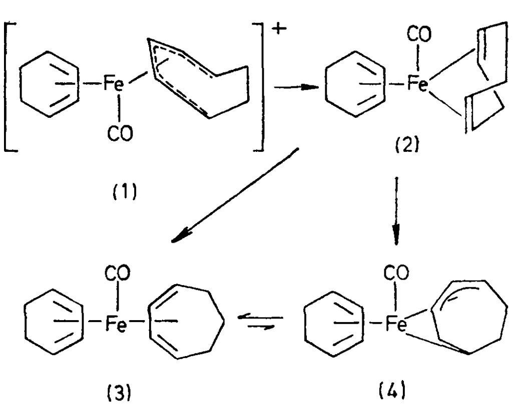
Cyclohepta-1,4-diene(cyclohexa-1,3-diene)(carbonyl) iron

By Brian F. G. Johnson, Jack Lewis,* Trevor W. Matheson, Ian E. Ryder, and Martyn V. Twigg
(*University Chemical Laboratory, Lensfield Road, Cambridge* CB2 1EW)

Summary Borohydride reduction of the complex cation $[(C_7H_9)Fe(CO)(C_6H_8)]^+$ affords $1,4\text{-}C_7H_{10}Fe(CO)(C_6H_8)$ which thermally isomerises into $1,3\text{-}C_7H_{10}Fe(CO)(C_6H_8)$ and h^4-$1,3,4,5\text{-}C_7H_9Fe(CO)(C_6H_8)$.

Nucleophilic addition to a co-ordinated dienyl grouping is predicted, on the basis of charge-density consideration, to occur at either the 1- or 3-position.[1] Addition to the 1-position is observed but no previous report of addition at the 3-position has appeared. Recent work has shown that, in contrast to prediction, attack may apparently occur at the 2-position to generate a h^4-1,3,4,5-bonding mode.[1,2] We now present experimental evidence which suggests that the initial nucleophilic attack can take place at the 3-position to produce an unstable 1,4-diene complex which then undergoes isomerisation to the 1- and 2- substituted derivatives.

Irradiation of $[C_7H_8Fe(CO)_3]BF_4$ in CH_2Cl_2 in the presence of cyclohexa-1,3-diene yields the cationic complex $[C_7H_9Fe(CO)C_7H_8]BF_4$ (**1**) in moderate yields. This complex was readily characterised by the usual analytical and spectroscopic methods. On the basis of ^1H and ^{13}C n.m.r. structure (**1**), in which the 3-position of the dienyl fragment is



trans to the carbonyl ligand, was confirmed. Reduction of (**1**) with $NaBH_4$ yielded the orange complex $C_7H_{10}Fe(CO)$-C_6H_8 (**2**) as the major product. In addition smaller amounts of the 1,3-diene complex (**3**) were also produced. The ratio of these products, (**2**)/(**3**), (*ca.* 9/1) indicates that hydride attack occurs preferentially at the 3-position. The proton-decoupled ^{13}C n.m.r. spectrum of (**2**) is different to those found for (**3**) and the σ,π-allyl complex (**4**) and shows seven non-tertiary carbon resonances. The uncoupled spectrum exhibits four low-field doublets and three higher-field triplets. These data are fully consistent with structure (**2**) which involves a co-ordinated 1,4-diene unit. The ^1H n.m.r. spectrum is compatible with this structure displaying a doublet of doublets at 4·31τ (2H) which may be assigned to the two *inner* protons of the C_6H_8 ligand.[3] Further support for this structural assignment comes from the thermal isomerisation which complex (**2**) undergoes. On warming heptane solutions of (**2**) the ν_{CO} band (1952 cm^{-1}) slowly disappears and is replaced by two new bands at 1961 cm^{-1} and 1946 cm^{-1}. These are assigned to complexes (**3**) and (**4**) respectively. The ^1H and ^{13}C n.m.r. spectra of the final solution are also interpreted in terms of a mixture of complexes (**3**) and (**4**). Complex (**4**) undergoes further rearrangement at higher temperatures (90°C) to give an equilibrium mixture of (**3**) and (**4**) containing *ca.* 90% of (**3**). The cyclohepta-1,3-diene complex (**3**) may be isolated by removal of the solvent under vacuum followed by sublimation *in vacuo.*

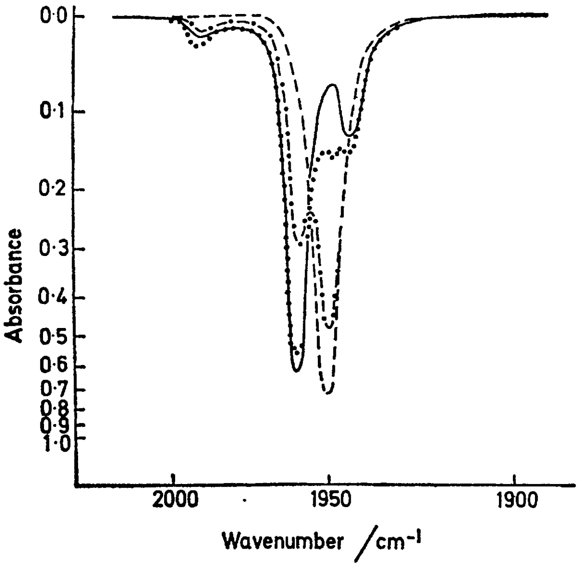


FIGURE. Changes in the i.r. spectrum during the thermal rearrangement (**2**) → (**3**) + (**4**) at 60° in n-heptane. Initial spectrum ----------, t = 8 min. .-.-.-.-.-., t = 18 min. ...., t = 77 min. ———.

The kinetics of the rearrangement of (**2**) were followed by monitoring changes in the i.r. spectrum (see Figure). Good first-order rate plots were obtained by monitoring the increase of absorbance at 1961 cm^{-1} or the decrease of absorbance at 1952 cm^{-1}, and at a given temperature both rate constants so determined agreed to within $\pm 5\%$. A linear Eyring plot over the temperature range 40—70°C was obtained: $\Delta H^\ddagger = 25{\cdot}1 \pm 0{\cdot}6$ kcal mol^{-1}, $\Delta S^\ddagger = 3 \pm 2$ cal mol^{-1} K^{-1}, $k_{obs} = 3{\cdot}6 \times 10^{-4}$ s^{-1} (50°C).

Reaction of complexes (**2**) and (**3**) with carbon monoxide revealed a surprising difference in labilities of the co-ordinated dienes. Thus whereas over prolonged periods complex (**2**) reacts with CO (1 atm., 20°C) to produce $C_6H_8Fe(CO)_3$; complex (**3**) requires considerably higher pressures and temperatures (80 atm., 60°C) to achieve a similar result.

We thank the Science Research Council for financial support.

(*Received*, 24*th January* 1973; *Com.* 094.)

---

[1] R. Edwards, B. F. G. Johnson, J. A. S. Howell, and J. Lewis, *J. Chem. Soc. Dalton*, in the press.

[2] R. Aumann, *J. Organometallic Chem.*, 1973, **47**, C29; *Angew. Chem. Internat. Edn.*, 1973, **12**, 574.

[3] S. Otsuka, A. Natamura, and K. Tain, *J. Chem. Soc.*, 1971, 154.