Regiospecific Rearrangements of η^2 and η^4-1,4-Diene Complexes of Iron(0); the Mechanisms of Metal-promoted 1,3-Hydrogen Shifts

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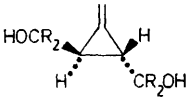
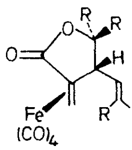
Summary Thermal rearrangements of η^2- and η^4-3-methylene-4-vinyldihydrofuran-2(3*H*)-one complexes of iron(0) yield isomeric 1,3-diene complexes *via* regiospecific 1,3-hydrogen shifts; the mechanistic implications with respect to metal-promoted olefin isomerisations are discussed.

A frequently proposed mechanism for the transition metal-promoted isomerisation of olefins involves the formation of allyl-metal-hydride intermediates.[1,2] The factors governing the formation of such species, their intimate structure, and the mechanism of their collapse to regenerate an olefin–metal system are only tenuously defined. Metal-promoted suprafacial 1,3-hydrogen shifts, normally thermally forbidden processes, have been proposed, on the basis of theoretical predictions, to provide a low-energy route for such isomerisations.[3] Experimentally it has been impossible to differentiate between the two alternative mechanisms in isomerisation systems where both may be occurring.

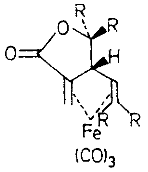
(−)-*trans*-2(*R*),3(*R*)-Bis(hydroxymethyl)methylene-cyclopropane (**1a**) reacted with $[Fe_2(CO)_9]$ to yield[4] (**2a**) $\{[\alpha]_D^{20}$ + 20° $\Delta\epsilon$ (340 nm) + 0·27} and (**3a**) $\{[\alpha]_D^{20}$ + 150°, $\Delta\epsilon$ (421 nm) − 0·13}.† Complex (**2a**) rearranged slowly in refluxing diethyl ether to yield as the only product (**4a**) {60%; m.p. 101—102 °C; ν_{CO} (hexane) 2065s, 2005s, 1992s, and 1776m cm^{-1}; $[\alpha]_D^{20}$ 0°; $\Delta\epsilon$ (410 nm) + 0·007}. The deuteriated complex (**2b**) similarly rearranged to (**4b**), with no deuterium scrambling. Optically active (**2a**) therefore rearranges regiospecifically, but with extensive racemisation. The most plausible mechanism for the rearrangement of (**2a**) is depicted in Scheme 1. Racemisation can only occur ***via*** the terminal σ-allylic intermediate (**5**), in which the two faces of the prochiral organic ligand becomes enantiotopic.



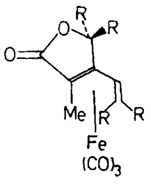
(1a) R = H
(1b) R = D



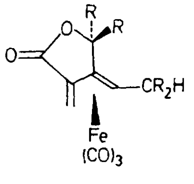
(2a) R = H
(2b) R = D



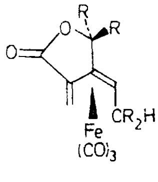
(3a) R = H
(3b) R = D



(4a) R = H
(4b) R = D



(6a) R = H
(6b) R = D



(7a) R = H
(7b) R = D

In contrast, complex (**3a**) rearranged rapidly in refluxing ether to yield a mixture of (**6a**) {30%; m.p. 121—123 °C; ν_{CO} (hexane) 2062s, 2004s, 1986s, and 1792m cm^{-1}; $[\alpha]_D^{20}$ + 120°; $\Delta\epsilon$ (391 nm) + 5·05}, and (**7a**) {70%; m.p. 109—111 °C; ν_{CO} (hexane) 2062s, 2004s, 1988s, and 1790 cm^{-1}; $[\alpha]_D^{20}$ + 42°; $\Delta\epsilon$ (390 nm) + 4·60]. Similarly (**3b**) yielded an identical

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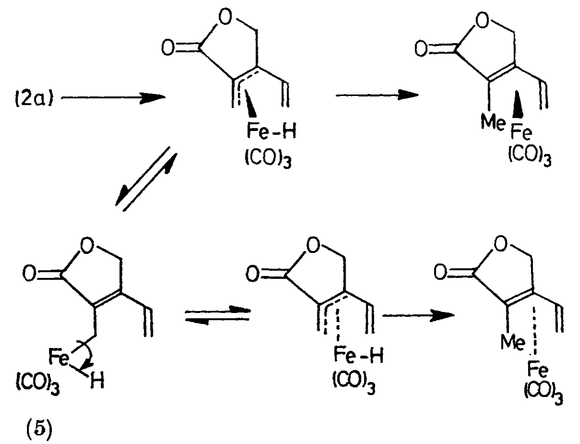
† (−)-(**1a**) was prepared by $LiAlH_4$ reduction[5] of the dimethyl ester of (+)-Feist's acid, which has been shown[6] to have the absolute configuration as drawn. The absolute configurations of (**2a**) and (**3a**) follow,[4] since a chiral carbon centre from (**1a**) is preserved in both products, and are as drawn. C.d. data given ($\Delta\epsilon$) are for the lowest energy optically active *d–d* transitions in all complexes.

ratio of (**6b**) and (**7b**), with no deuterium scrambling.‡ The ratio and optical activity of (**6a**) and (**7a**) were identical if the rearrangement of (**3a**) was carried out in refluxing hexane. Complexes (**6a**) and (**7a**) were not interconverted, nor did they show any loss of optical activity, after prolonged refluxing in hexane. No traces of complex (**4**) were ever observed under any of the above conditions.



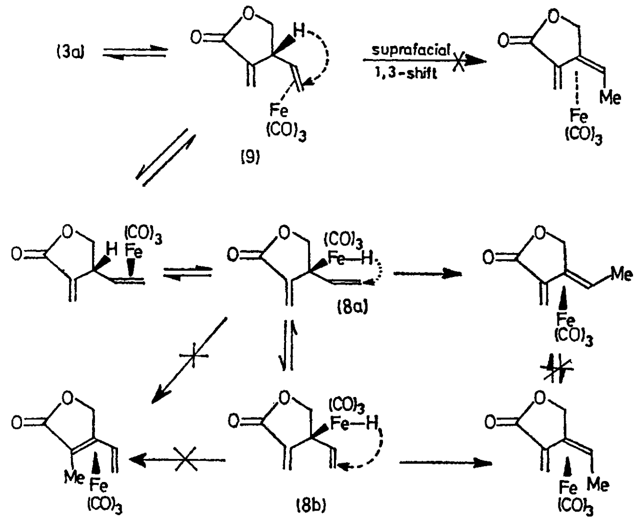
Scheme 1

Rearrangement of optically active (**3a**) occurs regiospecifically, yet without extensive racemisation; furthermore, both products (**6a**) and (**7a**) exhibit the same sign for the circular dichroism of the lowest energy *d–d* transition, indicating that both isomers possess the same absolute configuration.[7] The proposed rearrangement mechanism is depicted in Scheme 2.

Since racemisation does not occur, any terminal σ-allylic intermediate analogous to (**4**) must be discounted. However, the only intermediate which can give rise to both (**6a**) and (**7a**) having the same absolute configuration is the internal σ-allylic species, which can exist as two conformational isomers (**8a**) and (**8b**). Formation of (**8**) cannot occur *via* an intermediate π-allylic species, since any $\pi \to \sigma \to \pi$ transformation of such a species would favour the terminal σ-allyl rather than the internal σ-allyl (**8**),[8] and would consequently lead to racemisation. Formation of (**8**) must therefore arise *via* a direct insertion of the metal into the C–H bond.

The ratio of (**6a**) and (**7a**) produced depends upon the position of the conformational equilibrium between (**8a**) and (**8b**). However, collapse of (**8a**) or (**8b**) to the final product *via* a π-allylic species must be unlikely.

Moreover, intermediates (**8a**) and (**8b**) do not collapse to produce complex (**4**). Formation of (**6a**) and (**7a**) from (**8a**) and (**8b**) must therefore occur *via* a direct H-transfer from the metal to the terminal carbon atom of the vinyl olefin. Molecular models show that this terminal carbon atom can attain closer proximity to the metal than in the rigidly constrained vinylidene olefin. This flexibility within one-half of the molecule explains the formation of, and regiospecificity of the collapse of, (**8a**) and (**8b**); the rigidity within the other half presumably explains why intermediate (**8**) is not formed directly from complex (**2a**). It follows that where such flexibility exists, direct metal insertion into C–H bonds and direct H-migration from metal to carbon must be lower energy processes than formation of π-allylic metal systems.



Scheme 2

Finally, the first step in the isomerisation mechanism depicted in Scheme 2 generates the theoretically ideal intermediate (**9**) in which a metal assisted suprafacial 1,3-hydrogen shift should occur, if it is at all feasible.[3] Such a shift can only yield isomer (**7a**); isomer (**6a**) must be formed by the alternative route since the isomers are not interconvertible. Formation of (**7a**) *via* a metal-promoted suprafacial shift can only result in isomer (**7a**) having the opposite absolute configuration to (**6a**) (Scheme 2). This is not observed, conclusively demonstrating that the metal-promoted suprafacial 1,3-hydrogen shift cannot effectively compete with the allyl-metal-hydride mechanism as a low-energy isomeration process.

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‡ Satisfactory microanalytical, m.s. and ^{1}H and ^{13}C n.m.r. data have been obtained for all protio and deuterio-complexes reported.

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