Reactions of Co-ordinated Ligands. Part XIV.[1] Regiospecific Thermal Rearrangements of Tetracarbonyl-η^2-[3-methylene-*exo*-4-vinyldihydrofuran-2(3*H*)-one]iron(0) and Tricarbonyl-η^4-[3-methylene-*endo*-4-vinyldihydrofuran-2(3*H*)-one]iron(0) Complexes: the Mechanisms of Metal-promoted 1,3-Hydrogen Shifts

By **Michael Green** * and **Russell P. Hughes**, Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS

Tetracarbonyl-η^2-[3-methylene-*exo*-4-vinyldihydrofuran-2(3*H*)-one]iron complexes (1) rearrange regiospecifically at 35° *via* a 1,3-hydrogen shift to yield the corresponding substituted tricarbonyl(1,3-diene)iron complexes (4). Tricarbonyl-η^4-[3-methylene-*endo*-4-vinyldihydrofuran-2(3*H*)-one]iron(0) complexes (2) also rearrange regiospecifically at 35 °C to yield a 1 : 2.3 mixture of (5) and (6), isomeric with (4). Use of optically active complexes (+)-(1a) and (+)-(2a) defines the rearrangement of (+)-(1a) as proceeding with extensive racemisation, yet with slight retention of absolute configuration, and rearrangement of (+)-(2a) as proceeding with inversion of configuration. Kinetic results for the isomerisation of complexes (2) are reported, and the results are all discussed with reference to their implications concerning the mechanisms of metal-promoted olefin isomerisation reactions. A new 'σ-allyl metal hydride' mechanism is proposed as a low-energy isomerisation pathway.

THE transition-metal promoted isomerisation of olefins is one of the fundamentally important reactions of organometallic chemistry.[2] Two major mechanistic pathways are normally considered for such isomerisations; a metal-hydride addition–elimination mechanism, which in effect constitutes a 1,2-hydrogen shift,[3,4] and the so-called 'π-allyl metal hydride' mechanism, which involves a 1,3-hydrogen shift.[5] The latter mechanism has been the less well defined, although elegant studies by Casey and Cyr,[5] and by Whitesides

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[1] Part XIII. B. M. Chisnall, M. Green, R. P. Hughes, and A. J. Welch, *J.C.S. Dalton*, preceding paper.

[2] See for example, C. A. Tolman, 'Transition Metal Hydrides,' Vol. 1, E. L. Muetterties, ed., Marcel Dekker, New York, 1971, ch. 6.

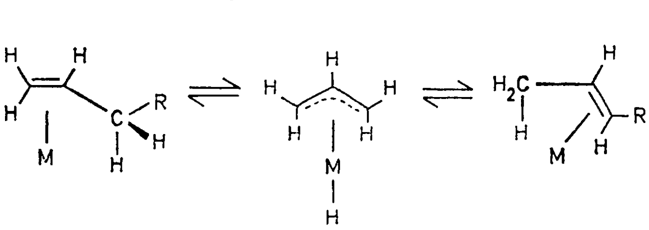
[3] C. P. Casey and C. R. Cyr, *J. Amer. Chem. Soc.*, 1971, **93**, 1280.

[4] C. P. Casey and C. R. Cyr, *J. Amer. Chem. Soc.*, 1973, **95**, 2240.

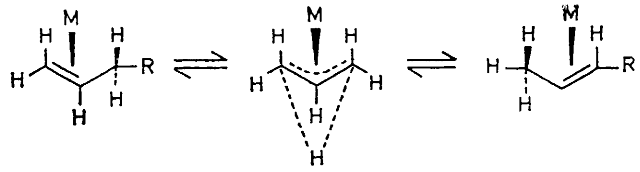
[5] C. P. Casey and C. R. Cyr, *J. Amer. Chem. Soc.*, 1973, **95**, 2248.

and Neilan,[6] have indicated that such a mechanistic pathway must exist. In particular, studies of the isomerisation of 3-ethylpent-2-ene and its 3-deuterio-analogue to give 3-ethylpent-2-ene, catalysed by $[Fe_3(CO)_{12}]$, have required π-allyl metal hydride intermediates to be invoked.[5] The π-allyl metal hydride mechanism is representatively depicted in Scheme 1(a).

An alternative [7,8] to the π-allyl metal hydride mechanism involves a sigmatropic 1,3-suprafacial hydrogen shift as depicted in Scheme 1(b). Notably, the migrating hydrogen is never involved in bonding to the metal, and migrates across the face of the olefinic ligand opposite to that on which the metal is bonded.[7,8] Although this process is thermally 'forbidden' by orbital symmetry considerations in the free olefin, it has been proposed that co-ordination of the olefin to a transition metal can lift this symmetry-imposed restriction and make a metal-promoted 1,3-suprafacial hydrogen shift an energetically viable alternative to the π-allyl metal hydride mechanism.[7,8]



(a) the π-allyl metal hydride mechanism



(b) metal-promoted sigmatropic 1,3-suprafacial hydrogen shift

SCHEME 1

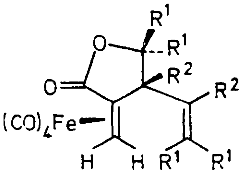
It must be noted, however, that since the net effect of both mechanisms is the same, in that a 1,3-hydrogen shift is effected, it is remarkably difficult to design a practical experiment to differentiate between the two possibilities. However, observations by Whitesides and Neilan,[6] based on the anticipated differences in isotope effects between the two mechanistic pathways, have indicated that the suprafacial shift mechanism may not be operating to a significant extent in the isomerisations of phenyl-substituted tricarbonyl(cyclohexa-1,3-diene)-iron complexes.†

This paper describes an isomerisation system in which it has been possible to distinguish between these two mechanistic possibilities. A preliminary account of this work has appeared.[9]

RESULTS

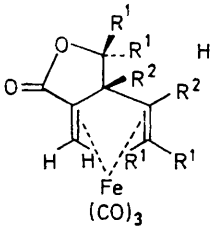
We have previously described the preparation, properties, and both spectroscopic and crystallographic characterisation of complexes (1a) and (2a), and the preparation of the deuterium-labelled analogous (1b,c) and (2b,c).[1] [These complexes are hereafter referred to as *rac*-(1a), *rac*-(2a), *etc.*]. The proposed mechanism of formation of these complexes from *trans*- or *cis*-2,3-bis(hydroxymethyl)methylenecyclopropanes and $[Fe_2(CO)_9]$ required [1] that the integrity of configuration at one of the two tetrahedral cyclopropane carbon atoms be retained. Thus, reaction of partially resolved (−)-*trans*-2(*R*),3(*R*)-bis(hydroxymethyl)methylenecyclopropane (3) [absolute configuration as drawn] with $[Fe_2(CO)_9]$ afforded optically active (+)-(1a) and (+)-(2a), which must have the absolute configuration as drawn. Circular dichroism data for all optically active complexes are listed in Table 1.

Prolonged reflux (16 h) of a solution of the tetracarbonyl complex *rac*-(1a) in diethyl ether afforded a single tricarbonyl complex, in 60% yield, shown by microanalysis, i.r. spectroscopy, mass spectrometry (see Experimental section), and ^1H n.m.r. (Table 2) and ^{13}C n.m.r. (Table 3) spectroscopy



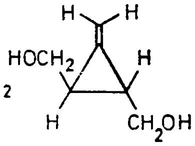
(1)

a; $R^1=R^2=H$
b; $R^1=D$, $R^2=H$
c; $R^1=H$, $R^2=D$

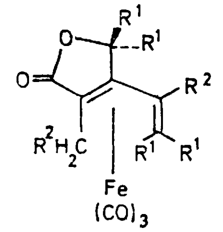


(2)

a; $R^1=R^2=H$
b; $R^1=D$, $R^2=H$
c; $R^1=H$, $R^2=D$

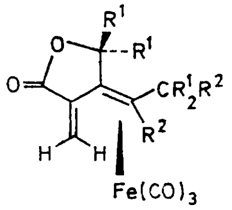


(3)



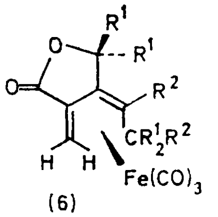
(4)

a; $R^1=R^2=H$
b; $R^1=D$, $R^2=H$
c; $R^1=H$, $R^2=D$



(5)

a; $R^1=R^2=H$
b; $R^1=D$, $R^2=H$
c; $R^1=H$, $R^2=H$



(6)

a; $R^1=R^2=H$
b; $R^1=D$, $R^2=H$
c; $R^1=H$, $R^2=D$

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† Whitesides and Neilan [6] consider the possibility of a sigmatropic 1,5-suprafacial hydrogen shift. This may equally well be represented by two consecutive 1,3-suprafacial hydrogen shifts.

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

[7] F. D. Mango, *Adv. in Catalysis*, 1969, **20**, 318.

[8] F. D. Mango, *Co-ordination Chem. Rev.*, 1975.

[9] M. Green and R. P. Hughes, *J.C.S. Chem. Comm.*, 1975, 619.

to be *rac*-(4a). Some decomposition was observed during this rearrangement. Similarly the tetradeuterio- and dideuterio-complexes *rac*-(1b) and *rac*-(1c), on refluxing in diethyl ether, afforded the analogous complexes *rac*-(4b) and *rac*-(4c) respectively. The ^{1}H n.m.r. (Table 2) and ^{13}C n.m.r. (Table 3) spectra of these complexes confirmed the positions of deuterium incorporation.

The rearrangement of (+)-(1a) was carried out under identical conditions and afforded a sample of (4a) which showed no detectable specific rotation at the D-line. The circular dichroism spectrum of this sample (Table 1), however, exhibited weak absorptions. Apparently, therefore, while the rearrangement of (+)-(1a) had occurred with extensive racemisation, this racemisation was not complete.

Similarly, rearrangement of a solution of *rac*-(2a) in refluxing diethyl ether proceeded to completion more quickly than that of *rac*-(4a) [4 h under identical conditions of concentration] to yield a mixture of two tricarbonyliron complexes, both isomeric with *rac*-(4a). The two products could not be separated by column chromatography, but formed visually different crystalline forms on crystallisation from hexane. These could be physically separated by

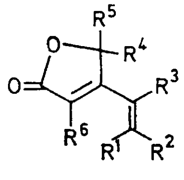
TABLE 1

Circular dichroism spectral data for complexes (+)-(1a), (+)-(2a), (+)-(4a), (+)-(5a), and (+)-(6a) (MeOH solution)

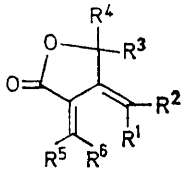
Complex	(+)-(1a)	(+)-(2a)	(+)-(4a)	(+)-(5a)	(+)-(6a)
$\lambda_{max.}$/nm ($\Delta\varepsilon$)	340 (+0.27)	421 (−0.13)	410 (+0.007)	391 (+5.05)	390 (+4.60)
	287 (−1.82)	312 (+0.73)	320 (−0.148)	339 (−5.54)	339 (−6.50)
	221 (+2.44)	245 (−0.14)	232 (+0.89)	229 (−3.92)	277 (−4.40)
		214 (+1.50)	203 (+1.78)	263 (−3.06)	240 (+3.83)
				225 (+10.00)	210 (−7.65)

TABLE 2

^{1}H N.m.r. data (CDCl$_3$; 34 °C; 100 MHz) for complexes (4), (5), and (6)



(4)

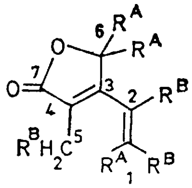


(5) and (6)

							τ(multiplicity); J/Hz					
Complex	R^1	R^2	R^3	R^4	R^5	R^6	R^1	R^2	R^3	R^4	R^5	R^6
(4a)	H	H	H	H	H	CH$_3$	8.65(dd) $J_{1,2} = 3$ $J_{1,3} = 9$	7.89(dd) $J_{1,2} = 3$ $J_{2,3} = 7$	3.96(dd) $J_{1,3} = 9$ $J_{2,3} = 7$	7.88(d) $J_{4,5} = 12.5$	5.22(d) $J_{4,5} = 12.5$	8.59(s)
(4b)	D	D	H	D	D	CH$_3$			3.96(bs)			8.59(s)
(4c)	H	H	D	H	H	CH$_2$D	8.65(d) $J_{1,2} = 3$	7.89(d) $J_{1,2} = 3$		4.88(d) $J_{4,5} = 12.5$	5.22(d) $J_{4,5} = 12.5$	8.59(s)
(5a)	H	CH$_3$	H	H	H	H	8.27(q) $J_{1,2} = 6$	8.42(d) $J_{1,2} = 6$	4.65(d) $J_{3,4} = 14.5$	4.91(d) $J_{3,4} = 14.5$	7.80(d) $J_{5,6} = 4$	9.68(d) $J_{5,6} = 4$
(5b)	H	CHD$_2$	D	D	H	H	8.27(d) $J_{1,2} = 6$	8.42(bd) $J_{1,2} = 6$			7.80(d) $J_{5,6} = 4$	9.68(d) $J_{5,6} = 4$
(5c)	D	CH$_2$D	H	H	H	H		8.42(bs)	4.65(d) $J_{3,4} = 14.5$	4.91(d) $J_{3,4} = 14.5$	7.80(d) $J_{5,6} = 4$	9.68(d) $J_{5,6} = 4$
(6a)	CH$_2$	H	H	H	H	H	8.82(d) $J_{1,2} = 7$	6.59(q) $J_{1,2} = 7$	4.64(d) $J_{2,4} = 14.5$	5.20(d) $J_{5,6} = 4$	6.55(d) $J_{5,6} = 4$	8.58(d)
(6b)	CH$_2$D	H	D	D	H	H	8.82(bd) $J_{1,2} = 7$	6.59(d) $J_{1,2} = 7$			6.55(d) $J_{5,6} = 4$	8.58(d) $J_{5,6} = 4$
(6c)	CH$_2$D	D	H	H	H	H	8.82(bs)		4.64(d) $J_{3,4} = 14.5$	5.20(d) $J_{3,4} = 14.5$	6.55(d) $J_{5,6} = 4$	8.58(d) $J_{5,6} = 4$

TABLE 3

^{13}C N.m.r. data for complexes (4) (CDCl$_3$; 34 °C; 25.15 MHz)



Complex	R^A	R^B	C^1	C^2	C^3	C^4	C^5	C^6	C^7	Fe(CO)$_3$
(4a)	H	H	38.77	83.36	111.27	57.82	14.01	70.38	180.62	208.05
(4b)	D	H		83.36	111.27	57.28	14.01		180.62	208.05
(4c)	H	D	38.77		111.27	57.82		70.38	180.62	208.05

hand. The two complexes were characterised by microanalysis, i.r. spectroscopy, mass spectrometry (Experimental section), and ^1H n.m.r. (Table 2) and ^{13}C n.m.r. (Table 4) spectroscopy, as the *syn*- and *anti*-isomers *rac*-(5a) and *rac*-(6a). The ratio of *rac*-(5a) : *rac*-(6a), determined by integration of the ^1H n.m.r. spectrum of the crude reaction mixture, was 1 : 2.3. When the rearrangement of *rac*-(2a) was carried out in refluxing hexane, instead of diethyl ether, the same ratio of *rac*-(5a) : *rac*-(6a) was obtained.

No interconversion between isomers was observed when solutions of *rac*-(4a), *rac*-(5a), or *rac*-(6a) in heptane were refluxed for 16 h. Similarly no traces of *rac*-(4a) were observed in the rearrangement of *rac*-(2a), and no traces of either *rac*-(5a) or *rac*-(6a) were observed during the rearrangement of *rac*-(1a).

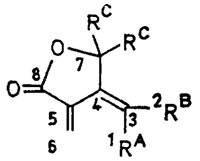
The tetradeuterio-complex *rac*-(2b) similarly rearranged to a 1 : 2.3 mixture of *rac*-(5b) : *rac*-(6b) on being refluxed in either diethyl ether or hexane. Similarly, the dideuterio-complex *rac*-(2c) rearranged in refluxing diethyl ether or hexane to afford a 1 : 2.3 mixture of *rac*-(5c) : *rac*-(6c). No scrambling of deuterium between sites was observed, within the limits of ^1H n.m.r. integration, after the deuteriated products had been refluxed for 16 h in heptane.

The rearrangement of (+)-(2a) was carried out under identical conditions in either refluxing diethyl ether or hexane, and afforded a 1 : 2.3 mixture of (+)-(5a) : (+)-(6a). Both isomers exhibited strong circular dichroism in their absorption spectra (Table 1). Furthermore, no loss of optical activity was observed on refluxing solutions of either (+)-(5a) or (+)-(6a) in heptane for 16 h.

A brief kinetic study of the rearrangements of both *rac*-(2a) and *rac*-(3c) in heptane at 321 K demonstrated no detectable kinetic isotope effect; $k_H/k_D = 1.05 \pm 0.1$, $k_{obs} = 5.6 \pm 0.3 \times 10^{-4}$ s^{-1}. First-order kinetics were observed over at least three half-lives for the reaction.

TABLE 4

^{13}C N.m.r. data for complexes (5) and (6) ($CDCl_3$; 34 °C; 25.15 MHz)



Complex	R^A	R^B	R^2	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	$Fe(CO)_3$
(5a)	H	CH_3	H		15.29	54.30	114.67	78.02	29.42	69.29	174.80	208.05
(5b)	H	CHD_2	D			54.30	114.67	78.02	29.42		174.80	208.05
(5c)	D	CH_2D	H				114.67	78.02	29.42	29.29	174.80	208.05
(6a)	CH_3	H	H	12.68		51.02	116.19	85.91	31.91	71.59	174.19	207.49
(6b)	CHD_2	H	D			51.02	116.19	85.91	31.91		174.19	207.49
(6c)	CH_2D	D	H				116.19	85.91	31.91	71.59	174.19	207.49

DISCUSSION

The tetracarbonyliron complexes (1) and the tricarbonyliron complexes (2) undergo remarkably regiospecific thermal rearrangements, under mild conditions, to yield different products. The use of deuterium-labelled complexes (1) and (2) unambiguously defines the rearrangement of each as proceeding *via* a pure 1,3-hydrogen (or deuterium) shift, and observation of first-order kinetics for the rearrangement of complexes *rac*-(2a) and *rac*-(2c) confirms the unimolecularity of this rearrangement.

Assignment of structural differences between isomers (5) and (6) is based on the well established observation that methyl groups, or protons in *syn*-positions on the terminal carbon atoms of a co-ordinated 1,3-diene, resonate, in the ^1H n.m.r. spectrum, at lower field than those corresponding moieties in *anti*-positions.[10] Notably the same trend is observed for the *syn*- and *anti*-methyl carbon resonances of complexes (5) and (6) (Table 4).

In order to assess the significance of the results of the rearrangements of the optically active complexes (+)-(1a) and (+)-(2a), it is necessary to assign the absolute configurations of the reactants and products. Based on the knowledge of the absolute configuration of the organic starting material (−)-*trans*-2(*R*),3(*R*)-bis-(hydroxymethyl)methylenecyclopropane (3) (see Experimental section), the absolute configuration of the resultant 3-methylene-4(*R*)-vinyldihydrofuran-2(3*H*)-one ligand in both (+)-(1a) and (+)-(2a) must be as drawn. The positions of the $Fe(CO)_4$ moiety in (+)-(1a) and the $Fe(CO)_3$ moiety in (+)-(2a) are known from the molecular structures of their racemic analogues.[1] The absolute configurations of (+)-(1a) and (+)-(2a) must therefore be as drawn, with the iron atoms bonded to opposite faces of the lactone ring system.

It has previously been established that for a variety of chiral transition-metal complexes, the sign of the circular dichroism (c.d.) observed for *d–d* transitions can be related to the absolute configuration of the complex concerned.[11,12] In particular, the absolute configurations of tricarbonyliron complexes of prochiral 1,3-dienes, and tetracarbonyliron complexes of prochiral olefins, have been successfully related to the sign of the c.d. of the lowest energy *d–d* transition.[11] It must be noted that the signs of the c.d. for *d–d* transitions must relate to the absolute configuration at the metal centre in the case of prochiral ligands. It is not surprising, therefore, that the signs of the c.d. for the lowest energy

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[10] G. F. Emerson, J. E. Mahler, R. Kochhar, and R. Pettit, *J. Org. Chem.*, 1964, **29**, 3620.

[11] A. Musco, R. Palumbo, and G. Paiaro, *Inorg. Chim. Acta*, 1971, **5**, 157.

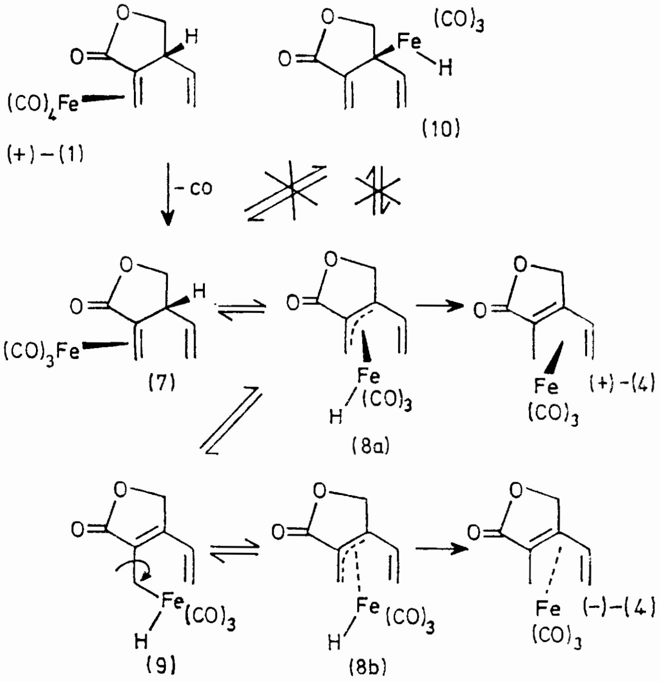
[12] A. D. Wrixon, E. Premuzic, and A. I. Scott, *Chem. Comm.*, 1968, 639; and references cited therein.

d–d transitions (Table 1) of (+)-(1a) [340 nm, positive] and (+)-(2a) [421 nm, negative] are opposite, even though the ligand has the same absolute configuration at its chiral carbon centre in both cases, since the metal atoms are situated on opposite faces of the ligand.*

Similarly the complexes (+)-(5a) and (+)-(6a), derived from the rearrangement of (+)-(2a), must have the same absolute configuration as one another,[11] since both exhibit strongly positive c.d. for their lowest energy *d–d* transitions. Observation of strongly positive c.d. places the $Fe(CO)_3$ moieties in both complexes (+)-(5a) and (+)-(6a) on the same face of the lactone ligand as the $Fe(CO)_4$ group in (+)-(1a), and, consequently, on the opposite face of the lactone ligand to the $Fe(CO)_3$ moiety in the precursor complex (+)-(2a). Thus, the transformation of (+)-(2a) into either (+)-(5a) or (+)-(6a), involves a migration of the iron atom from one face of the ligand to the other, *i.e.* the rearrangement proceeds with inversion of absolute configuration at the metal centre.

The sample of (+)-(4a), obtained by rearrangement of (+)-(1a), exhibits only very weak c.d. for the *d–d* transitions. The c.d. for the lowest-energy band at 410 nm is particularly weak, by a factor of *ca.* 10^{-2}, compared to the c.d. for the corresponding bands in (+)-(5a) and (+)-(6a). Since the three complexes are so similar structurally we have therefore concluded that extensive racemisation occurs during the rearrangement of (+)-(1a) to (+)-(4a).† However, the c.d. of the 410 nm band of (+)-(4a), though very weak, is positive in sign, placing the $Fe(CO)_3$ moiety in the dominant enantiomer on the same face of the lactone ring as the $Fe(CO)_4$ moiety in the precursor (+)-(1a). Rearrangement of (+)-(1a) therefore occurs with extensive, though not complete racemisation, and with slight retention of absolute configuration.

The mechanism which best fits the observations for the rearrangement of complexes (1)—(4) is depicted in Scheme 2, using the rearrangement of (+)-(1a) as an example. The first, and presumably rate-determining, step involves loss of a carbonyl ligand to generate the co-ordinatively unsaturated species (7) which can then undergo an oxidative addition reaction to produce the π-allylic iron hydride (8a).[5] Intermediate (8a) has two available options, apart from regenerating (7); it may directly undergo reductive elimination to afford (+)-(4a), or it may undergo a $\pi \longrightarrow \sigma$ rearrangement to yield a short-lived terminal σ-allylic species (9). Rotation during the lifetime of (9), as shown, followed by reformation of a π-allylic iron hydride (8b) generates the immediate precursor to (−)-(4a). Intermediate (9) therefore represents a racemisation intermediate. Since (9) can only be formed *via* the intermediacy of a π-allylic iron hydride, the observation of racemisation in this system implies that the π-allylic iron hydride (8a) must have a sufficiently long lifetime for the rate of $\pi \longrightarrow \sigma \longrightarrow \pi$ formation, and consequently racemisation, to compete effectively with the rate of reductive elimination to give the final product.



racemisation intermediate

SCHEME 2

An alternative internal σ-allylic species (10) could also be conceivably formed by a $\pi \longrightarrow \sigma$ transformation of (8a). However, it has been previously well established that the free energy of activation for formation of a σ-allylic species from a π-allylic precursor increases with the number of substituents present on the carbon atom which becomes σ-bonded to the metal.[13,14] Consequently formation of the primary carbon–metal σ bond in (9) from (8a) must constitute a much lower energy process than the formation of a tertiary carbon–metal bond in (10) from (8a). Species (10) must, therefore, be regarded as a relatively high-energy species to be formed *via* a π-allylic precursor.

The various equilibria possible as mechanistic pathways for the rearrangement of complexes (2) into a 1 : 2.3 mixture of (5) and (6) are depicted in Scheme 3, using the rearrangement of (+)-(2a) as an example. Migration of the iron atom from one face of the organic ligand to the other is required to bring it into proximity with the hydrogen atom which is to undergo the eventual 1,3-shift, and also to explain the absolute configurations

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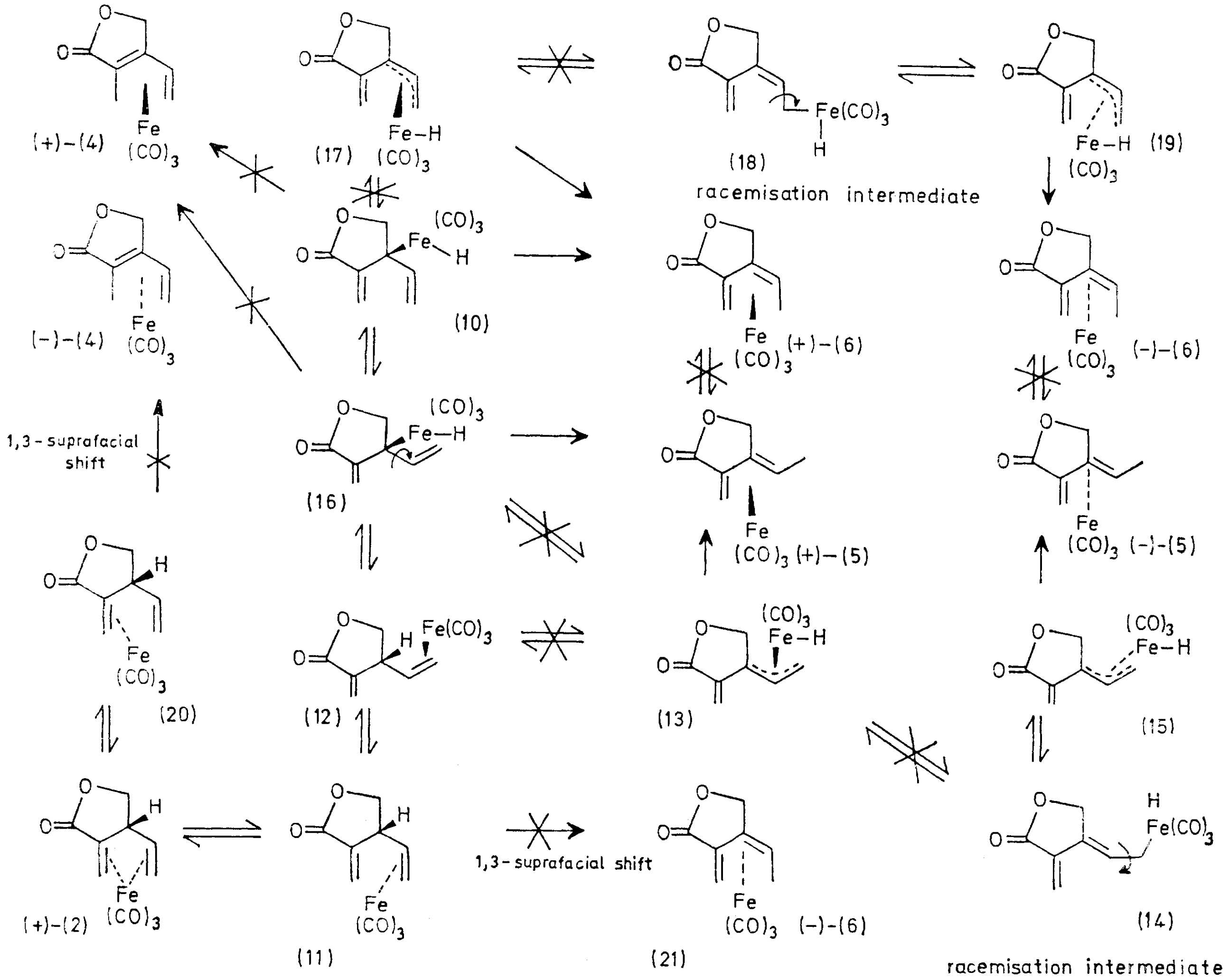
* This requires that the major source of dissymmetric perturbation at the metal centre is due to the prochiral lactone ring system rather than the single chiral carbon atom in (+)-(1a) and (+)-(2a).

† Attempts to obtain an optical assay of all the optically active complexes reported here by ^1H n.m.r. spectroscopy in the presence of all the commercially available Optishift reagents have unfortunately failed. The ^1H n.m.r. spectra are too complicated for any satisfactory resolution of enantiomers to be observed.

[13] J. W. Faller, M. E. Thomsen, and M. J. Mattina, *J. Amer. Chem. Soc.*, 1971, **93**, 2642.

[14] J. W. Faller and M. E. Thomsen, *J. Amer. Chem. Soc.*, 1969, **91**, 6871.

of the products obtained. This migration can be achieved by dissociation of the η^4-bonded ligand in (+)-(2a) to an η^2-bonded form as in (11); rotation about a carbon–carbon single bond is now possible, transferring the Fe(CO)$_3$ moiety from one face of the ligand to the other, and generating (12). Analogous processes have been proposed to explain the isomerisations of phenyl-substituted (cyclohexa-1,3-diene)iron tricarbonyl complexes[6] and the rearrangements of hexatriene iron tricarbonyl complexes.[15,16] Furthermore, since the rearrangements of *rac*-(2a) and *rac*-(2c) show no significant kinetic isotope effect, paralleling the results of Whitesides,[6] this initial dissociative–rotation step is probably rate-determining.



SCHEME 3

Transformation of (12) into a π-allylic iron hydride (13) seems, at first sight, the logical step immediately prior to the formation of (+)-(5) as shown (Scheme 3). Two problems arise; first (+)-(6), the *major product* cannot be formed directly from (13), nor can it be formed *via* (+)-(5) since the isomers are non-interconvertible; secondly, formation of a π-allylic species such as (13) must lead to the possibility of a low-energy $\pi \longrightarrow \sigma \longrightarrow \pi$ transformation *via* the terminal σ-allylic species (14), with consequent racemisation.

The only reaction pathway which can lead to the formation of both (+)-(5a) and (+)-(6a), having the same absolute configurations, must proceed *via* the internal σ-allylic intermediate (16), in which rotation of the vinyl group can lead to the conformer (10). As discussed previously, intermediate (16) cannot be formed *via* the intermediacy of a π-allylic species such as (13), since any $\pi \longrightarrow \sigma \longrightarrow \pi$ transformation of (13) would favour formation of (14) rather than (16), and would, consequently, lead to racemisation. Intermediate (16) must, therefore, form directly from the olefin complex (12) by a direct insertion of the Fe(CO)$_3$ moiety into the

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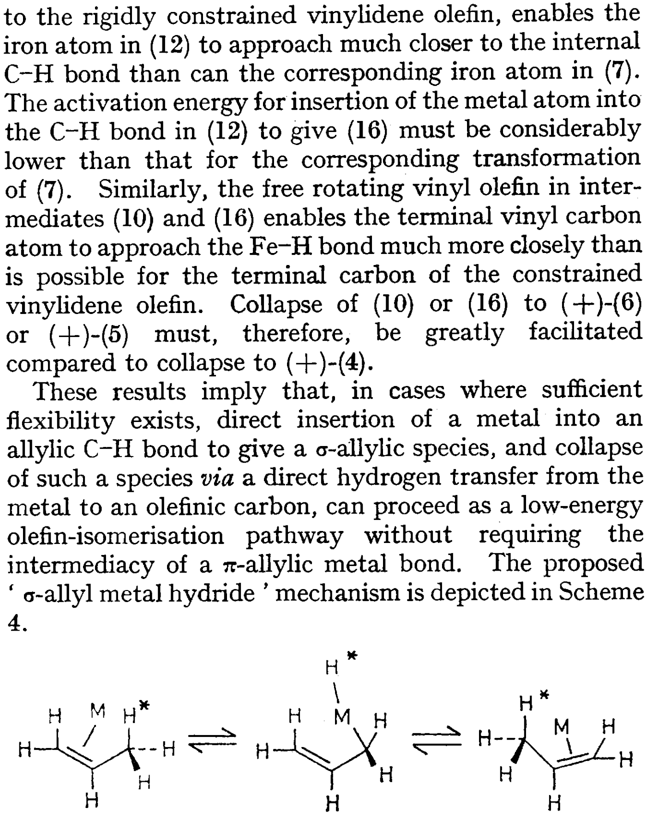
[15] H. W. Whitlock and R. L. Markezich, *J. Amer. Chem. Soc.*, 1971, **93**, 5290, 5291.

[16] H. W. Whitlock, C. Reich, and W. P. Woessner, *J. Amer. Chem. Soc.*, 1971, **93**, 2483.

C–H bond. Similarly, it must be extremely unlikely that collapse of (16) into (+)-(5) occurs *via* the intermediate formation of (13) since any significant lifetime for (13) should lead to racemisation *via* (14). It seems probable, therefore, that formation of (+)-(5a) from (16) and (+)-(6a) from (10) occurs *via* a direct hydrogen migration from the metal to the terminal vinyl carbon atom. The preference for formation of (+)-(6) rather than (+)-(5) must reflect some difference in thermodynamic stability associated with the rotational form of the vinyl olefin in (10) compared to that in (16).

Notably intermediates (10) and (16) show no propensity towards collapse to (+)-(4); nor can either (10) or (16) be formed directly from species (7) (Scheme 2), since the products from one system are never observed in the other. Molecular models of the intermediates (7), (12), (10), and (16) demonstrate quite unambiguously that the rotational flexibility of the vinyl olefin, compared to the rigidly constrained vinylidene olefin, enables the iron atom in (12) to approach much closer to the internal C–H bond than can the corresponding iron atom in (7). The activation energy for insertion of the metal atom into the C–H bond in (12) to give (16) must be considerably lower than that for the corresponding transformation of (7). Similarly, the free rotating vinyl olefin in intermediates (10) and (16) enables the terminal vinyl carbon atom to approach the Fe–H bond much more closely than is possible for the terminal carbon of the constrained vinylidene olefin. Collapse of (10) or (16) to (+)-(6) or (+)-(5) must, therefore, be greatly facilitated compared to collapse to (+)-(4).

These results imply that, in cases where sufficient flexibility exists, direct insertion of a metal into an allylic C–H bond to give a σ-allylic species, and collapse of such a species *via* a direct hydrogen transfer from the metal to an olefinic carbon, can proceed as a low-energy olefin-isomerisation pathway without requiring the intermediacy of a π-allylic metal bond. The proposed ' σ-allyl metal hydride ' mechanism is depicted in Scheme 4.



SCHEME 4 The ' σ-allyl metal hydride ' mechanism

The possibility of a metal-promoted sigmatropic 1,3-suprafacial hydrogen-shift mechanism has not yet been considered. Of the several possible intermediates available for the rearrangement of (+)-(2a) in Scheme 3, two such species, (11) and (20), comprise a co-ordinatively unsaturated metal fragment bonded in the theoretically ideal situation [7,8] for such a metal-promoted shift to occur. Furthermore both (11) and (20) are generated by simple $\eta^4 \rightarrow \eta^2$ co-ordination changes in the organic ligand, and as such are the first formed intermediates in any reaction of (+)-(2a). A 1,3-suprafacial hydrogen shift is indeed the only pathway available to species (20); however, no traces of complex (–)-(4), the only possible product, are ever observed in this reaction system. A 1,3-suprafacial hydrogen shift in (11) can only lead to (–)-(6a); this cannot be rationalised with the observed absolute configuration of both the reaction products.

These results allow the definite conclusion that any metal-promoted sigmatropic 1,3-suprafacial hydrogen shift in these systems is certainly not of sufficiently low energy to compete effectively with the σ-allyl metal hydride or the π-allyl metal hydride mechanisms for olefin isomerisation.

EXPERIMENTAL

All reactions were performed under an atmosphere of dry, oxygen-free nitrogen.

^{1}H N.m.r. spectra were recorded on a Varian Associates HA100 spectrometer at 100 MHz. ^{13}C N.m.r. spectra were recorded on a Jeol JNM-PFT-100 spectrometer, operating in the Fourier-transform mode, at 25.15 MHz. I.r. spectra were recorded on a Perkin-Elmer 257 instrument, using 1-mm path-length cells with CaF_2 optics. U.v. absorption spectra were recorded on a Unicam SP 1800 spectrometer.

Feist's acid (methylenecyclopropane-*trans*-2,3-dicarboxylic acid) was resolved with quinine, according to literature methods,[17] affording a crystalline diastereoisomer having a specific rotation $[\alpha]_D^{20} = -159.5°$ ($c = 0.44$ in 1 : 1 EtOH : H_2O). Acidification yielded a sample of Feist's acid having $[\alpha]_D^{20} = +130°$ ($c = 1.39$ in EtOH). Dextrorotatory Feist's acid has been shown to have the 2(*R*), 3(*R*) absolute configuration.[17] This sample of Feist's acid was converted into its dimethyl ester by treatment with diazomethane, and the diester was reduced with $LiAlH_4$, according to literature methods,[18] affording a sample of trans-2(R),3(R)-*bis(hydroxymethyl)methylenecyclopropane* having $[\alpha]_D^{20} = -56°$ ($c = 1.47$ in Et_2O).

The reaction of $[Fe_2(CO)_9]$ with (–)-*trans*-2(*R*),3(*R*)-bis(hydromethyl)methylenecyclopropane in diethyl ether was carried out exactly as described previously for the racemic dialcohol,[1] and yielded tetracarbonyl-η^2-[3-methylene-*exo*-4(*R*)-vinyldihydrofuran-2(3*H*)-one]iron(0) [complex (+)-(1a)] having $[\alpha]_D^{20} = +20°$ ($c = 1.0$ in CH_2Cl_2), and tricarbonyl-η^2-[3-methylene-*endo*-4(*R*)-vinyldihydrofuran-2(3*H*)-one]iron(0) [complex (+)-(2a)] having $[\alpha]_D^{20} = +150°$ ($c = 1.0$ in CH_2Cl_2).

Complexes *rac*-(1a), *rac*-(2a) and the deuterium-labelled complexes *rac*-(1b), *rac*-(1c), *rac*-(2b), and *rac*-(2c) were prepared as described previously.[1]

Thermal Rearrangement of the Tetracarbonyliron Complexes (1).—A solution of complex *rac*-(1a) (0.50 g, 1.7 mmol) in diethyl ether (50 cm^3) was refluxed for 16 h, after which time monitoring of the i.r. spectrum indicated that rearrangement was complete to yield a single tricarbonyl species. The resultant solution was filtered, and the filtrate evaporated to dryness. Recrystallisation of the residue from hexane (–30 °C) yielded complex *rac*-(4a) as yellow *needles* (0.30 g, 66%), m.p. 101—102 °C, ν_{CO} (hexane) 2 065s, 2 005s, 1 992s, and 1 776m cm^{-1}; *m/e* 264(*P*), 236(*P* – CO), 208(*P* – 2CO), and 180(*P* – 3CO) (Found: C, 45.3; H, 3.3. $C_{10}H_8FeO_5$ requires C, 45.4; H, 3.0%).

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[17] W. von E. Doering and H. D. Roth, *Tetrahedron*, 1970, **26**, 2825.

[18] J. J. Gajewski, *J. Amer. Chem. Soc.*, 1971, **93**, 4450.

An identical reaction of *rac*-(1a) in refluxing hexane (50 cm^3) yielded, after 16 h, an identical sample of *rac*-(4a).

Similarly, a solution of complex *rac*-(1b) (0.50 g, 1.7 mmol) in diethyl ether (50 cm^3) yielded, after 16 h at reflux, and an identical work-up procedure, the tetradeuterio-complex *rac*-(4b) as yellow *needles* (0.31 g, 69%), m.p. 102—104 °C; *m/e* 268(*P*), 240(*P* – CO), 218(*P* – 2CO), and 184(*P* – 3CO) (Found: C, 44.8; H, 3.0. $C_{10}H_4D_4FeO_5$ requires C, 44.8; H, 3.0%).

Similarly, a solution of complex *rac*-(1c) (0.50 g, 1.7 mmol) in diethyl ether (50 cm^3) yielded, after 16 h at reflux and an identical work-up procedure, the dideuterio-complex *rac*-(4c) as yellow *needles* (0.32 g, 71%), m.p. 102—103 °C; *m/e* 266(*P*), 238(*P* – CO), 216(*P* – 2CO), and 182(*P* – 3CO) (Found: C, 45.2; H, 3.0. $C_{10}H_6D_2FeO_5$ requires C, 45.1; H, 3.0%).

Similarly, a solution of complex (+)-(1a) (0.40 g, 1.4 mmol) yielded after an identical work-up procedure, the complex (+)-(4a) as yellow *needles* (0.25 g, 68%); $[\alpha]_D^{20} = 0°$ (c = 0.6 in CH_2Cl_2) (Found: C, 45.4; H, 3.3. $C_{10}H_8FeO_5$ requires C, 45.4; H, 3.0%).

Thermal Rearrangement of the Tricarbonyliron Complexes (2).—A solution of complex *rac*-(2a) (0.50 g, 1.9 mmol) in diethyl ether (50 cm^3) was refluxed for 4 h, when the original orange colour had faded to a pale yellow, and the i.r. spectrum indicated rearrangement to be complete. The solution was evaporated to dryness. The ^{1}H n.m.r. spectrum of the crude residue showed it to consist of a 1 : 2.3 mixture of complex *rac*-(5a) : complex *rac*-(6a). Recrystallisation of the residue from hexane (–30 °C) yielded a mixture of small yellow *prisms* (0.10 g, 20%) and yellow *needles* (0.30 g, 60%) which were separated by hand. ^{1}H N.m.r. spectroscopy showed the *prisms* to be pure complex *rac*-(5a), m.p. 121—123 °C; ν_{CO} (hexane) 2 062s, 2 004s, 1 986s, and 1 792m cm^{-1}; *m/e* 264(*P*), 236(*P* – CO), 208(*P* – 2CO), and 180(*P* – 3CO) (Found: C, 45.5; H, 3.3. $C_{10}H_8FeO_5$ requires C, 45.4; H, 3.0%) and the *needles* to be pure complex *rac*-(6a), m.p. 109—111 °C; ν_{CO} (hexane) 2 062s, 2 004s, 1 988s, and 1 790 cm^{-1}; *m/e* 264(*P*), 236(*P* – CO), 208(*P* – 2CO), and 180(*P* – 3CO) (Found: C, 45.4; H, 3.1. $C_{10}H_8FeO_5$ requires C, 45.4; H, 3.0%).

A similar rearrangement of complex *rac*-(2a) in refluxing hexane (2 h) yielded an identical 1 : 2.3 mixture of complex *rac*-(5a) : complex *rac*-(6a), as evidenced by integration of the ^{1}H n.m.r. spectrum of the crude reaction products.

A similar reaction of complex *rac*-(2b) (0.50 g, 1.9 mmol) in diethyl ether (50 cm^3) yielded, after 4 h at reflux and an identical work-up procedure, a 1 : 2.3 mixture of complex *rac*-(5b) : complex *rac*-(6b). Recrystallisation from hexane (–30 °C) afforded pure complex *rac*-(5b) as yellow *prisms* (0. 12 g, 24%), m.p. 122—124 °C; *m/e* 268(*P*), 240(*P* – CO), 218(*P* – 2CO), and 184(*P* – 3CO) (Found: C, 44.6; H, 3.2. $C_{10}H_4D_4FeO_5$ requires C, 44.8; H, 3.0%), and pure complex *rac*-(6b) as yellow *needles* (0.33 g, 66%), m.p. 109—110 °C; *m/e* 268(*P*), 240(*P* – CO), 218(*P* – 2CO), and 184(*P* – 3CO) (Found: C, 44.7; H, 3.3. $C_{10}H_4D_4FeO_5$ requires C, 44.8; H, 3.0%).

A similar reaction of complex *rac*-(2c) (0.50, 1.9 mmol) in diethyl ether (50 cm^3) yielded, after 4 h at reflux and an identical work-up procedure, a 1 : 2.3 mixture of complex *rac*-(5c): complex *rac*-(6c). Recrystallisation from hexane (–30 °C) afforded pure complex *rac*-(5c) as yellow *prisms* (0.11 g, 22%), m.p. 121—123 °C; *m/e* 266(*P*), 238(*P* – CO), 216(*P* – 2CO), and 182(*P* – 3CO) (Found: C, 45.3; H, 3.1. $C_{10}H_6D_2FeO_5$ requires C, 45.1; H, 3.0%) and pure complex *rac*-(6c) as yellow *needles* (0.33 g, 66%), m.p. 109—110 °C; *m/e* 266(*P*), 238(*P* – CO), 216(*P* – 2CO), and 182(*P* – 3CO) (Found: C, 45.2; H, 3.0. $C_{10}H_6D_2FeO_5$ requires C, 45.1; H, 3.0%).

A similar reaction of complex (+)-(2a) (0.50 g, 1.9 mmol) in diethyl ether (50 cm^3) yielded, after 4 h at reflux and an identical work-up procedure, a 1 : 2.3 mixture of complex (+)-5a: complex (+)-(6a). Recrystallisation from hexane (–30 °C) afforded pure complex (+)-(5a) as yellow *prisms* (0.13 g, 26%); $[\alpha]_D^{20} = +120°$ (c = 0.6 in CH_2Cl_2) (Found: C, 45.3; H, 3.1. $C_{10}H_8FeO_5$ requires C, 45.4; H, 3.0%) and pure complex (+)-(6a) as yellow *needles* (0.31 g, 62%); $[\alpha]_D^{20} = +42°$ (c = 0.6 in CH_2Cl_2) (Found: C, 45.4; H, 3.2. $C_{10}H_8FeO_5$ requires C, 45.4; H, 3.0%).

An identical reaction of (+)-(2a) in refluxing hexane, yielded after 2 h at reflux, an identical 1 : 2.3 mixture of complex (+)-(5a) : complex (+)-(6a). The separated complexes were found to have identical specific rotations to the samples obtained from the rearrangement in refluxing ether.

Tests for any Interconvertibility between Isomeric Complexes (4), (5), *and* (6).—A solution of complex (+)-(5a) (0.10 g, 0.38 mmol) in heptane (20 cm^3) was refluxed for 16 h. Evaporation yielded a quantitative return of (+)-(5a) having the same specific rotation. No traces of complexes (6a) or (4a) were observed by either i.r. or ^{1}H n.m.r. spectroscopy.

Identical results (*i.e.* a quantitative return of starting material) were obtained on refluxing solutions of either complex (+)-(6a) or (+)-(4a) in heptane for 16 h.

Similarly, a solution of the tetradeuterio-complex *rac*-(5b) (0.20 g, 0.75 mmol) in heptane (30 cm^3) was refluxed for 16 h. Evaporation yielded a quantitative return of *rac*-(5b) in which no deuterium scrambling had occurred, as evidenced by ^{1}H n.m.r. spectroscopy.

Identical results (*i.e.* a quantitative return of starting material) were obtained on refluxing similar solutions of complexes *rac*-(6b), *rac*-(5c), *rac*-(6c), *rac*-(4b), and *rac*-(4c) in heptane for 16 h.

Kinetics of the Rearrangement of Complexes (2).—The rate of rearrangement of a solution of complex *rac*-(2a) (0.035 g, 0.132 mmol) in heptane (50.0 cm^3) at 320 K was monitored by observing the rate of disappearance of the absorption band at 421 nm in the absorption spectrum of the starting material. This absorption band was found to obey Beer's Law over the range of concentrations used. A good first-order plot was observed over three half-lives of the reaction, after which the intensity changes in the 421 nm band became too small to provide reproducible readings. A value of k_H(obs.) = 5.6 ± 0.3 s^{-1} was calculated for the first-order rate constant. Examination of the reaction under a range of initial concentrations from 0.010 to 0.050 g (0.04—0.20 mmol) in 50.0 cm^3 of heptane yielded first-order plots with rate constants within the range $5.6 \pm 0.3 \times 10^{-4}$ s^{-1}.

The rate of rearrangement of complex *rac*-(2c) was monitored over an identical range of conditions and gave a mean value for k_D(obs.) = $5.1 \pm 0.3 \times 10^{-4}$ s^{-1}. The maximum value for k_H/k_D thus obtainable is 5.6/4.8 = 1.17 which is not considered to be significant.

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