

REGIOSELECTIVITY OF NUCLEOPHILIC ADDITIONS TO TRICARBONYL[η^5 -2-METHYL-2,4-CYCLOHEXADIEN-1-YL]IRON(1+)PF₆⁻: TEMPERATURE DEPENDENCE OF HYDRIDE REDUCTIONS

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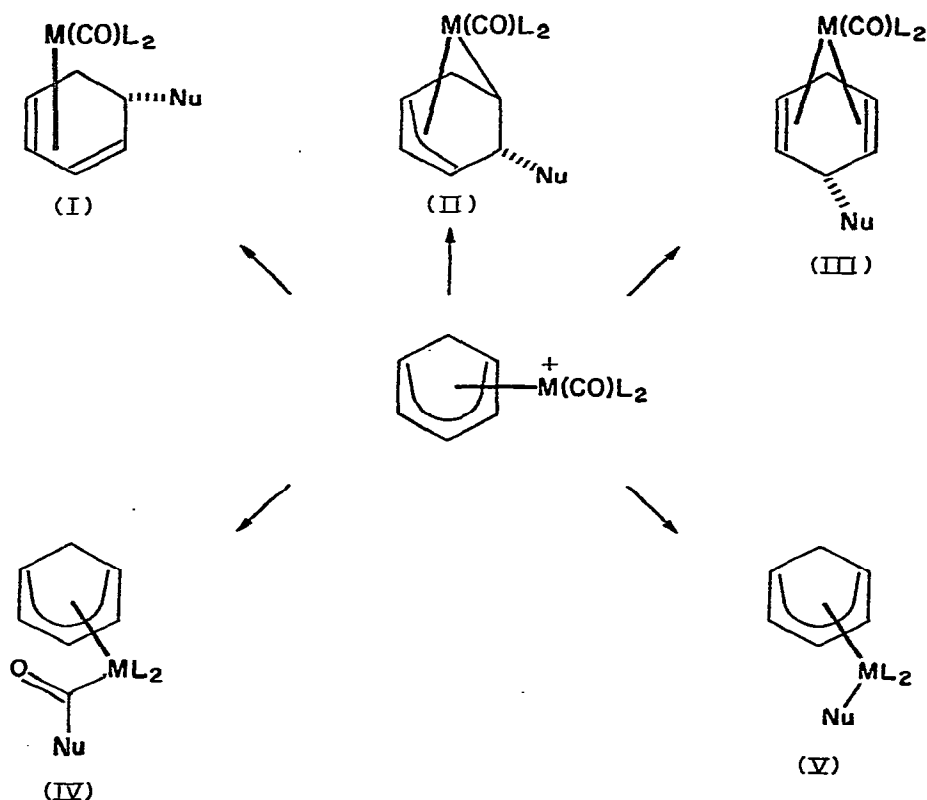
Summary

Reduction of [$(\eta^5\text{-CH}_3\text{C}_6\text{H}_6)\text{Fe}(\text{CO})_3$]⁺PF₆⁻ by NaBH₄, LiBH₄, LiEt₃BH and KBu₃BH becomes less regioselective at lower temperatures. Regioselectivity of reduction by 9-BBN, however, improves as the temperature is lowered. Factors affecting nucleophilic addition are discussed in terms of likely transition states for the competing processes.

Introduction

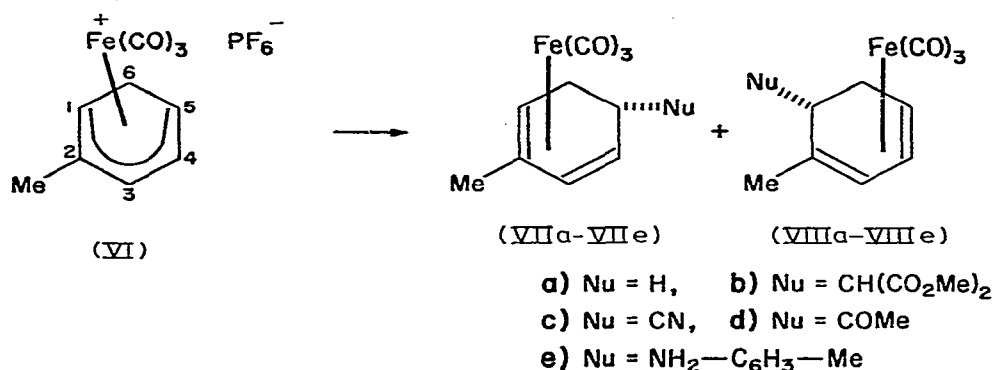
The addition of nucleophiles to cationic species stabilised by coordination to transition metals has been shown in many cases to give rise to synthetically useful C—C bond-forming reactions [1]. Our recent discussion of the chemistry of tricarbonyl[η^5 -cyclohexadienyl]iron(1+) salts has indicated [2,3,4] the potential utility of the complexes as precursors for specifically substituted organic ring systems. Such salts are now beginning to find application in organic synthesis [3,5]. If chiral salts are to be employed in synthesis, highly regioselective reactions must be developed for their manipulation. While some substituents direct most nucleophiles to a single position on the dienyl π system, others, for example a 2-Me group, afford comparatively little selectivity. The nature of the nucleophile also appears to be critical; even the strongly directing 2-OMe substituent fails to ensure regioselectivity in extreme cases [6]. We describe here the results of a study designed to probe further the factors affecting the regioselectivity of nucleophilic addition to η^5 -dienyl cations. A range of borohydride reducing agents was chosen to give variation of steric and reactivity properties. Surprisingly, regioselectivity of many reagents deteriorated as the temperature of reaction was lowered, though, in all cases, addition occurred at the termini of the dienyl system.

SCHEME 1



The course of nucleophilic addition to coordinated η^5 -dienyl cations may result in reaction at the metal, the dienyl system or the other ligands. Indeed, addition to the ring in the cyclohexadienyl series may occur at any of three types of sites. For metal carbonyl complexes, then, five types of addition process are possible (Scheme 1) and products I [7], II [8], III [9], IV [10] or V [11] have all been observed depending on the conditions, ring size and metal-ligand system involved. It is convenient, from the point of view of synthetic application, that tricarbonyl[η^5 -cyclohexadienyl]iron(1+) salts give final products of type I in almost all cases [1], though initial reversible attack at coordinated CO may occasionally be involved [12]. Iodide addition is exceptional and displaces CO to give V ($M = \text{Fe}$, $L = \text{CO}$, $\text{Nu} = \text{I}$) [11]. Some aspects of selectivity between products I–V have been discussed in terms of kinetic control [13,14]. In this paper we focus on the effect of temperature on the ability of reducing agents to distinguish the two termini of the dienyl system. The unsymmetrical salt VI was chosen for the study because the 2-Me substituent is only weakly directing, and isomeric mixtures of products were expected with many reagents. The stereochemistry of hydride addition was examined, and a survey made of selectivity of a number of carbon nucleophiles.

SCHEME 2



Results

Reductions were performed in 2/1 THF/MeCN, which appears to give homogeneous solutions at temperatures between reflux * (68°C) and -78°C. An excess of the reducing agent was used in all cases. The ratios of products VIIa and VIIIa (Scheme 2), as determined by GLC analysis, are shown in Table 1. The relative retention times were assigned by coinjection with authentic VIIa, obtained by unambiguous reduction of tricarbonyl[(1,2,3,4,5-η)-3-methyl-2,4-cyclohexadien-1-yl]iron(1+)PF₆⁻ [15].

Reaction of the salt VI with sodium borohydride at reflux gave a 3 : 2 mixture of VIIa and VIIIa, indicating preferential attack at C(5) (the less hindered site). Lowering the temperature, however, progressively favoured reaction at C(1) until, at -78°C, the ratio of VIIa to VIIIa became about 2 : 3. Lithium borohydride gave similar results at -78°C, but showed less preference for C(5) at higher temperatures. The greatest proportion of reaction at C(1) (the more hindered terminus of the dienyl system) was with BH₄⁻ reagents at low temperature. Reduction with diborane proceeded only at reflux *, but the dimethylsulphide complex, Me₂S · BH₃, reacted with VI at all temperatures, showing substantial selectivity for VIIa in each case.

The more bulky trialkylborohydride reagents were most regioselective at high temperature and reacted preferentially at C(5). In all these examples lowering the temperature resulted in poorer regioselectivity, with an increasing proportion of reaction occurring at C(1).

The opposite was true for the very bulky borane derivative, 9-borobicyclononane (9-BBN). Though considerably less selective than K-selectride at reflux, lowering temperature increased the preference of 9-BBN for reaction at C(5) and at -78°C no VIIIa could be detected in the product. The yield of reduc-

* Reduction of tricarbonyl[(1,2,3,4,5-η)-2,4-cyclohexadien-1-yl]iron(1+) tetrafluoroborate(1-) in MeCN at reflux in the absence of added nucleophile has recently been reported [32]. The salt VI was reduced slowly in THF/MeCN (2/1) at reflux, even in the absence of hydride reducing agent. Reactions performed at reflux, particularly with the very inactive hydride donor 9-BBN, may thus give anomalous results.

TABLE 1
RATIOS OF PRODUCTS WITH VARIOUS REDUCING AGENTS

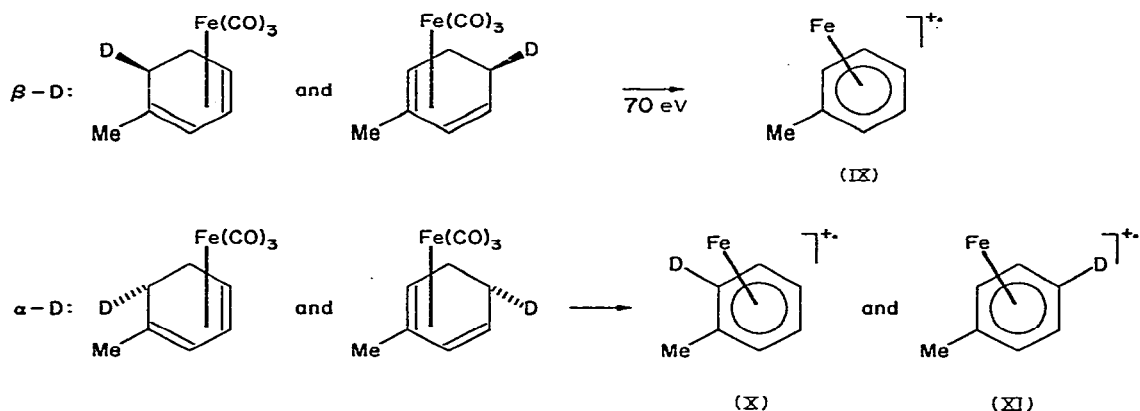
Reducing Agent (excess)	Temp. (°C)	Combined Yield (%)	Ratio of Products	
			VIIa	VIIIa
NaBH ₄	Reflux	53	60	40
	25	57	57	43
	-5	82	51	49
	-40	60	43	57
	-78	69	43	57
LiBH ₄	Reflux	33	52	48
	25	53	48	52
	-5	36	39	61
	-40	48	39	61
	-78	54	43	57
Superhydride	Reflux	43	69	31
	25	40	67	33
	-5	52	64	36
LiEt ₃ BH	-40	55	54	46
	-78	45	49	51
K-selectride	Reflux	28	78	22
	25	36	71	29
	-5	48	71	29
KBu ₃ BH	-40	54	72	28
	-78	30	68	32
Me ₂ SBH ₃	Reflux	26	68	32
	25	44	72	28
	-5	42	66	34
	-40	44	66	34
	-78	36	65	35
9-BBN	Reflux	13	68	32
	25	13	74	26
	-5	13	72	28
9-borobicyclo-[3.3.1]nonane	-40	8	76	24
	-78	14	>95	<5

tion products from K-selectride and 9-BBN was low. Thin layer chromatography was required to isolate the mixtures of VIIa and VIIIa for GLC analysis. Preparative scale reactions with the trialkylborohydride reagents revealed the formation of isomeric reductively coupled C—C dimers as by-products. The formation of the dimeric products would suggest that electron as well as hydride addition can occur, at least in this instance. It is possible that the reduction products VIIa and VIIIa could themselves be formed by initial electron addition. In the case of 9-BBN, the low yield of products was due to incomplete reaction. Starting material was recovered after four hours, even when a large excess of reducing agent was employed.

The stereochemistry * of reduction was determined using NaBD₄ and LiEt₃BD. The proportion of α - and β -deuterium incorporation was measured from

* The face of the cyclohexadiene ring bonded to the metal is termed the β -face; the opposite face is termed the α -face [4]. Thus substituents on the face opposite the metal are described as α -substituents.

the mass spectrum of the mixture of products. Each of VIIa and VIIIa show losses of 3 CO and H₂ in their fragmentation pattern. Whitesides and Arhart [16] have demonstrated that loss of H₂ from the β -face of the unsubstituted tricarbonyl[η^5 -cyclohexadienyl]iron(1+) cation is favoured by a factor of at least 100, and propose assistance by the metal to account for the very high selectivity of the process.



Thus C₁₀H₁₀O₃Fe and the β -isomers C₁₀H₉DO₃Fe give rise to the ion IX at 148 mass units, while the α -isomers C₁₀H₉DO₃Fe give ions X and XI at 149 mass units. The ratio of β and α -hydride (or deuteride) addition in the reduction of VI may be calculated from the ratio of peak heights at 148, and 149, if allowance is made for the percentage of deuterium incorporation. The percentage incorporation was determined by examination of the $M^{++} - \text{CO}$ ion: 206 for C₉H₁₀O₂Fe⁺⁺ and 207 for C₉H₉DO₂Fe⁺⁺. The incorporation for both NaBD₄ and LiBEt₃D was 92%. Borodeuteride proved highly stereoselective as expected [17], giving 96 $\pm$ 5% α -D products. Super-deuteride was less specific showing 45 $\pm$ 5% α -D and 55 $\pm$ 5% β -D incorporation. This result is in accord with spectroscopic and chemical determinations on other tricarbonyliron salts [4,18].

Addition of carbon nucleophiles was also examined. Highly regioselective addition of 1,2-bis(trimethylsiloxy)cyclopentene to VI has been demonstrated [3,19] by conversion of the product into a *p*-substituted benzene derivative. Reaction with the sodium enolate of dimethylmalonate in THF gave predominantly VIIb, though a trace of the other isomer was revealed by the presence of a small singlet in the ¹H NMR spectrum of the product at δ = 1.58 ppm. This corresponds to the expected position of resonance of the C(1) methyl group of VIIb. This assignment was confirmed by examination of the ¹³C NMR spectrum of the product. In addition to the carbon resonances of VIIb two small signals were observed at 88.4 and 82.1 ppm. These are assigned to the inner carbon atoms (C(2) and C(3)) of VIIb.

Potassium cyanide addition to VI gave a 2 : 1 mixture of VIIc and VIId. Attempts to separate these products by TLC were unsuccessful. Reaction of the mixture with MeMgI in ether [20] gave a mixture of the two acetyl compounds VIIe and VIIf, also in the ratio of 2 : 1. These, too, were inseparable by TLC but were identified by the presence in the ¹H NMR spectrum of four

singlets due to the two methyl groups of the two isomers. C-alkylation [21] of VI by *p*-toluidine in MeCN at reflux was found to be regioselective, giving only VIIe together with a small quantity of material derived from dialkylation of the aromatic ring.

Discussion

A number of factors that influence hydride addition to VI are clear from these results: (1a) addition of large nucleophiles at C(1) is disfavoured, presumably by the steric effect of the 2-Me substituent and the C(6) methylene group; (1b) the charge on the nucleophile has an important influence on the nature of the reactions: charged species are much more reactive than neutral ones; (1c) at lower temperatures charged hydride donors progressively favour C(1), the more hindered position; (1d) in contrast, regioselectivity of 9-BBN improves at low temperature. The regioselectivity of addition must relate to the relative energies of transition states for reactions at the two termini. This may depend on a variety of properties, for example: (2a) the charge distribution on the η^5 -dienyl system; (2b) changes to the molecular orbital coefficients at the coordinated carbon atoms, due to the introduction of substituents; (2c) the thermodynamic stabilities of the η^4 -coordination systems of the products; (2d) steric effects of substituents and (2e) the mechanism of addition. In the case of (arene)Cr(CO)₃ complexes, regioselectivity of nucleophilic addition has been related [22] to the conformation of the M(CO)₃ group. It is not clear whether this effect is present to an appreciable extent in η^5 -Fe(CO)₃ complexes, or contributes to the relative energies of the transition states. For tricarbonyl[(1,2,3,4,5- η)-2,4-cyclohexadien-1-yl]iron(1+)BF₄⁻ the preferred conformation of the Fe(CO)₃ group [23] would appear to exert an equal influence on each terminus of the dienyl system, though effects of substituents may distort possible interactions to favour one terminus. A crystal structure [24] of the 2-OMe salt, however, does not support this view.

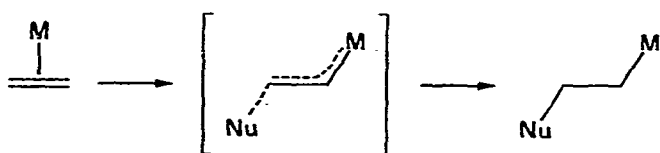
Discussion of the stereochemical data is necessary when considering (1a). The stereoselectivities of NaBH₄ and LiEt₃BH suggest that a different mechanism may operate with the highly reactive trialkylborohydride reagents. Hydride addition to a coordinated CO, and subsequent transfer to the dienyl ligand, has been proposed to account for the stereochemistry of reduction of acyclic dienyl salts [25]. In this light, the apparent increasing steric effects affecting addition by progressively more bulky reagents seem surprising, since the 2-Me group would be expected to have little steric influence on hydride addition via a coordinated CO, unless this process is fast relative to free rotation of the Fe(CO)₂CHO group. Alternatively, if direct (α) addition to the ring were highly regioselective for C(5), the observed ratios for reaction with LiEt₃BH and KBu₃BH might reflect the ratio of regioselective α -addition and random β -addition.

The greater regioselectivity observed with 9-BBN is common to other neutral reagents. Comparison of alkylations [26] with R₂Cd and R₂CuLi suggests that better selectivity is obtained with the neutral organocadmium reagents. Exceptions to such a rule are known. While the small charged CN⁻ ion shows very little selectivity, MeO⁻ is reported [27] to react solely at C(5). Neutral reagents

are less reactive than charged species (1b) and this itself may account for the greater selectivity, though it does not explain the differences in temperature dependence. The charge-distribution in the transition states may be of lesser importance when the nucleophilic species is neutral (compare (1c) and (1d)).

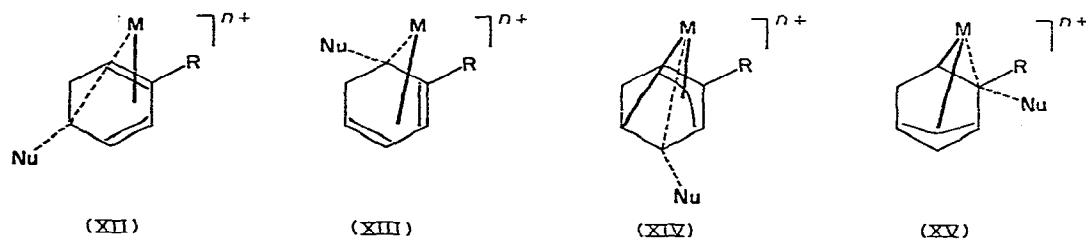
Attempts have been made to relate the site of nucleophilic addition to charge distribution. Correlations [27] have been made with ^{13}C NMR chemical shifts of the terminal carbon atoms of the dieny system, and, in an extensive theoretical discussion [14], Davis, Green and Mingos argue that the reaction of cationic polyene complexes with small, charged nucleophiles is likely to be charge controlled, and that regioselectivity is dominated by the relative positive charge on particular carbon atoms. Recently, an alternative has been suggested, namely that activation of coordinated olefins to nucleophilic addition is not primarily due to overall charge (though this is clearly a contributing factor), nor to the electron deficiency of the olefin through net donation of electron density to the metal, but rather to activation related to partial displacement of the metal-ligand bonding system towards one terminus in the transition state [28]. This is a consequence of the change from π to σ bonding during the addition process (Scheme 3).

SCHEME 3



In the case of the η^5 -dienyl $\text{Fe}(\text{CO})_3$ complexes this change is from η^5 to η^4 coordination (Scheme 2). Furthermore, it should be noted that η^5 -cyclohexadienyl complexes are bent, a property which has been attributed [29] to an interaction between the C-H σ -bond of the C(6) methylene group and the π -bonding system. This strain may be relieved, to some extent, in the η^4 products. For unsymmetrical cations an analogy with Scheme 3 would suggest competing transition states of the type indicated in Scheme 4.

SCHEME 4

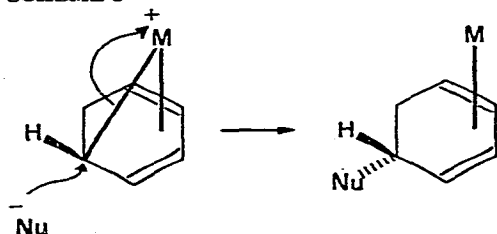


The relative energies of XII and XIII should be affected by the bulk of the R group (2d) and (indirectly) by the relative stabilities of the products (2c). Charge distribution would also be important, though distributions of charge in XII and XIII would be expected to differ from charge distributions in VI (see below). Finally one should note that for neutral nucleophiles in Scheme 4, $n = 1$; charged nucleophiles have $n = 0$. However, in the latter case, if an early tran-

sition state is assumed [30], then considerable polarisation should remain in XII and XIII, leaving a substantial positive charge on the metal.

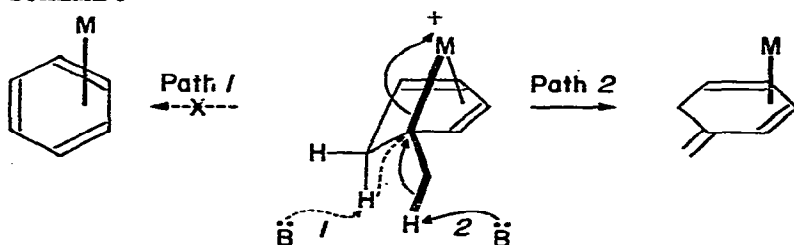
In contrast, analysis of the charge distribution in the starting material (2a) gives a poor indication of reactivity [30]. Both INDO [30] and extended Hückel [29] calculations indicate C(2) of the tricarbonyl[(1,2,3,4,5- η)-2,4-cyclohexadien-1-yl]iron(1+) salt to be the most positive position. This pattern of charge distribution is more akin to $C_6H_7^-$ (which has its lowest negative charge at C(2)), than $C_6H_7^+$ [29]. Furthermore, most of the positive charge appears to reside on the metal [29]. These observations are supported by inferences drawn from ^{13}C NMR chemical shifts. The resonances of the coordinated dienyl system are found in regions typical of sp^2 carbons or sp^3 carbons bearing hetero-atom substituents, certainly not the region expected for carbocations, and carbons 2 and 4 are usually the most deshielded [27]. On these grounds one might expect nucleophilic addition to be favoured at C(2) and C(4); for $[\eta^5\text{-cyclohexadienyl}]Fe(CO)_3^+$ complexes no such products have been observed. In this special case, the transition states XII and XIII must be completely favoured over XIV and XV. This has been attributed [8c] to better orbital overlap in the products. The transition states depicted in Scheme 4 have considerable similarity to the bonding system of the products, and may account for the observed formation only of products of type I ($M = Fe$, $L = CO$) due to inadequate orbital overlap in XIV and XV. If XII and XIII are polarised, with considerable positive charge on the metal, then in terms of charge separation they resemble the starting materials. An extreme representation of the process is made in Scheme 5.

SCHEME 5



The metal-carbon bond at C(1) or C(5), whatever its precise nature in terms of σ or π contributions, is broken in the course of the reaction allowing the M^+ portion to act in the fashion of a good leaving group in organic chemistry. It is interesting to note that elimination at the C(6) methylene group is not observed for such complexes [4], possibly because the geometry of the orbitals is unfavourable due to the bent nature of the complex. Elimination from a C(1) substituent is, however, a common and often undesirable outcome [31] of attempted nucleophilic addition (Scheme 6).

SCHEME 6



Conclusions

Charge densities in the cation can only be significant if (a) they indicate where charge is likely to localise in a transition state and (b) if changes in bonding in the transition state are possible, which permit such localisation. It appears that the charge distribution of the η^5 starting material does not provide a good basis for discussion of nucleophilic additions to VI. The proposed transition states XII and XIII represent early transition states (in accord with kinetic data [30]) in terms of charge separation, but do not resemble the starting material in terms of orbital interactions contributing to the metal–ligand bonding system. The regioselectivity must be related to this latter property, since charge separation in both XII and XIII would be expected to be similar. Thus factors (2c), (2d) and (2e) appear important for regiocontrol. The steric effect (2d) cannot explain the temperature dependence of reduction by borohydride. For a given reducing agent, variation of the contribution of the thermodynamic factor (2c) to the relative energies of XII and XIII may account for the temperature dependence observed. It is clear from the stereochemical evidence that point (2e) is critical, when different nucleophiles are compared. It must be emphasised that the precise nature of the nucleophile is paramount in determining whether the reaction has regioselectivity. Differences between nucleophiles must presumably alter the relative importance of factors contributing to the energies of XII and XIII; this would affect the nature of temperature dependence, as well as the degree of regiocontrol.

Experimental

Solutions of super-hydride (LiEt_3BH), super-deuteride (LiEt_3BD), K-selectride (KBu_3BH) and 9-BBN in THF were obtained from Aldrich Chemical Co. Ltd. The cations were prepared by the method of Birch and Haas [15]. Mass spectra were measured at 70 eV on an A.E.I. MS/902 instrument, and ^{13}C NMR spectra were recorded at 15.04 MHz on a Joel JNM FX60 Spectrometer. GLC analysis was performed with a Perkin-Elmer 881 gas chromatograph and a Hewlett-Packard 3380A integrator.

1. Reduction of tricarbonyl[(1,2,3,4,5- η)-2-methyl-2,4-cyclohexadien-1-yl]-iron(1+) hexafluorophosphate(1-) (VI).

Excess reducing agent was added to solutions of VI in THF/MeCN (2/1, v/v) at reflux (68°C), and 25, –5, –40 and –78°C, as described below.

Reduction with NaBH_4 . NaBH_4 (30 mg) was added in one portion to a stirred solution of VI (100 mg) in THF/MeCN (5 ml/2.5 ml). After 20 min the solvent was evaporated and the residue extracted with pentane (4 × 10 ml). The combined extracts were filtered through a pad of Al_2O_3 , washed with water (20 ml) and dried over MgSO_4 . Evaporation gave the mixture of VIIa and VIIIa as a yellow oil (53–82% yield).

Reduction with LiBH_4 . LiBH_4 (20 mg) was added in one portion to a stirred solution of VI (100 mg) in THF/MeCN as described for NaBH_4 , (33–54% yield).

Reduction with LiEt_3BH . A solution of LiEt_3BH in THF (1 M, 1 ml) was

added dropwise from a syringe to a stirred solution of VI (100 mg) in THF/MeCN (4 ml/2.5 ml). After 20 min the solvent was evaporated and the residue extracted with pentane (4 × 10 ml). The cloudy extracts were filtered and washed with water (4 × 10 ml), dried over MgSO_4 , concentrated and filtered through a small pad of SiO_2 . Evaporation gave the mixture of VIIa and VIIIa as a yellow oil (40–55% yield).

Reduction with KBu_3BH . A solution of KBu_3BH in THF (0.5 M, 2 ml) was added dropwise from a syringe to a stirred solution of VIa (100 mg) in THF/MeCN (3 ml/2.5 ml) as described for LiEt_3BH . The crude product was purified by prep. TLC (SiO_2 , hexane) to give the mixture of VIIa and VIIIa as a yellow oil (28–54% yield).

Reduction with $\text{Me}_2\text{S} \cdot \text{BH}_3$. A solution of $\text{Me}_2\text{S} \cdot \text{BH}_3$ in THF (10 M, 0.2 ml) was added to a stirred solution of VI in THF/MeCN (4.8 ml/2.5 ml). After 4 h the solvent was evaporated and the residue was extracted with pentane (4 × 10 ml). A mixture of VIIa and VIIIa was obtained by prep. TLC (SiO_2 , hexane) as a yellow oil (26–44% yield).

Reduction with diborane. A solution of diborane in THF (0.5 M, 2 ml) was added to a stirred solution of VI (100 mg) in THF/MeCN (3 ml/2.5 ml) at reflux. After 4 h the reaction was worked up as described for KBu_3BH . A 7 : 3 mixture of VIIa and VIIIa was obtained as a yellow oil (40% yield). Starting material was recovered when the reduction was attempted at lower temperatures.

Reduction with 9-BBN. A solution of 9-BBN in THF (1 M, 1 ml) was added dropwise from a syringe to a stirred solution of VI in THF/MeCN (4 ml/2.5 ml) as described for $\text{Me}_2\text{S} \cdot \text{BH}_3$. (8–13% yield). The reaction at -78°C was repeated on a preparative scale: a solution of 9-BBN in THF (1 M, 4 ml) was added to a solution of VI (740 mg) in THF/MeCN (26 ml/15 ml) and stirred at -78°C for 4 h. The solvent was evaporated and the residue extracted with pentane (4 × 10 ml). The product, obtained from prep. TLC (SiO_2 , hexane) and distillation (30°C , 10^{-3} mmHg), as a yellow oil (62 mg, 14%), was identical to an authentic sample of VIIa (NMR, GLC). The residue after pentane extraction was dissolved in MeCN. Addition of ether caused precipitation of unreacted VI (420 mg, 57%).

Reduction with LiEt_3BD . A solution of LiEt_3BD (1 M, 2 ml) was added to a stirred solution of VI (500 mg) in THF/MeCN (22 ml/12 ml) at -5°C . After 20 min the solvent was evaporated and the residue extracted with pentane (4 × 10 ml). The combined extracts were washed with water (4 × 10 ml) and dried over MgSO_4 . The mixture of products was partially separated by prep. TLC (SiO_2 , hexane). An inseparable mixture of monodeuterated (92%) VIIa and VIIIa (134 mg, 43%) (mass spectrum m/e 235, 207, 179, 177, 176, 149, 148 (100%), 92, 91), eluted ahead of hexacarbonyl[5,5'-di-(1,2,3,4- η)-2-methyl-1,3-cyclohexadiene]diiron(0), (XVI) and its isomers (88 mg, 28%); ^1H NMR (CDCl_3) δ : 1.8 (s), 1.25 (d), 2.12 (s), 2.5–3.0 (m), 5.0–5.3 (m) ppm. IR spectrum (cyclohexane): 2037, 1968 cm^{-1} . Mass spectrum m/e : 466, 296, 294, 233 (100%), 149, 148; $M^{++} - \text{CO}$: 437.9854. $\text{C}_{19}\text{H}_{18}\text{O}_5\text{Fe}_2$ calcd.: 437.9853.

Reduction with NaBD_4 . NaBD_4 (30 mg) was added in one portion to VI (300 mg) in THF/MeCN (10 ml/5 ml) at -5°C . After 20 min the reaction mixture was worked up as described for NaBH_4 to give a mixture of monodeuterated

(92%) VIIa and VIIIa (mass spectrum m/e : 235, 207, 179, 177, 149 (100%)) as a yellow oil (150 mg, 81%).

Reduction by heating at reflux. The salt VI (250 mg) was dissolved in THF/MeCN (12 ml/6 ml) and heated at reflux for 4 h. The solvent was evaporated and the residue extracted with pentane (4×10 ml), filtered, and evaporated to give a mixture of VIIa, VIIIa and XVI (55 mg, 35%). If the reaction was stopped after 20 min, I (177 mg, 71%) was recovered unchanged by precipitation with ether. The filtrate was evaporated and the residue extracted with pentane (5 ml) to give a trace of reduction products (5 mg).

2. GLC analysis of regioisomers

The isomers VIIa and VIIIa were separated on 2% OV17/Gas Chrom Q (50–120°C; 4° min⁻¹). VIIa (ca. 13.6 min) elutes before VIIIa (ca. 14.3 min).

3. Mass spectrometer analysis of stereochemistry

Slow scans in the region of 207 and 149 mass units were recorded for reduction products from NaBH₄, NaBD₄ and LiEt₃BD. The mean, normalised peak heights are tabulated below:

4. Tricarbonyl[*dimethyl*[(2,3,4,5- η)-4-methyl-2,4-cyclohexadien-1-yl]propanedioate]iron(0) (VIIb)

Sodium hydride dispersion in mineral oil (240 mg, 5.5 mmol of NaH) was washed with pentane (3×5 ml) and suspended in dry THF (20 ml). Dimethylmalonate (790 mg, 6 mmol) in THF (5 ml) was added slowly from a syringe. A clear solution of the sodio derivative was obtained. A portion of this solution (≈ 1 ml) was added dropwise to a stirred suspension of the salt VI (253 mg, 0.67 mmol) in THF (5 ml) at -5°C until dissolution of VI was complete. The mixture was then poured into a separating funnel charged with sat. aqueous NaCl (10 ml), water (10 ml) and ether (10 ml), and the aqueous phase was extracted with ether (3×10 ml). The combined extracts were washed with water (3×10 ml), dried over MgSO₄ and evaporated. The yellow oil was distilled (50–60°C, 10^{-3} mmHg) to give a mixture of VIIb and VIIIb (181 mg, 83%). ¹³C NMR (CDCl₃) δ : 21.8 (Me), 29.8 (C(6)), 37.0 (C(1)), 52.5 (OMe), 57.7, 59.6, 62.2 (C(2), C(5), C(1')), 84.6 (C(3)), 104.0 (C(4)), 168.7 (CO₂), 211.4 ppm (M–CO), VIIb, 82.1, 88.4 ppm (inner carbons of diene) VIIIb. A portion of this crude mixture was crystallised from pentane to give pure VIIb as a pale yellow solid, m.p. 72–74°C. ¹H NMR (CDCl₃) δ : 1.43 (dt, 1 H, $J = 14$, 3 Hz, H(6 α)), 2.07 (s, 3 H, Me), 2.14 (m, 1 H, H(6 β)), 2.71 (m, 1 H, H(2)), 2.82 (m,

TABLE 2

MASS SPECTROMETRIC ANALYSIS

Reducing agent	147–150 mass units				205–208 mass units			
	147	148	149	150	205	206	207	208
NaBH ₄	1	87	10	2	1	85	12	2
NaBD ₄	6	11	74	9	5	8	76	11
LiEt ₃ BD	3	51	41	5	4	8	77	11

1 H, H(5)), 3.01 (s, 1 H, H(1')), 3.05 (m, 1 H, H(1 β)), 3.68 (s, 3 H, OMe), 3.72 (s, 3 H, OMe), 5.21 (ppm (d, 1 H, $J = 6$ Hz, H(3))). IR spectrum (cyclohexane): 2041, 1975, 1967, 1755, 1739 cm^{-1} . Mass spectrum, m/e : 364, 326, 308, 280 (100%), 148, 91. Analysis: Found: C, 49.34; H, 4.24. $\text{C}_{15}\text{H}_{16}\text{O}_7\text{Fe}$ calcd.: C, 49.48; H, 4.43%.

5. *Tricarbonyl[(1,2,3,4- η)-5-cyano-2-methyl-1,3-cyclohexadiene]iron(0) (VIIc) and tricarbonyl[(1,2,3,4- η)-6-cyano-1-methyl-1,3-cyclohexadiene]iron(0) (VIIIc)*

Potassium cyanide (100 mg, 1.5 mmol), dissolved in the minimum volume of water, was added to a stirred solution of the salt VI (300 mg, 0.8 mmol) in MeCN (6 ml) at 25°C. After 10 min the solvent was removed on a rotary evaporator. The residue was extracted with hexane (4 $\times$ 10 ml). A mixture of VIIc and VIIIc was obtained as a yellow oil (192 mg, 90%). A portion of this material was distilled (45–50°C, 10^{-3} mmHg) for analysis. ^1H NMR (C_6D_6) δ : 1.32 (s, 1-Me), 1.48 (s, 2-Me), and 1.2–1.8 ppm (m, H(5), H(6), integrates for 6 H), 2.1–2.4 (m, H(1), H(4)) 4.4–4.7 ppm (m, H(2), H(3), integrates for 3 H); the ratio of signals at 2.3 and 4.6 ppm indicates a 2 : 1 mixture of VIIc and VIIIc. ^1H NMR (CDCl_3) δ 1.70 (s), 2.12 (s), 1.8–2.5 (m), 2.7–3.2 (m), 5.28 ppm (m). IR spectrum (liquid film): 2230 cm^{-1} ; (cyclohexane): 2046, 1979 cm^{-1} . Mass spectrum m/e : 259, 231, 203, 175, 173 (100%), 148, 91. Analysis: Found: C, 50.93; H, 3.53; N, 5.21. $\text{C}_{11}\text{H}_9\text{O}_3\text{NFe}$ calcd.: C, 51.00; H, 3.50; N, 5.41%. The same mixture was obtained by addition of VI in a small volume of MeCN to an aqueous solution of sodium cyanide.

6. *Tricarbonyl[(1,2,3,4- η)-5-acetyl-2-methyl-1,3-cyclohexadiene]iron(0) (VIIId) and tricarbonyl[(1,2,3,4- η)-6-acetyl-1-methyl-1,3-cyclohexadiene]iron(0) (VIIIId)*

The mixture of complexes (542 mg, 2 mmol) obtained in section 5 was dissolved in ether (40 ml) and added to a solution of MeMgI (prepared from Mg turnings (110 mg, 4.6 mmol) and MeI (700 mg, 4.9 mmol)) in ether (40 ml). The mixture was heated at reflux for 3 h and then stirred at room temperature overnight. The dark solution was poured into 5% aq. NH_4Cl (100 ml) and shaken vigorously. The aqueous layer was extracted with ether (2 $\times$ 30 ml). The extracts were dried (MgSO_4) and evaporated to leave a green residue which was chromatographed on silica with hexane/ether (1/1) to give a mixture of VIIId and VIIIId as a yellow oil (370 mg, 64%). ^1H NMR (CDCl_3) δ : 1.45 (s, 1-Me), 1.99 (s, 2-Me), 2.06 (s, 5-COMe), 2.08 (s, 6-COMe) and 1.8–2.4 (m, H(5 α), H(6 α), integrates for 8 H), 2.8–3.2 (m, H(1), H(4), H(5 β), H(6 β)), 5.15–5.55 ppm (m, H(2), H(3), integrates for 4 H). The ratio of signals at 3.0 and 5.4 ppm indicates a 2 : 1 mixture of VIIId and VIIIId. IR spectrum (liquid film): 1708 cm^{-1} ; (cyclohexane): 2040, 1970 cm^{-1} . Mass spectrum m/e : 276, 248, 220, 205, 203, 175, 173, 149, 148 (100%), 91. A semi-carbazone derivative (m.p. >350°C) was prepared for analysis: Found: C, 46.88; H, 4.95; N, 12.47. $\text{C}_{13}\text{H}_{15}\text{N}_3\text{O}_4\text{Fe}$ calcd.: C, 46.87; H, 4.54; N, 12.61%.

7. *Tricarbonyl[2-[(2,3,4,5- η)-4-methyl-2,4-cyclohexadien-1-yl]-4-methylbenzeneamine]iron(0) (VIIe) and hexacarbonyl[2,6-di-[(2,3,4,5- η)-4-methyl-2,4-*

cyclohexadien-1-yl]-4-methylbenzeneamine]diiron(0) (XVII)

A solution of the salt VI (395 mg, 1 mmol) in MeCN (25 ml) was added dropwise to a solution of *p*-toluidine (247 mg, 2.3 mmol) in MeCN (5 ml) at reflux over a period of 20 min. After a further 30 min the solvent was evaporated and excess *p*-toluidine removed from the residue by sublimation (45°C, 0.5 mmHg). The brown residue was extracted with boiling hexane (4 × 10 ml). A small amount of XVII (37 mg, 12% based on VI) m.p. 53–56°C, (¹H NMR, δ: 1.50 (d, 2 H, *J* = 16 Hz, H(6α)), 2.13 (s, 9 H, 2-Me and Ar-Me); 2.34 (dq, 2 H, *J* = 16 Hz, H(6β)), 2.94 (q, 2 H, *J* = 6 Hz, H(2)), 3.12 (m, 2 H, H(5)), 3.24 (m, 4 H, NH₂, H(1β)) 5.42 (d, 2 H, *J* = 6 Hz, H(3)), 6.59 ppm (d, 2 H, *J* = 2, Ar-H). IR spectrum (Nujol mull): 3470, 3380 cm⁻¹; (cyclohexane): 2041, 1975 cm⁻¹. Mass spectrum, *m/e*: 571, 543, 515, 487, 485, 427, 401, 399, 343, 337, 311, 309, 287, 253 (100%), 205, 197, 163, 107. Analysis: Found: C, 56.79; H, 4.58; N, 2.46. C₂₇H₂₅O₆NFe₂ calcd.: C, 56.78; H, 4.44; N, 2.45%) was separated from the more polar VIIe (yellow gum: ¹H NMR (CDCl₃) δ: 1.52 (d, 1 H, *J* = 16 Hz, H(6α)), 2.13 (s, 3 H, 2-Me), 2.17 (s, 3 H, Ar-Me), 2.31 (dq, 1 H, *J* = 16 Hz, H(6β)), 2.91 (q, 1 H, *J* = 6 Hz, H(2)) 3.1 (m, 1 H, H(5)), 3.2 (m, 2 H, NH₂, H(1β)), 5.35 (dd, 1 H, *J* = 6.2 Hz, H(3)), 6.31 (d, 1 H, *J* = 7.5 Hz, H(6) (Ar)), 6.65 (dd, 1 H, *J* = 7.5, 2 Hz, H(5) (Ar)), 6.70 ppm (m, 1 H, H(3) (Ar)). IR spectrum (liquid film): 3450, 3360 cm⁻¹; (cyclohexane): 2039, 1968 cm⁻¹. Mass spectrum, *m/e*: 339, 311, 283, 255, 253, 197, 163 (100%), 148, 107; *M*⁺ 339.0552. C₁₇H₁₇NO₃Fe calcd.: 339.0558) by prep. TLC on silica, eluting with hexane/ether (7/3).

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References

- 1 A.J. Birch and I.D. Jenkins in H. Alper (Ed.), *Transition Metal Organometallics in Organic Synthesis*, Vol. 1, Academic Press, New York, 1976, p. 1.
- 2 L.F. Kelly, A.S. Narula and A.J. Birch, *Tetrahedron Lett.*, 21 (1980) 2455.
- 3 A.J. Birch, P. Dahler, A.S. Narula and G.R. Stephenson, *Tetrahedron Lett.*, 21 (1980) 3817.
- 4 A.J. Birch, B.M.R. Bandara, K. Chamberlain, B. Chauncy, P. Dahler, A.I. Day, I.D. Jenkins, L.F. Kelly, T.-C. Khor, G. Kretschmer, A.J. Liepa, A.S. Narula, W.D. Raverty, E. Rizzardo, C. Sell, G.R. Stephenson, D.J. Thompson and D.H. Williamson, *Tetrahedron*, in press.
- 5 A.J. Pearson, P. Ham and D.C. Rees, *Tetrahedron Lett.*, 21 (1980) 4637; A.J. Pearson and C.W. Ong, *ibid.*, 21 (1980) 4641.
- 6 B.M.R. Bandara, A.J. Birch and T.-C. Khor, *Tetrahedron Lett.*, 21 (1980) 3625.
- 7 A.J. Birch, K.B. Chamberlain, M.A. Haas and D.J. Thomson, *J. Chem. Soc. Perkin I*, (1973) 1882.
- 8 (a) A.J. Deeming, S.S. Ullah, A.J. Domingos, B.F.G. Johnson and J. Lewis, *J. Chem. Soc. Dalton*, (1974) 2093; (b) R. Edwards, J.A.S. Howell, B.F.G. Johnson and J. Lewis, *ibid.*, (1974) 2105; (c) A.L. Burrows, B.F.G. Johnson, J. Lewis and D.G. Parker, *J. Organometal. Chem.*, 194 (1980) C11.
- 9 B.F.G. Johnson, J. Lewis, T.W. Matheson, I.E. Ryder and M.V. Twigg, *J. Chem. Soc. Chem. Commun.*, (1974) 269.
- 10 R.J.H. Cowles, B.F.G. Johnson, P.L. Josty and J. Lewis, *J. Chem. Soc. Chem. Commun.*, (1969) 392; E.G. Bryan, A.L. Burrows, B.F.G. Johnson, J. Lewis and G.M. Schiavon, *J. Organometal. Chem.*, 129 (1977) C19.
- 11 M.A. Hashmi, J.D. Munro, P.L. Pauson and J.M. Williamson, *J. Chem. Soc. (A)*, (1967) 240.
- 12 A.L. Burrows, PhD Thesis, University of Cambridge (1977).
- 13 S.G. Davies, M.L.H. Green and D.M.P. Mingos, *Nouveau Journal de Chimie*, 1 (1977) 445.
- 14 S.G. Davies, M.L.H. Green and D.M.P. Mingos, *Tetrahedron*, 34 (1978) 3047.

- 15 A.J. Birch and M.A. Haas, *J. Chem. Soc. C.*, (1971) 2465.
- 16 T.H. Whitesides, R.W. Arhart, *Tetrahedron Lett.*, (1972) 297.
- 17 A.J. Birch, P.E. Cross, J. Lewis, D.A. White and S.B. Wild, *J. Chem. Soc. (A)*, (1968) 332.
- 18 A.J. Birch and G. Kretschmer, unpublished results.
- 19 A.J. Birch, A.S. Narula, P. Dahler, G.R. Stephenson and L.F. Kelly, *Tetrahedron Lett.*, (1980) 979.
- 20 B.F.G. Johnson, J. Lewis, D.G. Parker, P.R. Raithby and G.M. Sheldrick, *J. Organometal. Chem.*, 150 (1978) 115.
- 21 A.J. Birch, A.J. Liepa and G.R. Stephenson, *Tetrahedron Lett.*, (1979) 3565.
- 22 T.A. Albright and B.K. Carpenter, *Inor. Chem.*, 19 (1980) 3092; A. Solladié-Cavallo and G. Wipff, *Tetrahedron Lett.*, 21 (1980) 3047.
- 23 T.A. Albright, P. Hofmann and R. Hoffmann, *J. Amer. Chem. Soc.*, 99 (1977) 7546.
- 24 P.M. Harrison, PhD Thesis, University of Sheffield (1968).
- 25 R.S. Bayoud, E.R. Biehl and P.C. Reeves, *J. Organometal. Chem.*, 174 (1979) 297.
- 26 A.J. Birch and A.J. Pearson, *J. Chem. Soc. Perkin I*, (1976) 954; A.J. Pearson, *Aust. J. Chem.*, 30 (1977) 345.
- 27 A.J. Birch, P.W. Westerman and A.J. Pearson, *Aust. J. Chem.*, 29 (1976) 1671.
- 28 O. Eisenstein and R. Hoffmann, *J. Amer. Chem. Soc.*, 102 (1980) 6148.
- 29 R. Hoffmann and P. Hofmann, *J. Amer. Chem. Soc.*, 98 (1976) 598.
- 30 D.W. Clack, M. Monshi and L.A.P. Kane-Maguire, *J. Organometal. Chem.*, 107 (1976) C40.
- 31 H. Alper and C.-C. Huang, *J. Organometal. Chem.*, 50 (1973) 213; A.J. Pearson, *J. Chem. Soc. Perkin I*, (1978) 495.
- 32 B.R. Reddy and J.S. McKennis, *J. Organometal. Chem.*, 182 (1979) C61.