonyl)iron cations of type I (where n = 1,2 or 3) in dichloromethane and in the presence of the appropriate 1,3-diene yields the cations II in yields of 70-80%. These cations were readily identified on the basis of their spectroscopic data. All show one carbonyl band at ca. 2020 cm^{-1} in their infrared spectrum, which shows little dependence on the olefins employed. Their ^{1}H NMR spectra are consistent with the presence of dienyl and diene



(I) (II)

Ia, $n = 1$, R = H
Ib, $n = 2$, R = H
Ic, $n = 3$, R = H
Id, $n = 1$, R = OMe

IIa, $n = 1$, $m = 2$; R = H, R' = H
IIb, $n = 1$, $m = 3$; R = H, R' = H
IIc, $n = 2$, $m = 0$; R = H, R' = Me
IId, $n = 2$, $m = 2$; R = H, R' = H
IIe, $n = 2$, $m = 3$; R = H, R' = H
IIf, $n = 3$, $m = 2$; R = H, R' = H
IIg, $n = 1$, $m = 2$; R = OMe, R' = H

species and assignments were made on the basis of selective proton decoupling studies on the complex IIa, Fig. 1.

Assuming an *idealised* octahedral geometry for these cations, e.g. complex IId, two isometic forms (A and B, Fig. 2) are expected [3]. These possibilities are not easily differentiated on the basis of the ^{1}H NMR data (Fig. 1). However, the fully proton decoupled ^{13}C spectrum under ambient conditions showed only seven non tertiary resonances, corresponding to carbon atoms a-g (see Fig. 2 and Table 1), expected for the symmetric isomer A. The spectrum was temperature-independent down to −60°, strongly suggesting that the seven resonances correspond to a ground state structure and not some rapidly equilibrating form. An additional resonance was observed at 224.3 ppm in the presence of $Cr(acac)_3$ as relaxation agent and corresponds to the coordinated CO group.

In contrast to the behaviour of six and seven membered diene systems, irradiation of the dienyls Ia and Ib in the presence of the eight membered

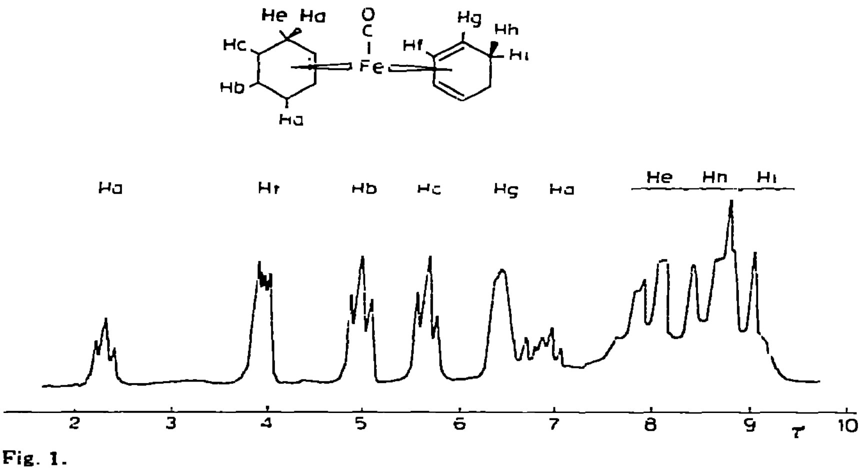
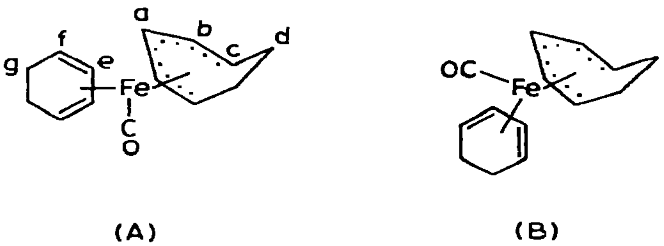


Fig. 1.



(A) (B)

Fig. 2. Possible structures for complex IId.

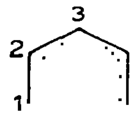


Fig. 3. Possible points of nucleophilic attack on a dienyl

rings, 1,3-cyclooctadiene, 1,5-cyclooctadiene and cyclooctatetraene followed a different course. Here disproportionation of the dienyl complexes was observed. Irradiation of the dienyl in the absence of any additional diene gave the same result. Thus, the reaction of complex Ia gave cyclohexadiene(tricarbonyl)-iron and benzene, whilst in constrast, irradiation of complex Ib yielded the monocarbonyl cation IIe.

All the cations undergo nucleophilic addition with a range of nucleophiles but the products obtained depend upon the ring size of the initial dienyl fragment and the nucleophile employed. The 6-membered dienyl cation IIa undergoes reduction with borohydride to give the bis(1,3-cyclohexadiene)monocarbonyl-iron. Treatment with borodeuteride showed that attack occurs at the 1-position of the dienyl (Fig. 3) to give the *exo* derivative. We find that with the 7-membered dienyl cation IId, attack by borohydride occurs in the 3-position leading to the (1,4-cycloheptadiene) complex III. This complex undergoes a subsequent rearrangement to give the 1,3-cycloheptadiene derivative. A previous report of this aspect of the work has been made [4]. Addition of cyanide to complex IId also leads to the 1,4-isomer. Reaction of IId with the methyllithium carbanion or the acetylacetonate anion apparently follows different courses to produce substituted 1,3-diene complexes. It is probable that attack of methyllithium does occur initially at the 3-position, but the product undergoes rapid isomerisation to the 2-substituted 1,3-derivative. In contrast the acetylacetonate anion attacks at the 1-position giving rise to a 5-substituted 1,3-derivative. The 8-mem-

TABLE 1

^{13}C NMR SPECTRUM OF COMPLEX IId ASSIGNED BY SELECTIVE PROTON DECOUPLING

Chemical shift (ppm) relative to TMS	Assignment	
24.1	d,g	
32.4		
77.9		b,c
88.8	f	
89.0		
97.7	e	
107.6	a	
224.3	CO	

bered dienyl cation IIf also undergoes attack by borohydride to give a species, which rearranges at room temperature. The PMR of this complex shows a resonance at τ 4.6 characteristic of a 1,4-diene. Sublimation of the complex in vacuo gives bis(1,3-cyclohexadiene)monocarbonyliron.

An unusual and important facet of the chemistry of the 1,4-diene complex III is the ease with which the 1,4-diene may be displaced by ligands such as tertiary phosphines or cyclooctatetraene.

Cyclooctatetraene(1,3-cyclohexadiene)monocarbonyliron shows a temperature-dependent proton NMR spectrum in which the cyclooctatetraene exhibits four resonances at $-85°$ [2]. The presence of two different diene groups bonded to the iron allows a comparison of the relative reactivity of the two ring systems. The cyclooctatetraene group shows a greater reactivity than the cyclohexadiene group. Thus the complex undergoes electrophilic attack by a proton to give the bicyclic dienyl complex and adds trityl to form the 1,2,3,4,5-*pentahapto*-6-triphenylmethyl-6-octenyl complex in complete analogy with the cyclooctatetraeneiron tricarbonyl complex [5-7].

Acknowledgements

We thank the S.R.C. for financial support.

References

1 E.K. Von Gustorf, J. Bruchkremer, Z. Pfarrer and F.W. Grevels, Angew. Chem., Int. Ed. Engl., 10 (1971) 260.
2 A. Carbonaro and A. Greca, J. Organometal. Chem., 25 (1970) 477.
3 M.R. Churchill and F.R. Scholer, Inorg. Chem., 8 (1969) 1950.
4 B F.G. Johnson, J. Lewis, T.W. Matheson, I.E. Ryder and M.V. Twigg, J. Chem. Soc., Chem. Commun., (1974) 269.
5 A. Carbonaro and F. Cambisi, J. Organometal. Chem., 44 (1972) 171.
6 A. Davidson, W. McFarlane, L. Pratt and G. Wilkinson, J. Chem. Soc., (1962) 4821.
7 B.F.G. Johnson, J. Lewis and W. Quail, J. Chem. Soc. Dalton Trans., submitted for publication.