Endo Addition to Dienylium Metal Complexes

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Various mechanistic studies have been carried out on reactions of 5-*exo*-substituted tricarbonyl(η-cyclohexa-1,3-diene)iron and the tricarbonyl(1—5-η-cyclohexadienylium)iron cation. These have shown that the corresponding *endo* complexes can be prepared provided that formation of the *exo* complex is reversible in the presence of acid, that the *endo* complex is sufficiently stable thermodynamically, and that formation of the *endo* complex is not unduly inhibited by bulkiness of the nucleophile. Formation and decomposition of the *endo* complexes are generally slower than those of the *exo* complexes, partly for steric reasons, the nucleophile having to pass close to the $Fe(CO)_3$ moiety on its way in or out. Reaction of the *exo* complex may be assisted by Fe–C bond formation coincidental with loss of the nucleophile.

NUCLEOPHILIC attack upon cyclohexadienyl or cycloheptadienyl transition-metal cationic complexes may result in addition to the co-ordinated organic ligand,[1] the metal,[1a] or the carbonyl group.[2,3] *X*-Ray studies [4] and spectroscopic and chemical evidence [1,5] indicate that with a few exceptions [6,7] stereospecific *exo* attack of nucleophiles on the co-ordinated organic ligand occurs. 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 reaction of tricarbonyl(cyclohexadienylium)iron with MeO^- in which the major product resulting from nucleophilic addition is the 5-*endo* derivative. In addition we report mechanistic studies to show that the *exo* complex is the kinetic product of the reaction and that the *endo* derivative is produced only when the formation of the *exo* derivative is reversible in the presence of acid. The formation and decomposition of the *endo* complexes are generally slower than for the *exo* complexes partly for steric reasons; the nucleophile passing close to the $Fe(CO)_3$ moiety on its way in or out. A brief report of this work has been made.[8]

RESULTS

Reaction of $[Fe(CO)_3(C_6H_7)]^+$ *with Methanol.*—Reaction of the salt $[Fe(CO)_3(C_6H_7)][BF_4]$ with methanol was followed by removing samples at various times from refluxing methanol for product analysis. Results (Table) show that

Product analysis of the reaction of $[Fe(CO)_3(C_6H_7)]^+$ in refluxing methanol

Reflux time/h	Yield (%)		
	exo-OMe	*endo*-OMe	$[Fe(CO)_3(C_6H_8)]$
0.3	98	2	0
0.7	89	10	1
1.0	75	23	2
1.5	52	43	5
23	31	56	13
40	27	52	21

formation of the 5-*exo*-OMe product is rapid but that it subsequently isomerises to give a pseudo-equilibrium mixture of the *exo* and *endo* complexes which is perturbed by formation of the unsubstituted diene complex tricarbonyl(η-cyclohexa-1,3-diene)iron. Some unreacted dienylium complex remained detectable throughout the reaction by means of its i.r. bands at 2 115 and 2 065 cm^{-1}. Isomerisation of the *exo*-OMe complex required the presence of acid, none occurring when the pure complex was refluxed in methanol but rapid reaction proceeding on addition of a drop of 40% aqueous HBF_4. Refluxing either the *exo* or *endo* complex in acidified methanol led to the same 1 : 2 *exo–endo* equilibrium mixture as was found after refluxing the dienylium cation but attainment of equilibrium beginning with the *endo* complex was much slower. No *endo* complex was found on refluxing the *exo* complex in acidified tetrahydrofuran (thf) or CH_2Cl_2, indicating that the presence of MeOH is also necessary and the reaction is not a simple intramolecular process. Acid was also required for the similar isomerisation in alcoholic solution of the 5-*exo*-OMe derivatives obtained from $[Fe(CO)_3(C_7H_8)]^+$ and $[Os(CO)_3(C_6H_7)]^+$, and of the 5-*exo*-OEt and -OPr^n derivatives of $[Fe(CO)_3(C_6H_7)]^+$. Refluxing the acidified solutions of the last two complexes for 20 h led to *exo–endo* mixtures in the ratio 3 : 2 and 3 : 1 respectively.

Reactions of 5-exo- *and* 5-endo-$[Fe(CO)_3(C_6H_7OMe)]$ *with Acid.*—Reactions of both the *exo*- and *endo*-OMe derivatives with aqueous HBF_4 in propionic anhydride yielded $[Fe(CO)_3(C_6H_7)]^+$ in almost quantitative yields. A more detailed study of the reaction with acid was undertaken, making use of the difference between the electronic spectra (Figure 1) of the *exo* or *endo* complexes (which are virtually identical) and the product to monitor the reaction in CH_2Cl_2. Trifluoroacetic acid, Htfa, was used as the acid. The same product was obtained from either the *exo* or *endo* complex. It was isolated as an orange oil and shown to be a mixture of the dienylium–trifluoroacetate salt and the trifluoroacetate-substituted diene complex $[Fe(CO)_3(C_6H_7O_2CCF_3)]$ by the occurrence of pairs of bands in the i.r. at 2 115 and 2 060 cm^{-1} and 2 050 and 1 960 cm^{-1}, respectively. Addition of an excess of Htfa to this mixture converted the substituted complex to the dienylium salt. The dependence of the electronic spectrum of the product mixture in CH_2Cl_2 on the concentration of Htfa was determined in order to provide appropriate values of absorbance for the analysis of the overall reaction with acid. This was studied by measuring the absorbance spectra of a series of solutions containing various amounts of acid.

Reaction of the *exo* complex led, virtually instantaneously, to an equilibrium mixture. The absorbance of the peak at 235 nm decreases steadily by about 40% as [Htfa] increases to 7×10^{-3} mol dm^{-3} but subsequent decrease on adding further acid is very much less pronounced. An analysis was undertaken in terms of the stoicheiometry

shown in equation (1) by making use of equation (2). A_0, A, and A_∞ are, respectively, the absorbances found in the absence of acid, those found in the presence of the known concentration [Htfa], and those that would have pertained if all the complex had existed as product mixture at that

$$5\text{-}exo\text{-}[Fe(CO)_3(C_6H_7OMe)] + \text{htfa} \overset{K}{\rightleftharpoons} \left\{ \begin{array}{c} [Fe(CO)_3(C_6H_7)]^+[tfa]^- \\ \rightleftharpoons \\ [Fe(CO)_3(C_6H_7O_2CCF_3)] \end{array} \right\} + \text{MeOH} \quad (1)$$

$$K = (A_0 - A)\,[\text{MeOH}]/(A - A_\infty)\,[\text{Htfa}] \quad (2)$$

value of [Htfa]. Htfa and the ion pair $\{[Fe(CO)_3(C_6H_7)]^+[tfa]^-\}$ are assumed to be undissociated in the weakly polar solvent CH_2Cl_2. The values of 10^3K calculated from absorbances at 240 nm of solutions with 10^3[Htfa] = 2, 3, 4, 5, and 6 mol dm^{-3} were 0.3, 1.2, 2.9, 3.8, and 6.3 respectively,

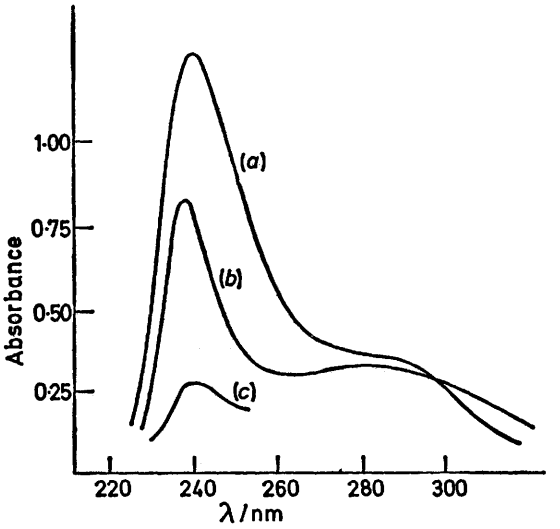


FIGURE 1 Spectra of 10^{-4} mol dm^{-3} 5-*exo*-$[Fe(CO)_3(C_6H_7OMe)]$ in CH_2Cl_2, (*a*) with no added acid, (*b*) [Htfa] = 5×10^{-3} mol dm^{-3}, and (*c*) [Htfa] = 2×10^{-1} mol dm^{-3}

[MeOH] being taken as equal to the concentration of the isomeric mixture of product complexes. A simple analysis in terms of a single equilibrium is, therefore, not in accord with the data. Since the discontinuity in the decrease in absorbance with increasing [Htfa] does qualitatively suggest a two-stage equilibrium, the absorbance change of the first stage was analysed in terms of the stoicheiometry in equation (3) by making use of equation (4). It seems reasonable to assume (see below) that the first stage of the overall reaction involves protonation of the *exo* complex at

$$5\text{-}exo\text{-}[Fe(CO)_3(C_6H_7OMe)] + \text{Htfa} \overset{K_1'}{\rightleftharpoons} 5\text{-}exo\text{-}[(C_6H_7OMeH)^+\cdot Fe(CO)_3\cdot tfa^-] \quad (3)$$

$$K_1' = (A_0 - A)/(A - A_\infty')\,[\text{Htfa}] \quad (4)$$

the O atom of the OMe group, and that the product would most probably exist as an ion pair as shown. A_0 and A are as defined above and A_∞' is the absorbance that would pertain if all the complex present existed as the ion pair. The approximate value taken for A_∞' was that at the discontinuity of the dependence of A on [Htfa]. Values of $10^2K_1'$ at 25 °C and 10^3[Htfa] = 1, 2, 3, 4, 5, and 6 mol dm^{-3} were 1.3, 1.5, 2.3, 3.4, 4.0, and 5.9 dm^3 mol^{-1} respectively. The increase with [Htfa] shown by these values is expected since equation (4) ignores the existence of the second stage of the equilibrium, that involving loss of MeOH from the protonated *exo* complex. The concentration of the product in equation (3) is therefore increasingly overestimated as [Htfa] increases, thus leading to increasingly erroneous and high values for K'. A correct estimate of K_1' can be made by extrapolation back to [Htfa] = 0, *i.e.* $K_1' = ca.\ 1 \times 10^2$ dm^3 mol^{-1}.

The behaviour of the *endo* complex is somewhat different. On addition of acid the spectrum undergoes a very rapid initial change which is followed by a further slow change, complete in a few minutes, as shown in Figure 2. The extent of the first change increases with [Htfa] to a limiting value which can be taken as A_∞'', the absorbance of the ion pair 5-*endo*-$[(C_6H_7OMeH)^+\cdot Fe(CO)_3\cdot tfa^-]$. Values of K_1'', the equilibrium constant for protonation of the *endo* complex at 25 °C, can be calculated from the expression $K_1'' = (A_0 - A)/(A - A_\infty'')$[Htfa]. Values of $10^{-1}K_1''$ were found to be 1.1, 1.0, 1.2, 1.2, 1.2, and 1.4 dm^3 mol^{-1} at 10^2[Htfa] = 1, 2, 3, 4, 5, and 6 mol dm^{-3}, respectively, from absorbance measurements at 235 nm. The excellent consistency of these values strongly supports the assumption of a simple protonation equilibrium in this case, and indirectly supports its assumed existence in the *exo* system as well.

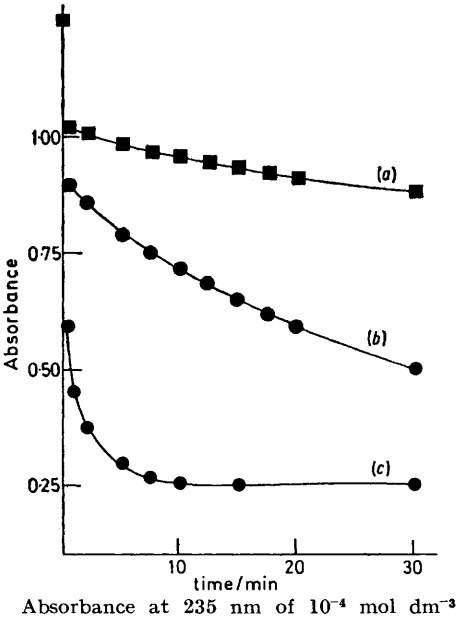


FIGURE 2 Absorbance at 235 nm of 10^{-4} mol dm^{-3} 5-*endo*-$[Fe(CO)_3(C_6H_7OMe)]$ in CH_2Cl_2 (5×10^{-2} mol dm^{-3}), before addition of acid (■) (*a*); at various times after addition of acid (●) to give [Htfa] = 1×10^{-1} mol dm^{-3} (*b*), and 2×10^{-1} mol dm^{-3} (*c*)

The extent of the slow subsequent reaction is also a function of [Htfa] and the observed first-order rate constants for approach to this final equilibrium at 25 °C are given by $10^4k_{obs.}$ = 4.0, 4.5, 5.7, 5.6, 5.5, 5.8, 7.5, 14.4, 16.8, and 48.3 s^{-1}, respectively, when 10^2[Htfa] is 2, 3, 4, 5, 6, 7, 8, 9, 10, and 20 mol dm^{-3}. Quantitative intepretation of these results is made difficult by the considerable variation with [Htfa] of the extent of protonation, of the extent of overall reaction, and of the exact nature of the products. The existence of some of the species as ion pairs is also likely to

lead to a complicated dependence on [Htfa] in such a non-polar solvent.

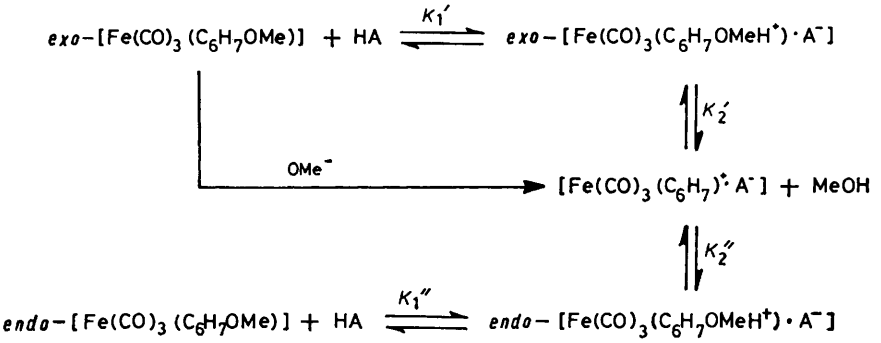
The existence of the protonated complexes, inferred above from the changes in the electronic spectra, was supported by complementary ^1H n.m.r. studies. Addition of an equivalent of [$^2H_1$]trifluoroacetic acid to the 5-*exo*-OMe complex in [$^2H_2$]dichloromethane at 0 °C led to a broadening, and shifting downfield, of the resonance due to the OMe protons. Further cooling to −60 °C led to three sharp resonances in that region at τ 6.53, 6.77, and 6.82. The first and last correspond, respectively, to CH_3OD and unreacted *exo*-OMe complex while that at τ 6.77 is consistent with the *exo*-OMe complex protonated at the O atom. This is supported by the isolation of the stable salt *exo*-[$Fe(CO)_3$-($C_6H_7NHMe_2$)][PF_6], the ^1H n.m.r. spectrum of which showed a CH_3 resonance at τ 7.13 as compared with one at τ 7.93 for its unprotonated analogue. The greater effect of the proton in the dimethylamino-complex is consistent with the greater strength of the N–H bond. Analogous spectra of acidified solutions of the *endo*-OMe complex showed, even at 0 °C, three sharp signals at τ 6.53, 6.62, and 6.77, the last being due to unreacted *endo* complex and that at τ 6.62 being assignable to the protonated form.

Interaction of [Eu(fod)$_3$] *with the* exo- *and* endo-OMe *Complexes.*—The complex [Eu(fod)$_3$] (fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionate) has been used successfully as a shift reagent for other organometallic compounds [9] and has been shown not to attach itself to co-ordinated CO.[10] Various amounts of this reagent were added to solutions of the *exo*- and *endo*-OMe [11] complexes and of the *endo*-OEt and -OPr^n complexes. The shift in the OMe or OCH_2 resonances depends linearly on [Eu(fod)$_3$], the relative gradients being, respectively, 100 : 10 : 5 : 1.

Temperature-dependent ^{13}C *N.M.R. Spectra.*—Free rotation of the $Fe(CO)_3$ moiety in the *exo*- and *endo*-OMe and -OPr^n complexes in $CDCl_3$ was investigated by variable-temperature ^{13}C n.m.r., [Cr(acac)$_3$] being used as a relaxation reagent (acac = acetylacetonate ion). At −80 °C two sharp signals in the intensity ratio 2 : 1 were obtained for all the complexes in the region 210—215 p.p.m. from $SiMe_4$. As the temperature was raised the signals broadened, coalescing at −45, −55, −60, and −55 °C, for the second *endo*-OMe and -OPr^n derivatives respectively. At higher temperature sharp signals of intensity 3 were obtained as expected.

DISCUSSION

The results described above suggest that the *exo* ⇌ *endo* equilibrium of the OMe complexes can be represented by Scheme 1. In the absence of acid the dienylium complex reacts rapidly with OMe^- to form only the *exo* isomer of the diene complex and this is also the initial product rapidly formed by reaction of the dienylium complex in MeOH. In the latter case, however, an equivalent of acid is released for every mole of *exo*-diene complex formed and the reaction is therefore reversible. Sufficient dienylium complex remains unreacted for the slower reaction with methanol, to form the *endo*-diene complex, to proceed until the overall equilibrium is established. Subsequent formation of [$Fe(CO)_3(C_6H_8)$] is not unexpected since it is also formed as a thermolysis product of 5-*exo*-[$Fe(CO)_3(C_6H_7OMe)$] in heptane at 140 °C.[12] If the conjugate base of the acid is a Lewis base, as is the case with Htfa, then an additional equilibrium involving the formation of the diene complex [$Fe(CO)_3(C_6H_7A)$] is possible.

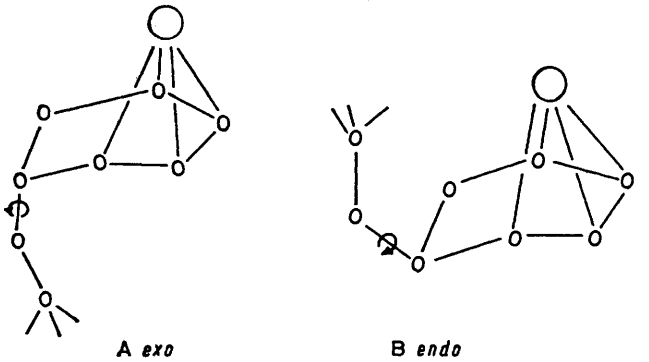


SCHEME 1

The ^1H n.m.r. spectra of *endo*- and *exo*-OMe complexes show that they can be protonated in the way described, resonances for each species containing an OMe group being clearly evident at lower temperatures. The *exo*-OMe system has to be cooled to −60 °C before the individual signals are clearly resolved, both the protonation equilibrium and the reversible loss of methanol being relatively rapid at 0 °C. The lower lability of the *endo* system is shown by the existence of individual resonances even at 0 °C. These findings are paralleled by those from studies of the u.v.–visible spectra in CH_2Cl_2. At 25 °C the protonation equilibria for the *exo* and *endo* complexes are both set up very rapidly, the equilibrium constant for protonating the *exo* complex being ten times greater than that for the *endo* complex. Subsequent loss of MeOH from the *exo* complex is also very rapid but loss from the *endo* complex is measurably slow. The protonated *endo* complex is therefore kinetically more stable towards loss of MeOH than is the corresponding *exo* complex, even though its thermodynamic stability relative to the unprotonated form is an order of magnitude lower. In MeOH the overall equilibrium is slightly in favour of the *endo* complex but the difference is quite small. This is consistent with the conformations A and B. The OMe group in the *exo* complex is in an axial position and is not subject to any steric strain. {The axial conformation is supported by crystallographically obtained structures of several similar 5-*exo*

derivatives, $[Fe(CO)_3(C_6H_7)]$}[4]. The OMe group is also able to rotate freely about the C–OMe bond. The OMe group in the *endo* complex is in an equatorial position and steric strain is only likely when the Me group is closest to the Fe atom as rotation about the C–OMe bond occurs. If anything, therefore, this suggests that the *endo* complex might be slightly less stable than its *exo* isomer but other effects could well offset this and the observed stability difference in MeOH is only *ca.* 2 kJ mol^{-1}. The smaller relative amounts of *endo* isomer of the $[Fe(CO)_3(C_6H_7OR)]^+$ complexes (R = Et or Pr^n) formed after reaction of the acidified *exo* complexes for 20 h in the appropriate alcohol suggest that a steric effect might be operating and the *exo* : *endo* ratio of 1 : 9 for $[Os(CO)_3(C_6H_7OMe)]$ [13] supports the suggestion that the *endo* complex is generally favoured except where steric inhibition is important.

The shift-reagent experiments also throw some light on the steric nature of these complexes. The $[Eu(fod)_3]$ is quite free to approach close to the O atom of the *exo*-OMe group, whatever the position of the Me group. In the case of the *endo* complex it can approach the O atom with complete freedom only when the Me group is forced down close to the $Fe(CO)_3$ moiety. On average it will not be as close to the O atom and its effect on the Me resonances will therefore be smaller, as observed. The

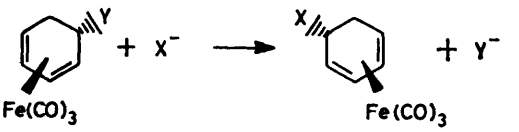


A *exo* B *endo*

monotonic decrease in the effect along the series *exo*-OMe > *endo*-OMe > OEt > OPr^n is fully consistent with this picture. These results also relate to the relative ease of protonation of the complexes in CH_2Cl_2. The protonated complexes will exist as ion pairs, the stability of which will be greater the closer the tfa^- ion can approach the H^+ attached to the O atom of the OMe group. For exactly the same reasons outlined for the shift-reagent effects, the tfa^- ion will be able to approach closer to the proton in the *exo* complex and this will contribute to the greater ease of protonation of this isomer.

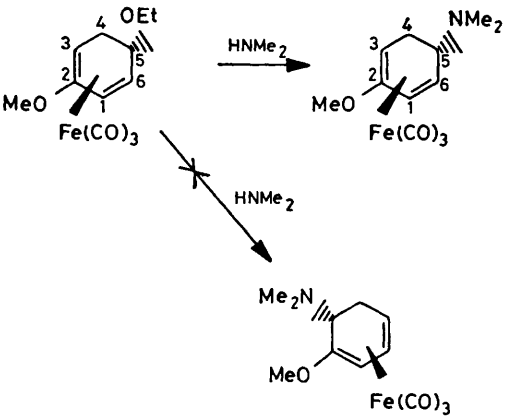
The ^{13}C n.m.r. studies show that the size of R in the *endo*-OR groups has no influence on the energy barrier for rotation so that any steric effects involved in the thermodynamic stabilities of the *endo*-OR complexes do not seem to be associated with interference between the R group and the carbonyl ligands. On the other hand the free-energy barrier for rotation in the *exo*-OPr^n complex is slightly lower than for the *exo*-OMe analogue (coalescence temperatures −60 and −45 °C respectively). This difference, which is almost within experimental error of determining coalescence temperature, *ca.* ± 5 °C, may be due to differing alkyl group–diene π-cloud interactions.

The displacement of an OR group by other nucleophilic groups throws some light on the mechanism of the isomerisation reactions. The displacements occur only



SCHEME 2

at the *exo* isomers where they proceed quite rapidly even in the absence of acid to form purely *exo* products. The *endo*-OMe complex does not react at all. The mechanism appears to involve dissociative loss of OR^- from the complex. An S_N2 reaction would be expected to be accompanied by inversion about the C atom in the ring and formation of *endo* products. An S_N2' reaction involving attack at C(3) and rearrangement of the double bonds as shown in Scheme 2 can be ruled out by the results shown in Scheme 3. Further indications of the dissociative mechanism are the retardation by free OEt^- of *exo* OEt^- displacement by OMe^-, and the relative slowness of the reaction in the less polar solvents thf and benzene. Acceleration observed in the presence of



SCHEME 3

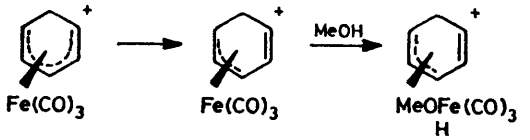
additional Na[OMe] and $Na[BH_4]$ can also be ascribed to salt effects on a dissociative process as found elsewhere.[14] The rapidity of this dissociative loss of the *exo* OMe^- group followed by 100% formation of *exo* products shows that the relative rates of formation of *endo* products during attack by highly nucleophilic groups must be very much smaller than in attack by the much less nucleophilic neutral alcohol molecules. Dissociative loss of the *endo* OMe^- group must be very slow in the absence of electrophilic assistance since no reaction with strong nucleophiles is found, even to form *exo* products.

The absence of any major differences in the relative

stabilities of the *endo*-OR complexes in their ground states shows that the relative unreactivity of the *endo*-OMe isomer must be due mainly to destabilisation of the transition states rather than to stabilisation of the ground state. This could be attributed to the movement of C(5) down into the plane of the four diene C atoms as the OMe^- group leaves, a movement that allows for greater p_π character of the orbital being emptied so that the loss of electron density can be made up for by delocalisation of the diene π electrons. This movement would force the departing OMe^- group closer to the $Fe(CO)_3$ moiety than if it had left simply from an sp^3 hybrid on C(5). If the OMe^- group does enter or leave from an sp^3 hybrid on C(5) then the energetic benefit of delocalisation and the making of an additional Fe–ring bond will have been lost and this will offset the absence of the unfavourable steric effect.

The relatively much greater rates of reaction of the *exo* complex can be explained by the absence of such unfavourable effects and/or by the participation of Fe–C bond making coincident with C–OMe bond breaking, *i.e.* anchiomeric assistance whereby electrons from the Fe^0 enter the p_π orbital on C(5) as it is vacated by the OMe^- group. This type of assistance is not available when the *endo*-OMe^- leaves. The importance of anchiomeric assistance of this type has been demonstrated quantitatively by Clinton and Lillya [15] who also showed the preference for *exo* addition and loss in analogous compounds. The relative importance of the various factors proposed above for our reactions is not obvious but we are inclined to favour anchiomeric assistance as the major one.

Alternative mechanisms for the reversible formation of the *endo* complexes can be envisaged. Initial formation of a co-ordinated CO_2R group, by nucleophilic attack at the C atom of a co-ordinated CO ligand, could occur and be followed by migration of the OR^- group onto the *endo* face of the ring. The exact mode of this transfer is not clear and the carbomethoxy complex $[Os(CO)_2(CO_2Me)(C_6H_7)]$ has been found to rearrange stereospecifically to form the 5-*exo*-$[Os(CO)_3(C_6H_7OMe)]$.[16] This must occur by dissociation of the OMe^- group and attack at the *exo* position that is relatively slow compared to reformation



SCHEME 4

of the carbomethoxy complex. Another possibility is the oxidative addition of MeOH to the Fe atom, a vacant co-ordination site for this purpose having been generated by rearrangement of the ring to the allylic form as shown in Scheme 4. Subsequent migration of the MeO^- to the *endo* face of the ring and loss of H^+ would have to be rapid. This mechanism would seem to require more energy than simple breaking, effectively, of one Fe–C bond since the ring has become only trihapto instead of pentahapto and some energy has to be provided for the oxidative addition. Direct nucleophilic attack at the metal followed by rearrangement could be proposed as a third alternative. When such direct attack has been inferred [17] it is the *exo* products that are subsequently formed, but this must be *via* Fe–nucleophile bond breaking followed by direct attack at the *exo* position. The simplest mechanism considered first appears to be the preferable one.

The properties of the 5-*exo* derivatives as a whole are also consistent with this mechanism. Those containing amino-groups undergo ready protonation but the subsequent loss of free amine occurs only when it is the weakest base used, aniline. (Even in this case the *endo* isomer is not formed, probably because so much acid has to be used to remove the aniline that no free aniline is present to attack the dienylium complex at its *endo* face.) This contrasts with those *exo* complexes containing O-donor substituents and is consistent with the generally easier process of ester hydrolysis compared with acid amide hydrolysis.[18] The 5-*exo* derivatives containing C-atom donors cannot be protonated at the C atom and the C–C bond is always much harder to break. Protonation at other positions in the *exo* group does not lead to formation of the dienylium complex except in the case of the 5-*exo*-$CH(COMe)_2$ complex when a large excess of acid leads to loss of acetylacetone, presumably in the enolic form initially. Removal of *exo* thiols is quite easy in the presence of acid but no *endo* complex can be formed. The thiol groups are larger than the corresponding alkoxy groups and it is possible that steric hindrance is sufficient to decrease the relative thermodynamic stability of the *endo* form to this extent. Alternatively, the larger size could slow down the rate of formation (and of decomposition, if formed) of the *endo* complex to the extent that its formation is not observed under the conditions used.

The results as a whole show, therefore, that the conditions necessary for *endo* addition to the dienylium ring are: addition to the *exo* face must be reversible in the presence of acid, the *endo* form must be sufficiently stable thermodynamically, and its formation must not be inhibited by, for example, the bulkiness of the nucleophile.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer, using either polystyrene film or carbon monoxide as calibrants. Mass spectra were recorded on an A.E.I. MS 12 spectrometer. Ultraviolet spectra were recorded on a Unicam SP 800 or 1800 spectrometer. Proton nuclear magnetic resonance spectra were recorded on Perkin-Elmer R12B and Varian Associates HA 100 and CFT 20 spectrometers. Carbon nuclear magnetic resonance spectra were recorded on a Varian Associates XL 100 spectrometer. Chemical shifts were measured in parts per million from tetramethylsilane.

Tricarbonyl(η-cyclohexa-1,3-diene)iron, tricarbonyl(1—5-η-cyclohexadienylium)iron tetrafluoroborate, tricarbonyl-(η-5-*exo*-methoxycyclohexa-1,3-diene)iron, and tricarbonyl-

(η-5-*endo*-methoxycyclohexa-1,3-diene)iron were prepared as previously described.[1c]

(*a*) *Product Analysis of the Reaction of Tricarbonyl*(1-5-η-*cyclohexadienylium*)*iron with Methanol.*—Tricarbonyl(1—5-η-cyclohexadienylium)iron tetrafluoroborate was refluxed in methanol for the required reaction time. The solution was then cooled, worked-up in the usual way, and the relative amounts of the 5-*exo*-methoxy and 5-*endo*-methoxy derivatives, and the tricarbonyl(η-cyclohexa-1,3-diene)iron, were determined after separation of the reduction mixture by chromatography on silica.

(*b*) *Acid Catalysed Isomerization of the* 5-exo-*Methoxy Derivative.*—Into a solution of methanol (5 cm^3) containing one drop of 40% aqueous HBF_4 solution was added tricarbonyl(η-5-*exo*-methoxycyclohexa-1,3-diene)iron (250 mg, 1.0 mmol) as a solution in methanol. The solution was refluxed for 20 h and then cooled and worked-up in the usual way. Separation of the reaction mixture on silica plates using diethyl ether–hexane (1 : 4) gave three bands in order of elution: (*i*) *tricarbonyl*(η-*cyclohexa*-1,3-*diene*)*iron* (21 mg, 0.10 mmol, 10%), (*ii*) *tricarbonyl*(η-5-endo-*methoxycyclohexa*-1,3-*diene*)*iron* (107 mg, 0.43 mmol, 43%), and (*iii*) *tricarbonyl*(η-5-exo-*methoxycyclohexa*-1,3-*diene*)*iron* (58 mg, 0.23 mmol, 23%).

(*c*) *Protonation of the* 5-exo *and* 5-endo-*Methoxy Derivatives.*—To a stirred solution of the methoxy derivative (500 mg, 2.1 mmol) in propionic anhydride (10 cm^3) at 0 °C was added dropwise an excess of HBF_4 over a period of 10 min. The resultant solution was stirred for a further 30 min, and diethyl ether was added to precipitate the dienylium salt. Filtration followed by washing with diethyl ether yielded the cyclohexadienylium iron salt (90%), identified by its spectroscopic properties.

(*d*) *Protonation of Tricarbonyl*(η-5-exo-NN-*dimethylamino-cyclohexa*-1,3-*diene*)*iron.*—To a solution of the amino-derivative in diethyl ether was added HPF_6 solution at 0 °C. The pale yellow cationic salt was precipitated, filtered off, and washed with diethyl ether (Found: C, 32.3; H, 3.2; N, 3.4; P, 7.9. Calculated for $C_{11}H_{14}F_6FeNO_3P$: C, 32.2; H, 3.4; N, 3.4; P, 7.6%).

(*e*) *Ultraviolet Spectroscopic Analysis of the Reaction of* tfa *with the* 5-exo- *and* 5-endo-*Methoxy Derivatives.*—Portions (3 cm^3) of solutions of the 5-*exo*- and 5-*endo*-methoxy derivatives in dichloromethane were removed, and different amounts (0.6—1.5 cm^3) of a 1 mol dm^{-3} solution of tfa were added using a microsyringe. The u.v. spectra of these reaction solutions were recorded in silica cells of path length 10 mm using a Perkin-Elmer SP1800 spectrophotometer, against a reference of dichloromethane also containing tfa. The solutions were maintained at 25 °C throughout the experiments by means of a water-flow thermostatting system. The absorbance measurements thus obtained were processed as described in the text.

Protonation studies were as discussed in the text.

(*f*) *Shift-reagent Studies on the* 5-exo- *and* 5-endo-*Alkoxy Derivatives.*—The shift-reagent studies on the 5-*exo*- and 5-*endo*-alkoxy derivatives were carried out by taking a 0.25 mol dm^{-3} solution of the appropriate alkoxy derivative in deuteriochloroform; increasing amounts of the shift reagent were sequentially added to the solution in 10 mg (10^{-5} mol dm^{-3}) portions at ambient temperature. The ^1H n.m.r. spectrum of the solution was recorded after each addition, using a Varian HA100 spectrometer with $SiMe_4$ as lock. The shift reagent used was tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-octane-4,6-dionate)europium(III).

(*g*) *Measurement of the Coalescence Temperatures of the Iron Tricarbonyl Moiety in the* 5-exo- *and* 5-endo-*Methoxy Derivatives.*—The investigations were carried out in the metal–carbonyl region of the ^{13}C n.m.r. spectra of the 5-*exo*- and 5-*endo*-methoxy derivatives, using a Varian XL100 FT spectrometer in the low-temperature mode. The appropriate alkoxy derivative was dissolved in deuteriochloroform solution containing [$Cr(acac)_3$] as a relaxation reagent. The solution was then placed in the spectrometer and cooled down to −80 °C. The spectrum was recorded and two peaks in the ratio 2 : 1 were typically observed in the region 210—215 p.p.m. down field from $SiMe_4$. This corresponds to the rotation of the metal moiety being frozen-out. The temperature was then raised in increments of 5 or 10 °C until the two peaks were observed to coalesce to give a single peak of relative intensity three; this corresponds to free rotation of the metal moiety. This temperature was taken as the coalescence temperature.

Preparation of Tricarbonyl(5-exo-*ethoxy*-2-*methoxycyclohexa*-1,3-*diene*)*iron.*—Tricarbonyl(2-methoxycyclohexadienyl)iron tetrafluoroborate was added to a rapidly stirring solution of sodium ethoxide (two-fold mol excess) in ethanol. The solution was stirred at 0 °C for 30 min, and then poured into water. The mixture was extracted with diethyl ether (three times), dried with $Mg[SO_4]$, filtered, and the solvent removed under reduced pressure. The residue was extracted with diethyl ether and chromatographed on silica plates using diethyl ether–hexane (1 : 4) as eluant to give the product (70%). N.m.r. data (see Scheme 3 for atom numbering): τ 4.73, H^3; 6.31, OCH_3; 6.65, OCH_2; 6.80, H^4; 7.23, H^5; 7.40, H^1; 7.80, H^6 *endo*; 8.34, H^6 *exo*; and 8.90, CH_3. I.r. data: 2 045, 1 974, and 1 969 cm^{-1}. Mass spectrum: M^+ 294; $C_{12}H_{14}FeO_5$ requires 294.

Solvolysis of Tricarbonyl(2-*methoxy*-5-exo-*methoxycyclohexa*-1,3-*diene*)*iron.*—The above compound (200 mg) was dissolved in thf (25 cm^3) and a ten-fold mol excess of dimethylamine solution was added. The solution was refluxed for 30 min. The mixture was poured into water, extracted with diethyl ether (three times), dried with $Mg[SO_4]$, and filtered. The residue was extracted with diethyl ether and chromatographed on silica plates using diethyl ether–hexane (1 : 4) as eluant. The only product isolated from the reaction after chromatography was tricarbonyl(5-*exo*-dimethylamino-2-methoxycyclohexa-1,3-diene)iron (70%). N.m.r. data: τ, 4.80, H^3; 6.32, OCH_3; 7.00, H^5; 7.10, H^4; 7.36, H^1; 7.95, $N(CH_3)_2$; 7.97, H^6 *endo*; and 8.73, H^6 *exo*. I.r. data: ν 2 047, 1 968, and 1 961 cm^{-1}. Mass spectrum: M^+ 293; $C_{12}H_{15}FeNO_4$ requires 293.

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