Preparation and Isomerisation of Carbonyl(η-cyclohepta-1,4-diene)(η-cyclohexa-1,3-diene)iron Complexes

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The reduction of $[Fe(C_6H_8)(C_7H_9)(CO)]^+$, (I), with $Na[BH_4]$ in water produces $[Fe(\eta\text{-}1,3\text{-}C_6H_8)(\eta\text{-}1,4\text{-}C_7H_{10})(CO)]$, (II), in good yield together with some $[Fe(\eta\text{-}1,3\text{-}C_6H_8)(\eta\text{-}1,3\text{-}C_7H_{10})(CO)]$, (III). On heating, (II) (as a solid or in solution) undergoes isomerisation to (III) and some $[Fe(\eta\text{-}1,3\text{-}C_6H_8)(1\text{-}\sigma, 3\text{—}5\text{-}\eta\text{-}C_7H_{10})(CO)]$. The kinetics of this first-order reaction have been studied in n-heptane over the temperature range 40—70 °C and the results compared with those for related systems. Reduction of (I) with $Na[BD_4]$ afforded the monodeuteriated η-cyclohepta-1,4-diene complex. Reactions of, and spectroscopic studies (particularly ^1H and ^{13}C n.m.r.) on, this complex indicate that nucleophilic addition has taken place at the *exo*-3-position, and that the *endo*-hydrogen atom migrates during the isomerisation process. Addition of cyanide ion to the complex cation also takes place at the *exo*-3-position, and the product rearranges to the η-2-substituted-1,3-diene complex *ca.* 5 times more rapidly than the unsubstituted complex. Complex (II) reacts with CO to give $[Fe(\eta\text{-}1,3\text{-}C_6H_8)(CO)_3]$ and with PPh_3 the complex $[Fe(\eta\text{-}1,3\text{-}C_6H_8)(CO)(PPh_3)_2]$ is formed *via* a second-order process.

UNTIL recently it was generally accepted that nucleophilic addition to a co-ordinated dienyl group occurred at either the 1- or 2-positions of the dienyl to give 1,3-diene and σ,η-allyl complexes.[1,2] Prior to our preliminary communications,[3,4] no report of attack at the 3-position of a co-ordinated dienyl group to give a 1,4-diene complex had appeared. We now report full details of this work together with a discussion of the factors affecting the rate of isomerisation of the 1,4-diene complex to the 1- and 2-substituted derivatives.

EXPERIMENTAL

All solvents were purified as previously described,[4] and deaerated by passing nitrogen through them immediately before use.

Carbonyl(η-*cyclohepta*-1,4-*diene*)(η-*cyclohexa*-1,3-*diene*)-*iron*, (II).—Sodium tetrahydridoborate (230 mg), dissolved in oxygen-free water (5 cm^3), was added slowly to a cold (0 °C) stirred oxygen-free mixture of carbonyl(1—5-η-cycloheptadienyl)(η-cyclohexa-1,3-diene)iron tetrafluoroborate,[4] $[Fe(C_6H_8)(C_7H_9)(CO)][BF_4]$ (2 g), water (10 cm^3), and diethyl ether (20 cm^3). After stirring for a further 30 min, the two layers were allowed to separate. The ether layer was dried over sodium sulphate and solvent removed under reduced pressure. Extraction of the residue with pentane (30 cm^3) gave a solution which was filtered under nitrogen, and cooled to −78 °C to give the desired orange product (0.88 g, 59%) (Found: C, 65.0; H, 6.8. $C_{14}H_{18}FeO$ requires C, 65.1; H, 7.0%).

Carbonyl(η-3-*cyclohepta*-1,3-*diene*)(η-*cyclohexa*-1,3-*diene*)-*iron*, (III).—Sublimation of (II) at 60 °C gave the red product (70%) (Found: C, 65.6; H, 7.0. $C_{14}H_{18}FeO$ requires C, 65.1; H, 7.0%).

Carbonyl(η-*cyanocyclohepta*-1,4-*diene*)(η-*cyclohexa*-1,3-*diene*)*iron*, (V).—An aqueous solution of KCN (5 cm^3, 10% w/v) was added over a period of 10 min to a mixture of $[Fe(C_6H_8)(C_7H_9)(CO)][BF_4]$ (300 mg) in water (10 cm^3) and diethyl ether (20 cm^3). The procedure adopted for the isolation of (II) afforded the product as a pink solid (75 mg, 30%) (Found: C, 63.8; H, 6.5; N, 5.3. $C_{15}H_{17}FeNO$ requires C, 63.6; H, 6.0; N, 4.9%).

Carbonyl(η-2-*cyanocyclohepta*-1,3-*diene*)(η-*cyclohexa*-1,3-*diene*)*iron*, (VI).—A benzene solution of (V) was warmed at 60 °C for 1.5 h. The solvent was removed under pressure and the residue extracted with n-pentane, and, after filtering under nitrogen, crystallisation from pentane at −78 °C gave the red solid product (1 g of parent dienyl gave 0.39 g, 47%) (Found: C, 64.3; H, 6.2; N, 4.4. $C_{15}H_{17}FeNO$ requires C, 63.6; H, 6.0; N, 4.9%).

Carbonyl(η-*cyclohexa*-1,3-*diene*)*bis*(*triphenylphosphine*)-*iron*, (VII).—Complex (II) (160 mg) and triphenylphosphine (215 mg) were dissolved in oxygen-free n-pentane (15 cm^3). After standing overnight (15 °C) the yellow precipitate was filtered off and dissolved in a large volume of oxygen-free n-pentane. After filtering, the volume of this solution was reduced to 20 cm^3 to give the orange product (170 mg, 55%) (Found: C, 75.4; H, 5.8. $C_{42}H_{38}FeOP_2$ requires C, 75.0; H, 5.5%).

Mass spectra were obtained with a MS 12 instrument. I.r. spectra were recorded on a Perkin-Elmer 257 instrument and n.m.r. spectra on Perkin-Elmer 12B and Varian Associates HA100 and XL100 spectrometers. Elemental analyses were by the analytical service of this department.

Kinetics.—The procedure for monitoring the isomerisation of complex (II) and its derivatives was based on that described previously.[5] Complex (II) (*ca.* 5 mg) was weighed into a volumetric flask (10 cm^3) filled with argon. After dissolving the complex in n-heptane and making the total volume up to 10 cm^3, the solution was transferred to a Pyrex reaction tube fitted with a rubber septum cap, a side arm, and a tap. The solution was degassed by four or five freeze–pump–thaw cycles before filling the tube with high-purity argon. The reaction tube was then placed in a thermostatted bath of poly(arylalkyl)glycol with a temperature control better than ±0.1 °C. Aliquot portions were withdrawn through a stainless-steel tube by applying an excess pressure of argon, and their i.r. spectra in the carbonyl-stretching region were recorded on a Perkin-Elmer 257 instrument (slit = 7) using 1 mm path length sodium chloride cells. Although good first-order rate plots were obtained up to 2—3 half-lives, reproducibility was initially poor, but this was improved by degassing the reactant solutions at least four times rather than twice. A second source of error resulted from the

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[1] R. Edwards, B. F. G. Johnson, J. A. S. Howell, and J. Lewis, *J.C.S. Dalton*, 1974, 2105.

[2] R. Aumann, *J. Organometallic Chem.*, 1973, **47**, C29; *Angew. Chem. Internat. Edn.*, 1973, **12**, 574.

[3] B. F. G. Johnson, J. Lewis, T. W. Matheson, I. E. Ryder, and M. V. Twigg, *J.C.S. Chem. Comm.*, 1974, 269.

[4] J. Ashley-Smith, D. V. Howe, B. F. G. Johnson, J. Lewis, and I. E. Ryder, *J. Organometallic Chem.*, 1974, **82**, 257.

[5] B. F. G. Johnson, J. Lewis, and M. V. Twigg, *J.C.S. Dalton*, 1974, 241.

difficulty in estimating infinite-time absorbance values resulting from the overlap of the i.r. bands of the reactant and product. This was overcome by utilising a weighted non-linear least-squares program (written in Algol W and run on the Cambridge IBM 370 computer) in which A_0, A_∞, and $k_{obs.}$ (A = absorbance at $t = 0$ and ∞ respectively) are treated as unknowns with weights assigned assuming a constant fractional error in A. This procedure using 12—15 data points over 2—3 half-lives gave reproducible results.

In reactions with PPh_3, a solution of the ligand in n-heptane of known concentration was used to dissolve the complex, and subsequent operations were performed as described above.

TABLE 1

^{13}C N.m.r. spectra

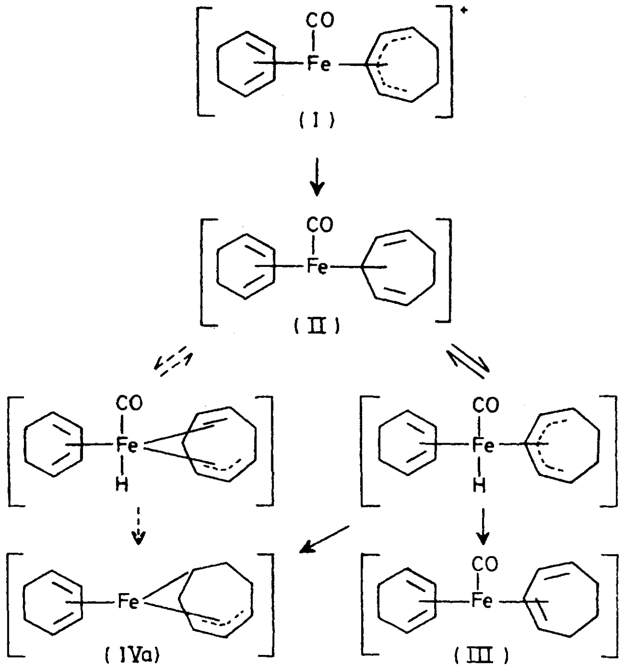
Complex (II)			Complex (III)			Complex (IV) [a]
Chemical shift [b] (δ/p.p.m.)	Multiplicity [c] [J(C–H)/Hz]	Assignment [d]	Chemical shift [b] (δ/p.p.m.)	Multiplicity [c] [J(C–H)/Hz]	Assignment [d]	Chemical shift [b] (δ/p.p.m.)
22.8	t[130]	3	23.8	t[130]	6	20.3
24.4	t[125]	6,7	24.8	t[125]	5,7	29.2
27.6	t[125]	5′, 6′	29.8	t[115]	5′, 6′	32.8
37.1	d[165]	1, 5	60.1	d[140]	1, 4	54.7
52.8	d[150]	2, 4	61.7	d[160]	1′, 4′	73.2
71.2	d[180]	1′, 4′	82.4	d[165]	2′, 3′	95.1
89.5	d[170]	2′, 3′	83.7	d[165]	2, 3	97.9
			230.9 [e]		CO	

[a] Low concentration prevented complete assignment. [b] Relative to tetramethylsilane. [c] t = Triplet and d = doublet. [d] A prime refers to a six-membered ring. [e] Obtained in the presence of 0.04 mol dm^{-3} $Cr[pd]_3$ as relaxation agent (pd = pentane-2,4-dionate).

RESULTS AND DISCUSSION

The reduction of the carbonyl(1—5-η-cycloheptadienyl)(η-cyclohexa-1,3-diene)iron cation, (I), by sodium tetrahydridoborate in an aqueous medium is sensitive to the concentration of $Na[BH_4]$. An exact 1 : 1 molar ratio of the reactants is required for complete reaction without excessive decomposition. The product of this reaction is a mixture of two monocarbonyl complexes, (II) and (III) (9 : 1). On warming a solution of complex (II) in n-heptane at 60 °C for 1 h, the complex underwent isomerisation to a mixture of (III) and (IV) in the ratio of *ca.* 10 : 1. Nucleophilic addition to the 1-, 2-, and 3-positions of a co-ordinated dienyl group is expected to give a 1,3-diene, a σ,η-allyl, or a 1,4-diene complex respectively. Apart from a resonance at τ 4.31 associated with the two inner olefin protons of cyclohexa-1,3-diene, the ^1H n.m.r. spectrum of complex (II) showed no other resonance in the range τ 0—6.9. Since the reported spectra of σ,η-allyl complexes all exhibit allylic resonances in the τ 5.0—6.5 region, it appeared that complex (II) was the 1,4-diene derivative and this was confirmed by measurement of its ^{13}C n.m.r. spectrum. Thus the fully proton-decoupled ^{13}C n.m.r. spectrum of complex (II) in C_6D_6 showed only the seven non-tertiary carbon resonances expected for structure (II) (Table 1), and assignment of the resonances was made on the basis of selective proton-decoupling studies, selective deuteriation (see below), and comparison with the ^{13}C n.m.r. spectrum of (III) (Table 1).

The fully proton-decoupled ^{13}C n.m.r. spectrum of the mixture of complexes (III) and (IV) obtained on heating a solution of (III) showed seven non-tertiary resonances in addition to those due to (III), four of which appeared in the co-ordinated olefin region and three in the methylene region (Table 1). Although both the unsymmetric σ,η-allyl, (IVa), and the symmetric dienyl–allyl arrangement of carbonyl(1—5-η-cycloheptadienyl)-(1—3-η-cyclohexenyl)iron (IVb) might be expected to give rise to more than seven ^{13}C resonances, it is possible that some of these could be hidden under those of complex (III). The ^1H n.m.r. spectrum of this mixture showed two new resonances at τ 5.2 and 7.0 besides those due to (III). This is consistent with structure (IVa), but structure (IVb) could also give rise to resonances in this region. However, a neutral dienyl complex such as (IVb) would be expected to exhibit an ^1H n.m.r.



SCHEME 1

resonance associated with the central dienyl proton in the τ 4.1—4.9 region which is clear in our spectrum, indicating that complex (IV) has a σ,η-allyl structure, (IVa).[6] No n.m.r. evidence was obtained for the presence of metal hydride species.

Reduction of (I) with $\mathrm{Na[BD_4]}$ gave a monodeuterioderivative of complex (II) (95% D from mass spectroscopy). The 22.8 p.p.m. resonance in the ^{13}C n.m.r. spectrum of this complex was replaced by a very weak deuterium-coupled triplet, enabling this resonance to be assigned to the unique methylene carbon atom of the η-cyclohepta-1,4-diene. After heating the solution at 60 °C for 1 h, the ^{13}C n.m.r. spectrum of the resulting deuteriated derivative of (III) was measured. The resonances at 83.7 and 82.4 p.p.m. in the ^{13}C n.m.r. spectrum of (III) had been assigned to carbon atoms 2,3; 2′,3′ * on the basis of selective proton decoupling: a comparison with the spectrum of the deuteriated derivative showed the resonance at 83.7 p.p.m. to have decreased in intensity by a factor of two relative to the resonance at 82.4 p.p.m., enabling assignment of the higher-field resonance to carbons 2,3. This was further supported by the ^{1}H n.m.r. spectrum of (III) in which the integrated ratio of the inner diene to the other proton of 4 : 14 decreased to 3 : 14 for the deuteriated derivative. Treatment of the deuteriated derivative of complex (II) with trityl tetrafluoroborate gave the undeuteriated cation (I). Normally, the *exo*-hydrogen is abstracted by trityl from a methylene group adjacent to a co-ordinated olefin and this, together with the formation of a 2-deuteriated-1,3-diene complex on rearrangement of complex (II), indicates *exo* addition of the nucleophile [7] to complex (I), and *endo*-metal isomerisation of (II) (see below).

In contrast to the reaction of cation (I) with $\mathrm{Na[BH_4]}$ in aqueous media, the only carbonyl complexes formed in boiling tetrahydrofuran were approximately equal small amounts of tricarbonyl(η-cyclohexa-1,3-diene)iron and tricarbonyl(η-cyclohepta-1,3-diene)iron. It is noteworthy that a small amount of tricarbonyl complex accompanies the aqueous reduction even at 0 °C. Addition of cyanide ion to cation (I) also occurred at the 3-position of the dienyl to give an easily crystallised η-1,4-diene complex, (V). On heating, this complex rearranged to the η-2-substituted-1,3-diene complex, (VI), consistent with nucleophilic addition at the *exo* position, and isomerisation occurring *via endo*-metal hydrogen transfer.

The ability of transition metals to activate olefinic rearrangements is illustrated by the tricarbonyl(η-cyclohepta-1,3,5-triene) complexes of chromium and molybdenum. The free ligand possesses a boat conformation and has been shown by studies on the deuteriated derivative to undergo a 1,5-sigmatropic shift which gives rise to scrambling around the ring, and is thought to involve the axial (*exo*) proton.[8] The chromium and molybdenum complexes undergo a similar process, but in these it is the *endo*-proton which migrates, and the rate is considerably faster than in the free ligand.[9–11]

Kinetic Studies.—Free cyclohepta-1,4-diene has only recently been prepared and is comparatively stable towards heat, with the only Woodward–Hoffmann-allowed rearrangement being a sterically unfavourable 1,3-antarafacial sigmatropic shift.[11,12] In contrast, isomerisation of complex (II) to (III) takes place smoothly in n-heptane over the temperature range 40—70 °C. This reaction was followed by monitoring changes in the i.r. carbonyl-stretching region (Figure 1). Both loss of the reactant and appearance of product are first-order processes and the two rate constants so obtained at a given temperature are the same within experimental error. This, together with the fact that complex (II) isomerises in the solid state, suggests that the overall process is an intramolecular reaction. Above room temperature, complex (II) is very oxygen sensitive, but when the solutions were thoroughly degassed reproducible kinetic results were obtained. Observed first-order rate constants are given in Table 2 and the derived activation parameters are similar to those for other intramolecular

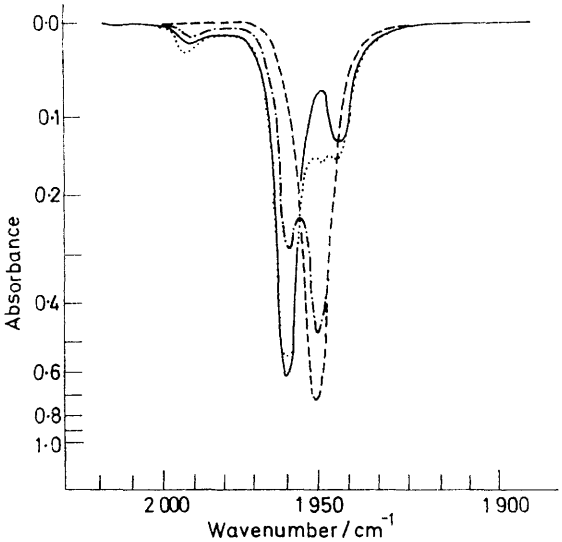


FIGURE 1 Changes in the i.r. carbonyl-stretching region during the thermal isomerisation of (II) to (III) and (IV) at 60 °C in n-heptane: (— — — —), initial spectrum; (— · — · —), after 8 min; (· · · ·), after 18 min; (——), after 77 min

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* A prime refers to a six-membered ring.

[6] D. Jones, C. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1962, 4458; G. Winkhaus, C. Pratt, and G. Wilkinson, *ibid.*, 1961, 3807.

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[10] T. H. Whitesides and R. W. Arhart, *J. Amer. Chem. Soc.*, 1971, **93**, 5296; H. Alper, P. C. LePort, and S. Wolfe, *ibid.*, 1969, **91**, 7554; T. H. Whitesides and R. W. Arhart, *Tetrahedron Letters*, 1972, 297.

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[12] E. Vogel, K. H. Ott, and K. Gajek, *Annalen*, 1961, **644**, 172.

metal-assisted isomerisations.[8,13] Isomerisation of complex (II) to (III) is accompanied by the formation of a small amount of (IVa) [ν(CO) 1 946 cm^{-1}]. The ratio of the two products appears not to be markedly dependent on temperature [(III) : (IVa) = 6 ± 1 : 1 at 50 °C] indicating that the difference in enthalpies of activation is small, and suggests a similar mechanism for the formation of the two products. On heating the mixture of these two complexes, at 90 °C a further slow rearrangement of (IVa) to (III) took place until equilibrium concentrations were reached with (III) : (IVa) *ca.* 9 : 1. Similarly, heating a solution of complex (III) at 90 °C over several days gave rise to a small concentration of (IVa).

TABLE 2

First-order rate constants for the isomerisation of complex (II) in n-heptane under argon

θ_c/°C	$10^5k_{obs.}$/s^{-1}	$10^5k_{calc.}$ [a]/s^{-1}
70.0	355	362
70.0	348	362
70.0	365	362
70.0	372	362
60.0	119	117
60.0	124	117
60.0	117	117
60.0	115	117
60.0	127	117
50.0	37.9	35.4
50.0	33.9	35.4
50.0	35.2	35.4
50.0	39.2	35.4
40.0	9.64	9.90
40.0	9.14	9.90

Activation parameters [b]: $\Delta H^{\ddagger} = 25.1 \pm 0.3$ kcal mol^{-1}; $\Delta S^{\ddagger} = 3.2 \pm 0.9$ cal K^{-1} mol^{-1}.

[a] Calculated from the derived activation parameters. [b] Error limits are standard deviations corrected for the number of degrees of freedom so that doubling them produces 95% confidence limits.

The increased reactivity towards isomerisation of cyclohepta-1,4-diene on complex formation clearly shows that the metal assists the isomerisation process by providing a more favourable mechanism. Removal of a proton to the metal from either the unique methylene gives a 1—5-η-dienyl, or from one of the other methylenes gives a 1,2:4—6-η-allyl intermediate (see Scheme 1). Transfer of the proton back to the dienyl group could take place at either the 1-, 2-, or 3-positions, but only (III) and (IVa) are stable at the temperatures employed. However, the 1,2:4—6-η-allyl complex would only give the parent (II) or the σ,η-allyl complex (IVa). The formation of (III) indicates that the process involving the 1—5-η-dienyl intermediate *is* occurring, but no evidence concerning the involvement of the 1,2:3—5-η-allyl species was obtained. The observed rate constant for isomerisation of the 3-deuteriated derivative of (II) is the same as that for the undeuteriated complex (Table 4). This lack of a kinetic-isotope effect provides further evidence for *exo* addition to cation (I), and removal of the *endo*-proton during the isomerisation of (II) to (III) (see above).

During the isomerisation of (II) a band at 1 994 cm^{-1} increased in intensity, reached a maximum of *ca.* 5% of the initial concentration of complex (II), and then slowly decreased to zero absorbance. The species responsible for this band is very oxygen-sensitive. Attempts to fit quantitatively the absorbance–time data for this band to its being an intermediate in a consecutive reaction were unsuccessful. However, an approximate fit could be made on the basis of Scheme 2.

TABLE 3

^{1}H N.m.r. spectra, i.r. CO-stretching frequencies, and observed parent-ion mass numbers of the η-cyclohepta-1,4- and -1,3-diene complexes

Complex	Proton [a]	τ [b]	$\tilde{\nu}$(CO) [c]/cm^{-1}	m/e
(II)	2′, 3′	4.31 (d of d) [d]	1 952	258
	1′, 4′	7.29 (m)		
	2, 4	7.71 (m)		
	1, 5	7.91 (m)		
	CH_2	8.30 (m)		
		8.85 (m)		
(III)	2, 3 and 2′, 3′	5.85 (m)	1 961	258
	1′, 4′	7.60 (m)		
	1, 4	8.00 (m)		
	CH_2	8.30 (m)		
		8.90 (m)		
(V)	2′, 3′	4.63 (d of d) [d]	1 968	283
	3	6.28 (t)		
	1′, 4′	7.30 (m)		
	2, 4	7.75 (m)		
	1, 5	8.46 (m)		
	CH_2	8.80 (m)		
		9.07 (m)		
(VI)	2′, 3′ and 3	5.50 (m)	1 977	283
	1′, 4′	7.60 (m)		
	1, 4	8.30 (m)		
	CH_2	9.00 (m)		
(VII)	PPh_3	2.2—2.6 (m)	1 888	e
	2′, 3′	5.26 (d of d)		
	1′, 4′	7.76 (m)		
	CH_2	8.65 (m)		

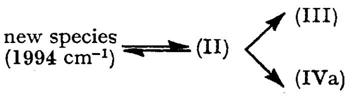
[a] Positions on the six-membered ring are indicated by primes. [b] Recorded in C_6D_6 at 28 °C, using C_6H_6 as internal standard. [c] Using n-hexane solutions. Instrument calibrated against CO. [d] Recorded at 10 °C. [e] No parent ion was observed.

TABLE 4

First-order rate constants for the isomerisation of complex (II) and its 3-*exo*-deuterium and cyano-derivatives in n-heptane

	$10^5k_{obs.}$/s^{-1}		
θ_c/°C	(H)	(D)	(CN)
60.0	119	116	800
60.0	124	112	
60.0	117	115 *	
60.0	115	112 *	
60.0	127		
40.0	9.9		51
40.0	9.9		

* Obtained by monitoring the appearance of the product, others by monitoring the disappearance of the reactant.



SCHEME 2

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[13] J. Evans, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1972, 2668.

The η-3-cyanocyclohepta-1,4-diene complex, (VI), isomerises more rapidly than the unsubstituted complex (II) (Table 4). This rate enhancement need not necessarily be associated with the electron-withdrawing nature of the cyano-group. Models suggest, and by analogy with cyclo-octa-1,5-diene complexes, the highly strained η-cyclohepta-1,4-diene ring is likely to be in the boat conformation. In this conformation there are probably steric interactions between the methylene groups. Substitution of a hydrogen for a more bulky group would increase this and hence the rate of isomerisation. This is supported by the observation that the bulky, but electron donating, methyl derivative does not form a stable η-cyclohepta-1,4-diene complex; apparently this complex rapidly rearranges to the 2-substituted cyclohepta-1,3-diene complex.[4]

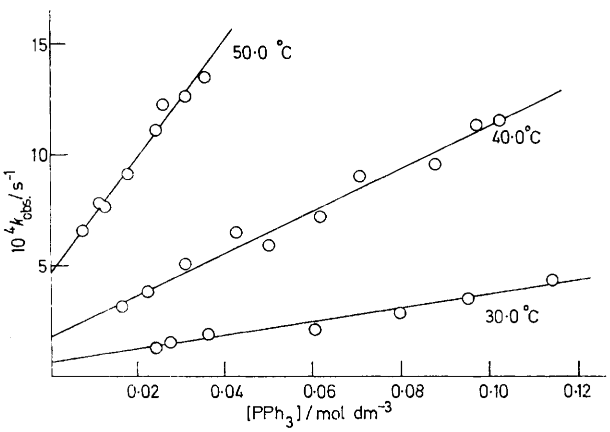

FIGURE 2 Plots of $k_{obs.}$ against triphenylphosphine concentration for the displacement of cyclohepta-1,4-diene from complex (II)

The products of reaction between tricarbonyl(η-diolefin)iron complexes and Group 5B Lewis bases are very dependent on the nature of the bonding in the complex, the ring size of the olefin, and the attacking base.[14] Complex (II) reacted at room temperature with an excess of triphenylphosphine to give a yellow solution that had a single absorption in the i.r. carbonyl-stretching region at 1 888 cm^{-1}. From this solution a pure air-stable orange complex was obtained which did not display a parent ion in its mass spectrum nor any fragments containing cycloheptadiene. These observations, together with its ^{1}H n.m.r. spectrum (Table 3) and elemental analysis, are consistent with this product being carbonyl(η-cyclohexa-1,3-diene)bis(triphenylphosphine)iron, (VII). Similarly, reaction of (II) with CO over prolonged periods (1 atm, 20 °C) * resulted in loss of cyclohepta-1,4-diene to give tricarbonyl(η-cyclohexa-1,3-diene)iron. The reaction of (II) with PPh_3 in n-heptane was followed at three temperatures by monitoring the loss of absorbance at 1 952 cm^{-1} due to the reactant complex. Good first-order rate plots were obtained, and observed pseudo-first-order rate constants increased with increasing triphenylphosphine concentration. Plots of the observed first-order rate constants against $[PPh_3]$ were linear (Figure 2). From these results, values of the intercepts (k_1) and the second-order rate constants (k_2) were calculated by a least-squares analysis in which each rate constant was assumed to have the same fractional error (Table 5). At the higher temperatures used, considerable quantities of the reactant isomerised to (III) which under these conditions did *not* react with PPh_3.[14] The values of the intercepts on the plots of $k_{obs.}$ against $[PPh_3]$ are therefore expected to correspond to the rate of the unimolecular isomerisation of complex (II). Although the precision of the k_1 values is not good, perhaps because of the oxygen sensitivity of the reactant complex, the agreement with the independently measured rate constants for the isomerisation is tolerable (Table 5).

TABLE 5

Derived rate constants for the reaction of complex (II) with triphenylphosphine in n-heptane under argon

$\theta_c/°C$	$10^3k_2{}^a/dm^3\ mol^{-1}\ s^{-1}$	$10^4k_1{}^a/s^{-1}$	$10^4k_{iso}{}^b/s^{-1}$
30.0	3.02 ± 0.70	0.6 ± 0.4	0.3 ± 0.1
40.0	9.49 ± 1.36	1.8 ± 0.6	1.0 ± 0.1
50.0	26.4 ± 3.6	4.7 ± 0.7	3.5 ± 0.1

Activation parameters for the second-order process: $\Delta H^‡ = 20.37 \pm 0.68$ kcal mol^{-1}; $\Delta S^‡ = -3 \pm 2$ cal K^{-1} mol^{-1}.

[a] Error limits are standard deviations at the 95% confidence level. [b] k_{iso} = rate constant for isomerisation of complex (II) in the absence of PPh_3. The data were calculated from results in Table 1.

The second-order rate constants are of better precision and enable reasonable estimates of the activation parameters for this process to be made. These, together with the second-order rate constants, are given in Table 5 and are similar to those for the second-order displacement of cyclo-octa-1,3-diene by PPh_3 from tricarbonyl(η-cyclo-octa-1,3-diene)iron.[14] The value of the entropy of activation is considerably less negative than is usual [15] for a bimolecular process and is suggestive of a mechanism involving a pre-equilibrium in which one olefin–metal bond is broken followed by attack on the co-ordinatively unsaturated species by the phosphine.[16] However, if this were the case, a limiting rate constant would be obtained at very high phosphine concentrations. This limiting behaviour was not observed over the triphenylphosphine concentration range accessible in this study.

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* 1 atm = 101 325 Pa, 1 cal = 4.184 J.

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