Stereochemical Requirements for Thermally Induced Hydrogen Migrations in Tricarbonyl(η-methoxycyclohexa-1,3-diene)iron Complexes [1]

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Tricarbonyl(η-5-*exo*-methoxycyclohexa-1,3-diene)iron has been shown to undergo a thermal reaction to a mixture of the 1- and 2-methoxy-isomers plus a small amount of tricarbonyl(η-cyclohexa-1,3-diene)iron. Tricarbonyl(η-5-*endo*-methoxycyclohexa-1,3-diene)iron does not react under identical conditions. These results have been interpreted in terms of a reaction mechanism in which migration of only the C^5 *endo*-hydrogen occurs.

THE chemistry of organic ligands bound to transition metals has attracted considerable attention in recent years.[2,3] Of particular interest are attempts to ascertain whether certain transformations of the ligand occur in a stepwise or in a concerted fashion.[4] Substituted cyclohexa-1,3-diene complexes of iron tricarbonyl have been shown to undergo thermally induced isomerizations which appear to result from an allowed 1,5 suprafacial hydrogen migration [equation (1)].[5,6] On the basis of isotope-effect studies, Whitesides and Neilan [5] concluded that, for the case (Ia) $\rightleftharpoons$ (IIa), the reaction involves an intermediate metal deuteride and thus occurs in a stepwise manner. Even for reactions of (Ia) and (IIa) which result in deuterium scrambling, the possibility of a 1,5 sigmatropic shift of the C^5 *exo*-hydrogen was not considered a likely process. Instead, these workers advanced a mechanism in which scrambling resulted from a process involving complexing of the iron tricarbonyl group to the aromatic ring. Further experiments showed that the phenyl group was a necessary structural feature for deuterium scrambling.

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[1] K. E. Hine, B. F. G. Johnson, and J. Lewis, *J.C.S. Chem. Comm.*, 1975, 81.

[2] *Cf.* J. A. S. Howell, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1974, 295 and earlier parts in this series.

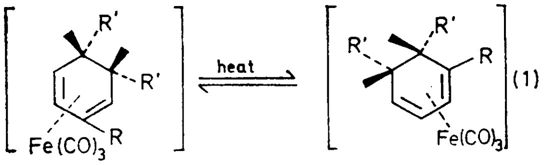
[3] (*a*) A. J. Birch, K. B. Chamberlain, M. A. Hass, and D. J. Thompson, *J.C.S. Perkin I*, 1973, 1882; (*b*) M. Brookhart, R. E. Dedmond, and B. F. Lewis, *J. Organometallic Chem.*, 1974, **72**, 239; M. A. Hass, *Organometallic Chem. Rev.*, 1969, **A4**, 307 and refs. therein.

[4] For example, F. D. Mango and J. H. Schachtschneider in 'Transition Metals in Homogeneous Catalysis,' ed. G. N. Schrauzer, Marcel Dekker, New York, 1971; L. A. Paquette, *Accounts Chem. Res.*, 1971, **4**, 280.

[5] T. H. Whitesides and J. P. Neilan, *J. Amer. Chem. Soc.*, 1973, **95**, 5811.

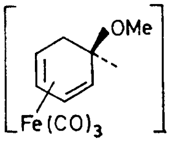
[6] R. E. Ireland, G. C. Brown, jun., R. H. Sanford, jun., and R. C. McKenzie, *J. Org. Chem.*, 1974, **39**, 51.

Our approach to the question of *exo* versus *endo* migration of hydrogen has been to examine the relative

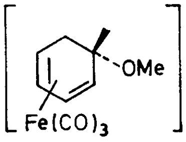


(Ia) R = Ph, R' = D (IIa) R = Ph, R' = D
(Ib) R = OMe, R' = H (IIb) R = OMe, R' = H
(Ic) R = OCD$_3$, R' = H (IIc) R = OCD$_3$, R' = H

thermal reactivity of 5-*exo*- and 5-*endo*-methoxycyclohexa-1,3-diene complexes of iron tricarbonyl, (III) and (IV) respectively. We have shown previously that the



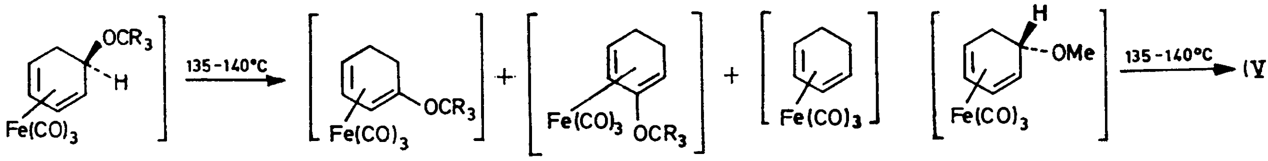
(III)



(IV)

reaction of [OMe]$^-$ with [Ru(dienyl)(CO)$_3$]$^+$ systems leads to preferential attack on a CO ligand to yield [Ru(dienyl)(CO)$_2$(CO·OMe)] derivatives followed by [OMe]$^-$ migration to the organic ring.[7] Recently Maitlis [8] and Lewis [9] and their co-workers showed that nucleophilic addition to diene derivatives of Pd^{II} and Pt^{II} can also lead to the formation of *endo* derivatives.

Thermal isomerization of (III) to the 1-methoxy-isomer, (Ib), can occur only *via* migration of the C^5 *endo*-hydrogen, presumably through a metal hydride intermediate.[5,10] However, isomerization of (IV) to (Ib) can proceed only *via* migration of the C^5 *exo*-proton. In both cases, movement of the C^6 hydrogens is a degenerate process and does not lead to the product. The isomers (III) and (IV) were chosen for this study since both can be easily prepared in good yield from the readily available tricarbonyl(η-cyclohexadienyl)iron tetrafluoroborate, the latter stereoselectively by simply heating the salt under reflux in methanol.[11] The stereochemistry about C^5 has been rigorously established for these isomers. Furthermore, thermal isomerization of either (III) or (IV) should not be complicated by side reactions or interaction of the substituent with Fe(CO)$_3$.



(III) R = H (Ib) R = H (IIb) R = H (V) (IV)
(VI) R = D (Ic) R = D (IIc) R = D

RESULTS

Preparation of the Complexes.—Complex (III) was prepared according to the procedure of Lewis and his co-workers.[12] The *endo* isomer (IV) was obtained *via* a procedure recently developed in this laboratory.[11] Both complexes were purified by chromatography prior to use.

Thermolysis of (III) *and* (IV).—Heating a solution of (III) in n-heptane in a sealed tube at temperatures between 135 and 140 °C resulted in three products. Typically, 50% of the starting material reacted in *ca.* 36 h under these conditions. Although product ratios varied slightly, separation of the mixture gave, for example, recovered starting material (50%), (Ib) (20%), (IIb) (25%), and tricarbonyl(η-cyclohexa-1,3-diene)iron, (V) (5%), with overall yields of 65—70% based on the amount of recovered oil. The three products were identified by their ^{1}H n.m.r., i.r., and mass spectra in comparison to those obtained for authentic complexes prepared by standard literature procedures.[3a,12] Only a trace amount (1%) of another product, probably (IV), could be detected by t.l.c. analysis. The conversion of complex (III) into (Ib) and (IIb) could be increased by using longer reaction times and higher temperatures. However, the amount of decomposition also increased.

Under identical conditions in a sealed tube (n-heptane solution, 135—140 °C) the *endo* isomer (IV) underwent a comparatively slower reaction to give only (V). After 36 h, t.l.c. analysis revealed the presence of mostly (IV), a small amount of (V), and about the same amount of other minor products with different R_F values to those of (Ib) and (IIb). Hydrogen-1 n.m.r. analysis of this crude mixture did not reveal the presence of singlets at δ 3.58 and 3.43 p.p.m. due to the OMe groups of (IIb) and (Ib) even when the amplitude of the instrument was adjusted to send the OMe singlet of (IV) far off-scale. Separation of the crude mixture led to a 70% overall recovery of the oils in the relative amounts (IV) (*ca.* 96%), (V) (*ca.* 2%), and other compounds (*ca.* 2%). The minor products were not extensively eluted under conditions which easily eluted (Ib) and (IIb).

Thermolysis of the OCD$_3$ *Derivative of* (III).—In order to examine whether the hydrogens of the methyl group of (III) are involved in any way, the OCD$_3$ analogue, (VI), of (III) was studied. Heating an n-heptane solution of (VI) at 135—140 °C for 44 h afforded a mixture of starting material (39%) and three products, identified as (Ic) (30%), (IIc) (23%), and (V) (8%). Mass-spectral or ^{1}H n.m.r. evidence indicated that no deuterium had been incorporated into (V)

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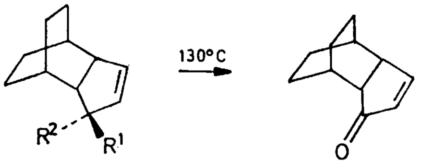
[12] A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc.* (*A*), 1968, 332.

and that no deuterium loss from the methyl groups of (Ic) and (IIc) had occurred.

DISCUSSION

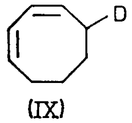
It is clear from these results that the rate of isomerization of simply substituted cyclohexa-1,3-diene complexes of iron tricarbonyl can be influenced to a large extent by the stereochemical relation between the iron carbonyl moiety and the C^5 hydrogen bond. Only in the case where the migrating hydrogen occupies a position on the same side as the metal atom will reaction occur to place the substituent on a double bond. In a related study Cowherd and von Rosenberg[13] observed that the allylic alcohol (VIIa), but not the epimer (VIIb), could be isomerized to the ketone (VIII) in the presence of $[Fe(CO)_5]$. These workers suggested that an (η-allyl)-tricarbonylhydridoiron intermediate was formed only in the case of (VIIa) since it was assumed that the iron carbonyl ' catalyst ' could approach the olefinic bond only from the *exo* side. In our study we were able to unambiguously define the relation between the iron atom and the migrating centre by starting with complexes whose stereochemistry has been rigorously determined.



(VIIa) R^1 = H, R^2 = OH (VIII)
(VIIb) R^1 = OH, R^2 = H

Since the stereochemical requirements of this reaction suggest that the metal is in some way directly involved, it is attractive to consider that an (η-allyl)tricarbonylhydridoiron intermediate, suggested earlier by Whitesides and Neilan,[5] is formed in the first step of this reaction. Analogous species have also been proposed to explain olefin isomerizations catalysed by transition-metal carbonyls.[14] However, in at least one case, that of the $[Co(CO)_4D]$-assisted isomerization of allylbenzene to β-methylstyrene, the results suggested that a metal hydride was not involved.[15]

Inspection of a molecular model of (IV) indicates that there is no apparent steric interaction to prevent a suprafacial 1,5 sigmatropic shift of hydrogen across the ' top ' surface of the cyclohexadienyl ligand. It would appear therefore that the concerted reaction in this case is relatively too high in energy to effectively compete with a stepwise process. Typically, 1,5 sigmatropic shifts of hydrogen in related diene systems, not complexed to metals, take place readily at 100—150 °C. For example, 7-methylcyclohepta-1,3,5-triene was converted[16] into a mixture of the 1-, 2-, and 3-methyl isomers at 129 °C, and equilibration of the deuterium atom in (IX) takes place at 150 °C in 24 h.[17] Numerous other examples can be found in the recent literature.[18]

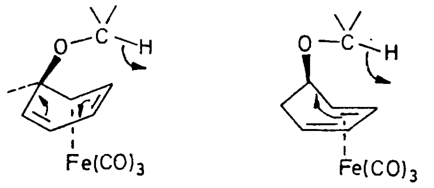


(IX)

The lack of any detectable isomerization of (IV) may be the result of two factors. Complexing the diene system to $Fe(CO)_3$ may prevent the 5-methoxycyclohexa-1,3-diene ring from adopting a conformation favourable for a 1,5 shift. In addition, one might expect the presence of the iron atom to alter the symmetry of the dienyl system in such a way as to render this process forbidden in the ground state.[19]

The formation of (IIb) and (IIc) most likely arises from a subsequent thermal reaction of the initially formed complexes (Ib) and (Ic). Ireland *et al.*[6] showed that (Ib) and (IIb) interconvert in refluxing di-n-butyl ether to give a 3 : 7 mixture. Independent experiments in this laboratory have confirmed this result. The observation that little or no (III) is formed from (Ib) would appear to reflect the greater thermodynamic stability of a substituted olefinic system over a corresponding unsubstituted one. Alternatively, the lability of the C^5 *endo*-proton may be greater when alpha to the methoxy-group.

An interesting reaction is the formation of (V) from (III). The most reasonable mechanism for this reaction is the intramolecular process shown below; this involves a cyclic transition state consisting of six or eight electrons. The eight-electron transition state is produced in a formally non-allowed electrocyclic ground-state process according to orbital-symmetry conservation.[18] However, the presence of the metal may provide a relatively low-energy path for the ' non-allowed ' thermal reactions as demonstrated recently by Petit and his co-workers.[19] The six-electron, formally ' allowed ', process would proceed *via* initial formation of a complexed 1,4-diene intermediate.[14] Intramolecular ' retro-ene ' reactions of this nature have been reported



Eight-electron process Six-electron process

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by Berson and other workers in studies of the thermal reactions of certain allyl methyl ethers.[20]

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were recorded on a Varian HA100 instrument using CCl_4 as solvent and $SiMe_4$ as internal reference. The i.r. spectra were obtained on a Perkin-Elmer 257 instrument using dry hexane as the solvent. Mass spectra were recorded on A.E.I. MS 12 or MS 9 instruments, normally at 50 eV and between 40 and 50 °C.*

n-Heptane was treated with concentrated alkali, distilled, and then dried over sodium wire. Diethyl ether was run through a short column of basic alumina, activity I or II, just prior to use. All Carius tubes were washed with hot concentrated alkali, then with distilled water until the washings were neutral. The tubes were dried by storing them in an oven at *ca.* 150 °C overnight. Failure to treat the glassware in this manner led to irreproducible results and extensive decomposition of the iron tricarbonyl complexes. The following complexes of iron tricarbonyl were prepared by literature procedures: cyclohexa-1,3-diene;[12] 5-*exo*-methoxycyclohexa-1,3-diene;[12] 5-*endo*-methoxycyclohexa-1,3-diene;[11] and 1-methoxy- and 2-methoxy-cyclohexa-1,3-diene.[3a] All the complexes had spectroscopic data (^1H n.m.r., i.r., and mass) in agreement with those reported in the original papers. All the preparative reactions were in nitrogen-purged solvents in an inert atmosphere. The thermolyses were in the absence of direct light.

Tricarbonyl(η-5-exo-$[^2H_3]$*methoxycyclohexa*-1,3-*diene*)*iron*, (VI).—To a solution of sodium (30 mg) in CD_3OD (5 cm^3) was added tricarbonyl(η-cyclohexadienyl)iron tetrafluoroborate (220 mg) over a period of 10—15 min. The resulting yellow solution was stirred at 40 °C for 20 min and then the solvent was removed under reduced pressure at room temperature. The remaining mixture was extracted with diethyl ether and the oil was chromatographed immediately on silica plates using a 15% diethyl ether–pentane solvent as eluant. The yellow oil (179 mg) had the following spectral properties: i.r., ν(CO) at 2 051, 1 982, and 1 979 cm^{-1}; m/e 253 $[M]^+$, 225 $[M - CO]^+$, 197 $[M - 2CO]^+$, and 169 $[M - 3CO]^+$; ^1H n.m.r., δ 3.00 (2 H) $H^{1,4}$, 5.52 (2 H) $H^{2,3}$, 3.78 (1 H) H^5, 2.22 (1 H) H^6, and 1.47 p.p.m. (1 H) H^6.

Thermal Reaction of Tricarbonyl(η-5-exo-*methoxycyclohexa*-1,3-*diene*)*iron*, (III).—The pure complex (300 mg) was dissolved in n-heptane (15 cm^3) and placed in a Carius tube (25—30 cm^3). The solution was degassed by three freeze–pump–thaw cycles on a vacuum line which maintained a pressure of 10^{-2}—10^{-3} mmHg. The tube was sealed *in vacuo* and placed in an oven at 135—140 °C for 36 h. The resulting mixture was filtered through $Mg[SO_4]$ and the solvent removed very carefully, without heating, under reduced pressure. T.l.c. analysis showed that three products had been formed and indicated the presence of unchanged (III). The crude oil (240 mg) was then chromatographed immediately on silica plates using diethyl ether–pentane solution as eluant. The three products were, in order of elution, (*i*) (V) (9 mg) [ν(CO) at 2 046 and 1 973 cm^{-1}; δ 5.28 (2 H) $H^{2,3}$, 3.24 (2 H) $H^{1,4}$, and 1.66 p.p.m. (4 H) $H^{5,6}$], (*ii*) (IIb) (45 mg) [ν(CO) at 2 045, 1 975, and 1 969 cm^{-1}; δ 5.09 (1 H) H^3, 3.46 (1 H) H^1, 2.78 (1 H) H^4, 3.58 (3 H) OMe, and 2.65 p.p.m. (4 H) $H^{5,6}$], and (*iii*) (Ib) (36 mg) [ν(CO) at 2 042, 1 973, and 1 965 cm^{-1}; δ 5.27 (1 H) H^2, 5.00 (1 H) H^3, 2.90 (1 H) H^4, 3.43 (3 H) OMe, 2.2 (1 H), and 1.6—1.85 p.p.m. (3 H) $H^{5,6}$]. Unchanged starting material (90 mg) was eluted last [ν(CO) at 2 051, 1 982, and 1 979 cm^{-1}].

Thermal Reaction of Tricarbonyl(η-5-endo-*methoxycyclohexa*-1,3-*diene*)*iron*, (IV).—As above, the pure complex (200 mg) in n-heptane (15 cm^3) was placed in a Carius tube and heated at 135—140 °C for 36 h. The resulting crude orange oil (138 mg) was analyzed by t.l.c. and ^1H n.m.r. before chromatography. Both methods indicated that (IV) was essentially unchanged. Separation, as above, gave pure (V) (2 mg) [ν(CO) at 2 046 and 1 973 cm^{-1}] and (IV) (95 mg) [ν(CO) at 2 054, 1 992, and 1 972 cm^{-1}; δ 5.22 (2 H) $H^{2,3}$, 3.3 (2 H) $H^{1,4}$, 3.05 (1 H) H^5, 3.18 (3 H)OMe, 1.88, and 1.54 p.p.m. (2 H) H^6], plus several milligrams of an oil which was not examined further. The R_F value of the complex was quite different from those of (Ib) and (IIb).

Thermal Reaction of (VI).—The pure complex (350 mg) was heated at 137 °C for 44 h as described above. Filtering the reacted mixture through $Mg[SO_4]$ gave a clear yellow solution. Removal of the solvent at room temperature yielded an orange oil (204 mg) which consisted of three main products and starting material as judged by t.l.c. analysis. Separation on silica gave (*i*) (V) (12 mg) (^1H n.m.r. and mass spectra identical to those obtained previously and to those reported in the literature [21,22]), (*ii*) (IIc) (39 mg) [ν(CO) at 2 045, 1 975, and 1 970 cm^{-1}; δ 5.06 (1 H) H^3, 3.44 (1 H) H^1, 2.74 (1 H) H^4, and 1.8 p.p.m. (4 H) $H^{5,6}$]; (*iii*) (Ic) (50 mg) [ν(CO) at 2 042, 1 973, and 1 965 cm^{-1}; δ 5.27 (1 H) H^2, 5.00 (1 H) H^3, 2.95 (1 H) H^4, and 1.6—2.2 p.p.m. (4 H) $H^{5,6}$], and (*iv*) (VI) (65 mg).

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* 1 eV ≈ 1.60 × 10^{-19} J, 1 mmHg ≈ 13.6 × 9.8 Pa.

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