Tetrahedron Letters No.34, pp. 3705-3706, 1968. Pergamon Press. Printed in Great Britain.

REMOVAL OF OMe FROM TRICARBONYL-1- OR -2-METHOXYCYCLOHEXA-1,3-DIENEIRON COMPLEXES : A NOVEL PREPARATION OF TRICARBONYL-π-CYCLOHEXADIENYLIRON SALTS

A.J. Birch and M. Haas
Research School of Chemistry, Australian National University
P.O. Box 4, Canberra, A.C.T. Australia.

(Received in UK 14 March 1968; accepted for publication 27 May 1968)

Tricarbonyl-1- and -2-methoxycyclohexa-1,3-dieneiron derivatives are readily available, although usually as mixtures, by reaction of iron carbonyls with the 1-methoxycyclohexa-1,4 dienes produced by reduction of methoxybenzenes with metal-ammonia solutions[1]. π-Dienyl salts, still containing OMe, can be obtained from these by hydride abstraction[1] in a manner analogous to the similar production of π-dienyl salts from alkylcyclohexa-1,3-dieneiron complexes[1,2]. Such salts can also be obtained from neutral complexes by removal of other anions such as OMe from positions allylic to the complexed diene system. Usually mixtures are thus obtained, not readily separated.

We now report another method involving removal of OMe from the 1- or 2-position of the complexed dienes above, which is useful because of the ready availability of the starting-materials, because the products are independent of the mixed nature of the original complexes and because the products usually differ from the isomers obtainable by hydride abstraction from the related alkylcyclohexa-1,3-dieneiron complexes. They may in some cases also be pure salts. The process, involving a rapid reaction in cold concentrated sulphuric acid, followed by precipitation of any salt by addition of excess dry ether, can also be used to equilibrate the isomeric neutral alkylcyclohexa-1,3-dieneiron complexes. For example (I,R=H) gives (III,R=H) in 70% yield (isolated as the hexafluorophosphate salt), and a mixture of (I,R=H)(33%) and (II,R=H)(67%) gives (III,R=H) in the same yield, indicating probable equilibration of the neutral complexes or of a protonated intermediate. That equilibration can occur is shown by the conversion, with 92% recovery, of a mixture of (IV,R=H)(50%) and (V,R=H)(50%) into a mixture of the same compounds in the ratio 67:33. Similarly a mixture of (IV,R=Me)(67%) and (V,R=Me)(33%) gives, with 95% recovery, the same substances in the ratio 86:14, unaltered by further treatment and presumably indicative of a thermodynamic equilibrium.

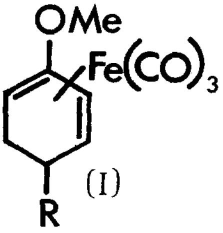
The structures are chiefly based on analyses and NMR spectra[1]; the nature of mixtures being readily defined by the latter[1].

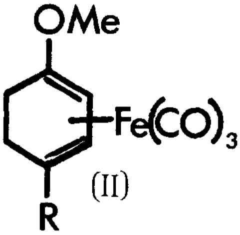
Examples of pure salts obtained are from the mixture of (I,R=Me)(54%) with (II,R=Me) (46%) which gives pure (VI); and from the mixture of isomers obtained[1] from 1-methoxy-3-methylcyclohexa-1,4-diene and pentacarbonyliron which gives pure (III,R=Me). The mixed complexes from 1-methylcyclohexa-1,4-diene gives, by hydride abstraction, a mixture of these two salts, together with a third isomer.

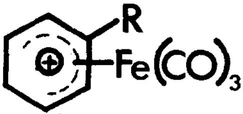
Reduction of (III,R=Me) with borohydride gives pure (IV,R=H), not directly obtainable from 1-methylcyclohexa-1,4-diene[1], while (VI) gives equal proportions of the two neutral complexes (IV,R=H) and (V,R=H) by addition of hydride to both terminal positions.

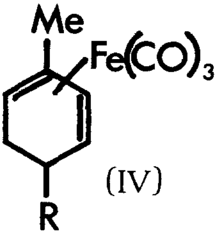
The process probably involves reversible protonations leading to equilibration of various diene complexes via the π-allyl complexes, the isomer of type (VII) undergoing rapid and irreversible loss of OMe to give, in this case, the salt (III,R=H). Even if the type (VII) is only a minor component of equilibria, the irreversibility of the final stage will lead to complete conversion into the salt.

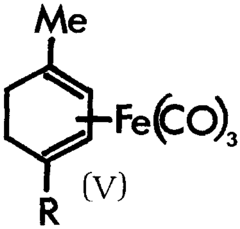
Further discussions of the mechanism and relation between precursors and products will be published elsewhere.

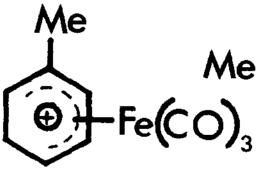

(I)

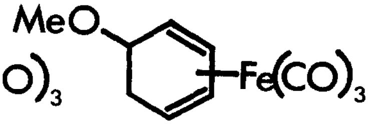

(II)


(III)


(IV)


(V)


(VI)


(VII)

REFERENCES

1. A.J. Birch, P.E. Cross, J. Lewis, D.A. White and S.B. Wild, J.Chem.Soc. (A), 332 (1968) and references therein.

2. R. Pettit and G.F. Emerson, Advances in Organometallic Chemistry, Vol.1, p.30 Academic Press N.Y. (1964).