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Preliminary communication

THE DIFFERENT STERIC ENVIRONMENTS OF THE 5-*exo*- AND 5-*endo*-SUBSTITUENT FOR A PAIR OF ISOMERIC TRICARBONYL(METHOXYCYCLOHEXA-1,3-DIENE)IRONS

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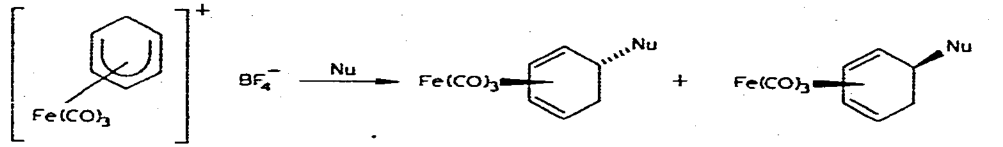
Summary

A shift reagent has been employed to demonstrate the sterically-hindered environment of the methoxy group in tricarbonyl(5-*endo*-methoxycyclohexa-1,3-diene)iron relative to that of the methoxy group in the 5-*exo* analogue.

We are currently investigating the reaction of nucleophiles towards tricarbonyl(cyclohexadienyl)iron tetrafluoroborate (I). It has been shown that the initial product of reaction is the 5-*exo*-substituted species (II) [1]. However, for Nu = $^-$OMe, $^-$OEt and $^-$O-n-Pr, a second species may be obtained, namely the 5-*endo*-substituted compound (III) [2]:



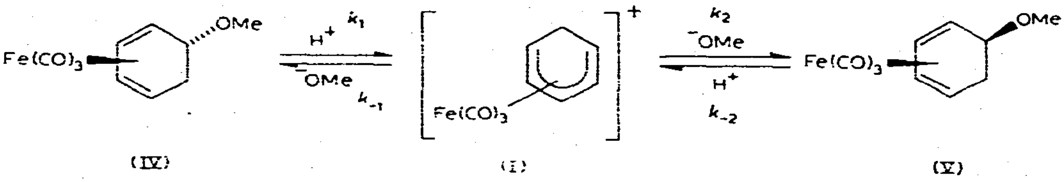
(I) (II) (III)

e.g. Nu = $^-$OMe, $^-$OEt, $^-$O-n-Pr, $^-$CN, $^-$CH(CO$_2$Et)$_2$, HNMe$_2$, $^-$SMe

Nu = $^-$OMe, $^-$OEt, $^-$O-n-Pr

Thus, when I is stirred in methanol under nitrogen at room temperature, tricarbonyl(5-*exo*-methoxycyclohexa-1,3-diene)iron (IV) is rapidly formed in good yield. However, if the resultant solution is heated to reflux, a second species, tricarbonyl(5-*endo*-methoxycyclohexa-1,3-diene) iron (V) is observed, and the relative ratio of V/IV increases with time until an equilibrium of 60%

V, 40% IV is attained. That this is a true equilibrium was shown by treating a pure sample of V with acidified methanol at reflux, whence the same final ratio of V/IV was obtained, although the rate of attainment of equilibrium was much slower from this direction ($k_{-2} < k_1$, Scheme 1) and it is envisaged that the exchange process proceeds via a common intermediate I viz.:



That the *endo* isomer less readily underwent reaction is thought to be due to steric hindrance on the *endo* face towards protonation* of the methoxy substituent. The *exo* isomer should be relatively free from steric constraints and will thus protonate more readily.

Although this view is quite widely held, it has as yet never been subjected to an experimental determination. In order to demonstrate the different steric environments enjoyed by the isomeric pair, IV and V we undertook a europium shift experiment.

To a deuterochloroform solution of a mixture of the isomers (60% *exo*, 40% *endo*, 0.06 g in 0.5 ml, 0.48 mol l^{-1}) was added sequentially ~0.01 g,

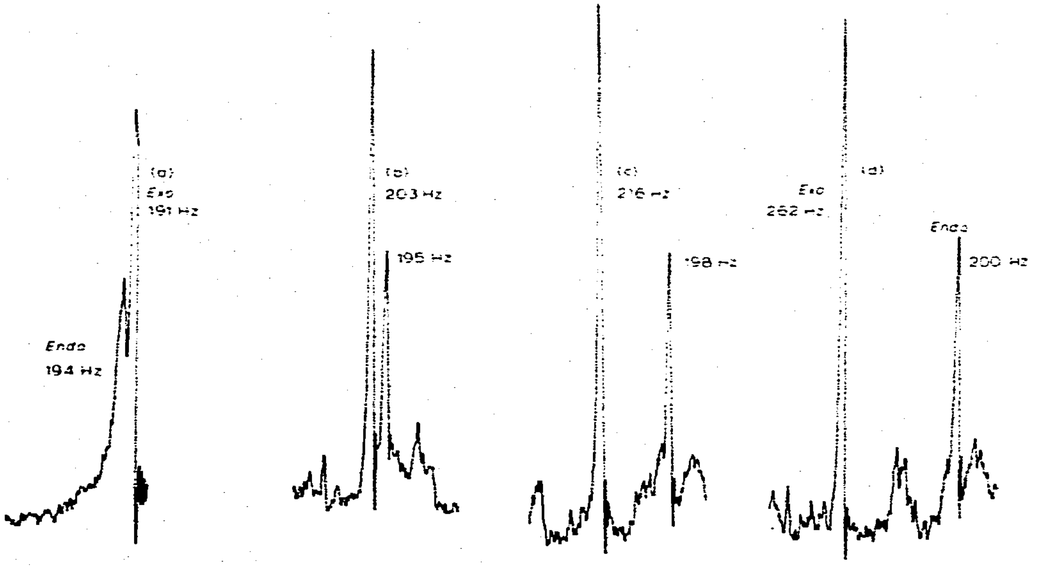


Fig. 1. Effect of $Eu(fod)_3$ on methoxy resonances of a $CDCl_3$ solution containing 60 mg (60% *exo*, 40% *endo*) tricarbonyl(5-methoxycyclohexa-1,3-diene)iron (TMS ref.) (a) No shift reagent, (b) +0.011 g $Eu(fod)_3$, (c) +0.017 g $Eu(fod)_3$, (d) +0.029 g $Eu(fod)_3$.

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*In a polar solvent such as methanol, the proton will be heavily solvated, and this together with its counter ion BF_4^- gives the protonating species considerable bulk.

10^{-5} mol, portions of (tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionate)europium(III) [Eu(fod)$_3$]. The results obtained are shown in Fig. 1. With no shift reagent added (a), the *exo*-methoxy resonates at a slightly higher field than its *endo* counterpart due to the shielding effect of the π-orbitals of the diene [3]. On addition of 0.01 g of Eu(fod)$_3$ the *exo*-methoxy is shifted to lower field by 12 Hz, whilst the *endo*-methoxy barely moves ~1 Hz (b). Successive additions of Eu(fod)$_3$ (c,d) serves to magnify the shift differences of the two isomers.

The above result argues in favour of the *endo*-methoxy being sterically shielded relative to the *exo*-methoxy, and thus gives good support for the observed differing rates of protonation.

References

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2 K. Hine, B.F.G. Johnson and J. Lewis, J. Chem. Soc. Chem. Commun., (1975) 81.
3 cf. P.L. Pauson, G.H. Smith and J.H. Valentine, J. Chem. Soc. C, (1967) 1057, 1061.