endo-Addition of Nucleophiles to Tricarbonyldienyliron Complexes

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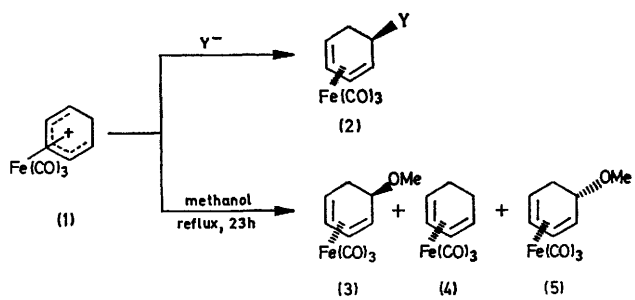
Summary Reaction of (tricarbonyl)cyclohexadienyliron with nucleophilic reagents (*e.g.* MeO^-) gives the 5-*endo*-derivatives as the ultimate product.

NUCLEOPHILIC attack upon cyclohexadienyl or cycloheptadienyl transition-metal cationic complexes may result in addition to the co-ordinated organic ligand,[1] the metal,[1a,2] or the carbonyl group.[3] *X*-Ray studies,[4] spectroscopic, and chemical evidence[1,5] indicate that with few exceptions[6,7] stereospecific *exo* attack of nucleophiles on the co-ordinated ligand occurs [*e.g.* (**1**) → (**2**), $Y^- \equiv$ nucleophile] Such stereospecificity has generally been attributed to steric or electronic factors and does not appear to be influenced by the nature of the nucleophile or reaction conditions. However, we report here a new reaction of the complex (**1**) in which the major product resulting from nucleophilic addition is the 5-*endo* derivative.

Refluxing a solution of (**1**) in nitrogen-purged MeOH (0·5 g/25 ml) for 23 h yielded, after conventional work-up, a mixture of three products which were readily separated by chromatography on silica. The two minor components were identified as the 5-*exo*-methoxycyclohexa-1,3-diene complex (**3**) and the cyclohexa-1,3-diene complex (**4**) on the basis of their spectroscopic properties, in comparison to those of authentic samples prepared by published procedures.[1] The third product was a yellow, reasonably air-stable oil whose i.r. spectrum, ν(CO) (hexane) 2054, 1992, and 1972 cm^{-1} and mass spectrum, *m/e* 250 (M^+), 222 ($M - CO)^+$, 194 ($M - 2CO)^+$, and 166 ($M - 3CO)^+$, indicated that it was a tricarbonyl iron compound, isomeric with (**3**). The ^1H n.m.r. spectrum [δ (100 MHz, CCl_4; Me_4Si internal reference; $\sigma = 0{\cdot}0$): 1·54 (6-*endo*-H), 1·88 (6-*exo*-H), 3·05 (5-H), 3·18 (OMe), 3·3 (1- and 4-H), and 5·22 (2- and 3-H); $J_{1,2} = J_{3,4} = 7$, $J_{2,3} = 3{\cdot}8$, $J_{4,5} = 2{\cdot}8$, $J_{5,6} = 1$, $J_{5,6\text{-}endo} = 3$, $J_{6\text{-}exo,6\text{-}endo} = 16$, $J_{1,6\text{-}exo} = 6{\cdot}5$, and $J_{1,6\text{-}endo} = 2$ Hz] was assigned with the aid of spin-decoupling experiments. It is fully consistent with the assigned structure (**5**) and is distinctly different from the ^1H n.m.r. spectra obtained for both the 1-methoxy- and 2-methoxy-cyclohexa-1,3-diene-tricarbonyliron isomers.[1c]. Protonation of (**5**) with HBF_4 in propionic anhydride at 0° yielded (**1**) (92%), identified by its spectroscopic and chemical properties.



When the progress of the reaction between (**1**) and methanol was monitored carefully by t.l.c. analysis, it was observed that after 20 min all the cation had reacted to give (**3**) and only a small amount of (**5**). After 1·5 h both (**4**) and (**5**) were formed and the relative amount of (**3**) had decreased. In separate experiments (**3**) was observed to give rise to (**5**) when stirred at 20° in a solution of methanol (250 mg/5 ml) containing one drop of HBF_4 solution. After 23 days the ratio of complexes (**5**) : (**3**) was 65 : 35 (^1H n.m.r.) and no further change in the relative amounts occurred upon continued stirring.†

Preliminary studies indicate that this approach to preparing 5-*endo* derivatives may be general. We have pre-

† We have established that this conversion is not affected by the presence of MeO^-.

pared, for example, the 5-*endo*-ethoxy and 5-*endo*-malononitrile derivatives of (**5**) as well as tricarbonyl-5-*endo*-methoxycyclohepta-1,3-dieneiron in good yield. Thus far, attempts to prepare *endo* derivatives of the bicyclo[5,1,0]-octadienyl complex in this manner have yielded products resulting from opening of the cyclopropane ring.[8]

In spite of the fact that the steric or electronic factors do not favour the formation of 5-*endo*-derivatives, it is clear from these results that (**5**) can be formed from (**1**) in good yield under moderate conditions. Initial attack of the nucleophile may take place not only on the co-ordinated dienyl group but also upon a carbonyl group in (**1**) to yield a dienyl ester complex, as in the case of the analogous ruthenium complex.[3] A subsequent intramolecular transfer of the methoxy group to the *endo* side of the cyclohexadienyl ring would give (**5**). In agreement, we find that the ruthenium dienyl ester complex which may be readily separated and characterised does undergo isomerisation to give specific *endo*-addition. Alternatively, (**5**) may be formed from (**3**) *via* an S_N1 or S_N2 type of reaction which, typically, can result in inversion about the reactive centre.[9]

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