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ORGANOMETALLIC COMPOUNDS IN ORGANIC SYNTHESIS—XI

THE STRATEGY OF LATERAL CONTROL OF REACTIVITY: TRICARBONYLCYCLOHEXADIENEIRON COMPLEXES AND THEIR ORGANIC SYNTHETIC EQUIVALENTS

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Abstract—The concept is discussed of superimposed lateral control of reactivity, stereochemistry and structures, by attachment of complexed metal atoms to olefinic systems. This differs from classical endogenous control of synthesis by classical anionoid and cationoid groups in the skeleton, and its application has many theoretical and practical advantages. It is illustrated by considerations of reactions of substituted tricarbonylcyclohexa-1,3-dieneiron derivatives; notably the derived dienyliron salts, which are defined as equivalents of specifically substituted aryl cations or as cyclohex-2-enone cations, dependent on the structures and reaction sequences. The effects are noted of classical substituents on the positions and on the rates of reactivity of some complexed dienyl cations; both regio- and stereospecificities are dependent on the nature of the anion involved and the conditions. Probable mechanisms are discussed. Other effects of lateral control include those on the classical reactivities of attached groups (such as hydrolysis of CO_2Me) and on adjacent groups, such as stereochemistry of reduction of the 3-carbonyl in the ergosterone complex. Some useful new C–C bond-forming reactions made possible by the approach are noted.

STRATEGIES OF ORGANIC SYNTHESIS

To achieve appropriate reactivities for the junction of component molecules, classical organic synthesis requires the presence of appropriately reactive groups. This requirement leaves structural remnants in the new skeleton, often not the structures desired which must then be attained by further manipulations. This strategy may be termed endogenous control of reactivity and steric selectivity; reactions are frequently not completely regio- or stereospecific. It was pointed out in the first discussion of the strategy now termed convergent synthesis,[1] that a major problem is to modify appropriately the structures resulting from the initial reactivity requirements. Increasing functionality in target molecules accentuates the problem, since groups required for synthetic activation are frequently identical in type with those required as substituents, which implies the use of competitive reactions or roundabout protection methods.

Many of these problems can, in principle, be overcome in appropriate structures by superimposing the required control of activation and stereochemistry in the form of laterally attached groups consisting of complexed transition metal atoms. The fundamental activation needed can then be independent of a requirement for classical anionoid and cationoid substituents in the skeleton, the presence of which may, however, be important in influencing the regiospecificities of reaction. Steric control, due to molecular shape as is possible with classical globular molecules,[2] or of an entirely different type resulting from the reactivities superimposed by the complexing group itself, is unusual in relation to most classical processes in being frequently complete. Superimposed control can be exercised to bring about reactions on the same, or the opposed, side to the metal according to the mechanism and to kinetic or thermodynamic control of products.

In order to permit the use in synthesis of such principles, previous work in these laboratories,[3,4] has been concerned with preparations and reactions of some $Fe(CO)_3$ complexes, a series which we now discuss as illustrative but not exclusive examples of the application of the strategy. The type of thinking expressed is general to olefin π-complexes, but particular applications require close considerations of the appropriate metals and ligands.

We call this strategy "lateral control of reactivity, stereochemistry and structure". The use of such groups is analogous to that of external scaffolding in erecting a building. It also has affinities with the ideas of enzyme chemistry, although the exact processes are very different. The concept can be extended, in slightly different terms, to the classical coordination complexes and the effects in them of a metal atom on the reactivities of the organic complexing group.

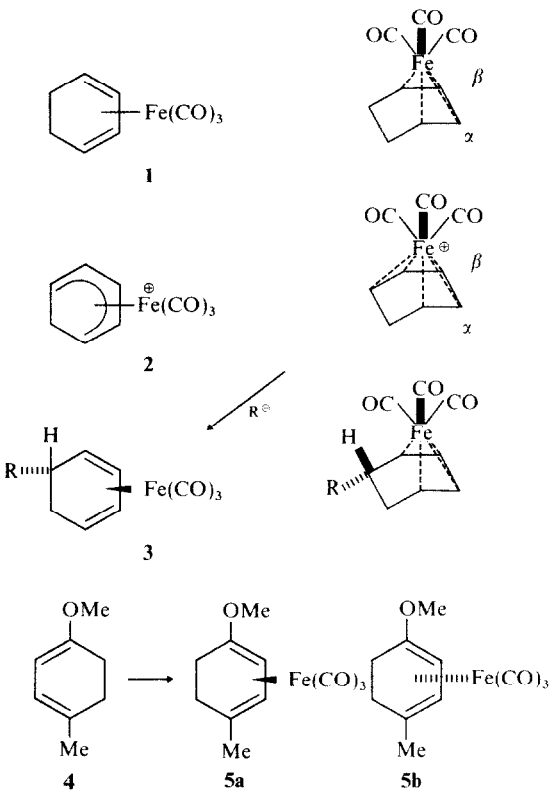
Characteristics of cyclohexa-1,3-diene or dienyl $Fe(CO)_3$ *complexes*

A general characteristic of $Fe(CO)_3$ π-complexes with cyclohexa-1,3-dienes such as **1** is that the metal is joined simultaneously to a number of carbons, four in the neutral diene complexes and five in the cationic

complexes (**2**), the complexed portion of the molecule being globular in type with a β-face of the ring (carrying the metal) and an α-(opposed) face. Reaction capabilities differ completely between the two ring faces. Also, because of the obligatory C–Fe bonding, the carbons involved are necessarily cisoid. This is inevitable inside a ring but is also true of open-chain compounds, and, for example, also prevents externalisation of complexed unsaturation from a ring, giving another dimension of synthetic control of structures. Addition and removal of the complexing group in one step[3] contrasts with classical methods in that four directed bonds are formed and broken simultaneously in the η^4–η^5 series or two in the η^2–η^3 series.

An outstanding feature of induced reactivity conferred by complexing is the ability to form cations of the η^5 type **2**. Cationoid processes can therefore be carried out independently of any need for the presence of classical cationoid groups such as carbonyl. Such cations can indeed contain typical anionoid groups such as OMe. These formal equivalents of stabilised mesomeric carbocations usually react in kinetically controlled processes with anionoid (nucleophilic) reagents solely on the α-face, with the partial exception of some hydride reductions noted later, resulting in the steric control of the newly formed centre, e.g. as in **3**.

Control can extend to the production of a newly fully resolved chiral centre if the cation is optically resolved.[5,47] All complexes of unsymmetrically substituted dienes such as **5a**, **5b** and the derived cations unless symmetrical, are capable of existing as enantiomers whether or not the diene itself is chiral. This permits in principle one solution of an old problem: to use one resolved centre to induce another, of known configuration, and then to remove the first.



The stereospecificity of formation of a new C–C or other bond, in a reaction involving an asymmetric cation of known configuration, results in enantiospecific generation of a new centre, of known configuration, resolved to the extent that the initial cation is resolved. Removal of metal and attached groups from the neutral product then abolishes the inducing asymmetry. This applies to any sterically defined process including formation of C–H or C–D when an asymmetric centre results. In the following account, an asterisk (*) with a formula number indicates an absolute configuration[5] rather than one component of a racemic mixture.

Availability of complexes

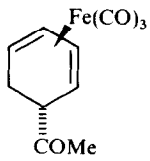
In order to utilise these and other characteristics in organic (as distinct from organometallic) synthesis, it is necessary to be able: (1) to add and to remove the lateral complexing group efficiently; (2) to prepare efficiently and in states of purity a wide range of complexes with specific substitutions; (3) to examine and understand the regio- and stereospecificities of reactions in relation to mechanisms involving structures of complexes and reagents, and conditions. A number of aspects of these topics have already been discussed[3] and will not be pursued further here except to note that no cation is mentioned in this review unless it can be obtained in a state of purity. Reagents of choice for removal of $Fe(CO)_3$ are $Me_3NO \cdot 2H_2O$[6] or $CuCl_2$.[7]

In considering synthetic strategies, it is necessary to distinguish in practice between the use of the complexes as reagents and to perform steps in later stages of a long sequence. The dominant factor in the first type of usage is ease of formation, and in the second case is yield. In particular, unconjugated dienes from Birch reductions of aromatic compounds can be used directly for simple preparations, but often mixtures or poor yields result which require to be separated or isomerised. For high yields of defined products, after a long synthetic sequence, it would be desirable to form a complex from a preformed specifically substituted conjugated diene.

Kinetic and thermodynamic control of products

To define the regio- and stereospecificity of reactions it must be established whether products are determined by a rate, or an equilibrium (or partial equilibrium) position. Equilibration can be attained either by reversals of the addition to a cation, or by enolisations of groups such as CHCOR or $CHCO_2Me$ in a η^4 complex. An example of the latter seems to be the Friedel–Crafts acetylation of the cyclohexadiene complex, originally thought[8] to give the 5α-COMe (**6**). Repetition of the work[9] shows initially the formation of the 5β-COMe (**7**) isomerisable with base into the known 5α-COMe (**6**). The yield in the acylation with the $Fe(CO)_3$ complex is about 45%, but by use of the less electron-withdrawing $Fe(CO)_2PPh_3$ the acetylated product is formed in 75% yield.[9] This is one pointer to possible synthetic control by manipulating the metal ligands appropriately.

Examples of equilibration by reversal are shown with anions like OMe[10,28] or OH.[11] The ratio 40α:60β (**8**, **9**) for the 5-OMe cyclohexadiene complex is surprising and possibly indicates stabilisation of β-OMe by orbital interaction, of an unknown character.



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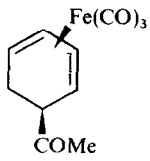

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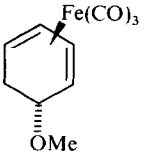

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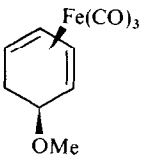

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rather than the expression of simple classical hindrance.[9] Reversal of 5α- C–C formation in some products of reaction of carbon nucleophiles with cations is known by means of sulphuric acid[12] but this process regenerates the cation and does not produce a steric isomer equilibrium. We assume for new C–C or C–H formation in reactions with cations that the products are kinetically controlled; for other more reversible nucleophiles the results may depend on conditions which have not been closely examined except in the case quoted.[10] Kinetic control (apparently α-) is possible in such cases, but depends on the use of irreversible experimental conditions. It is not clear at present that reversal will affect regio as well as stereospecificities, but it would be expected.

Regiochemistry

Electrophilic reactions on substituted cyclohexadiene complexes in relation to directive effects have been little examined.

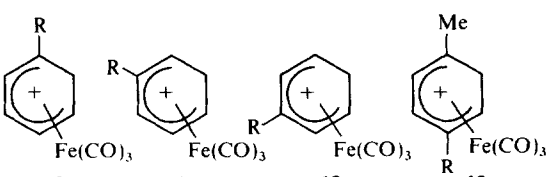
The substituted complexed cations are formally, stabilised specifically protonated benzenes which, unlike these parents, do not readily undergo deprotonation but react at C-1 or C-5 with anionoid (nucleophilic) reagents. In contrast to some larger rings[13] or derivatives of other metals,[14] in the cyclohexadienyl $Fe(CO)_3$ cation series reaction does not occur on C-2, C-3 or C-4, although if it is regarded as a mesomeric carbonium ion reaction at C-3 is formally possible. The stability of the complexed cations is attributable to charge delocalisation over the orbitals of a 3-dimensional π-system, and the relative reactivities of the two termini of the carbon system must be due to modifications by the substituents of the entire molecular orbital system. Substituents therefore do not necessarily show in any simple form the electronic effects of classical organic chemistry. Whilst this must be borne in mind, the addition of nucleophiles to a large number of organometallic cations has been surveyed and the conclusion made that the addition of hard nucleophiles to 18-electron cations may be considered charge, rather than orbitally controlled.[15] A rough correlation does seem to exist between ^{13}C NMR shifts and selectivities[16] which may provide useful indications of trends. Also, experimental selectivity between the termini depends not only on the nature and position of the substituent, but on the type of the reagent and the conditions as noted below. One readily interpretable classical effect of substitution is steric inhibition by a substituent on a position to which electronic effects would normally direct reaction.

The cation cannot be regarded as a classical carbonium ion, since a significant part of the charge is located on Fe.[17] Also the siting of a counter anion, and possible conformations of polar CO groups may have at present unknown effects on charge localisation in reactions. "Free" cations of this type must also differ from those based on classical polarisations of groups like carbonyl, in requiring little activation energy, at least in reactions with anions. The more reactive the anion the less should be the selectivity induced by substitution in the cation. Results quoted below agree qualitatively with the proposition that the weaker the acid corresponding to the anion used the less selective is that anion. However, complications in both regio- and stereoselectivity may result from changing mechanisms; if, for example, a reagent interacts first with the $Fe(CO)_3$ and is then transferred to the carbon system, as with hydride via a formyl complex.[18]

Problems of regio-control depend on the nature of the substituents. With 1-CO_2Me (**10**, R = CO_2Me) or 2-OMe (**11**, R = OMe) the 5-product results[3,4] except when very reactive anions are used.[19,20] However, with a weakly directive group like 2-Me (**11**, R = Me) selectivity is dependent on the nature of the reagent: allylsilanes,[21] 1,2-bis TMS 1-cycloalkenes[22] and aromatic amines[23] are known to react exclusively at C-5. With $NaBH_4$ in MeCN, selectivity is low, and attempts to increase this by lowering temperatures, surprisingly, resulted in decreased selectivity. The ratios of 1-Me:2-Me product are: 0.70 (82°); 0.79 (25°); 0.96 (−5°); 1.08 (−40°).

Improvements in selectivity may be affected by simple modifications of structures. In the case of borohydride reduction in acetonitrile of the 2-isopropoxy-5-methyl cation (**13**, R = O-*i*-Pr), undesired reaction at the 1-terminus is reduced but not completely suppressed [6%, compared to 10% for the corresponding 2-methoxy cation (**13**, R = OMe)[24]].

For synthetic uses it is desirable to know something of changes in rate of cation reactions due to substitution. The effects of the substituents OMe, Me, CO_2Me on overall reaction rates of the tricarbonylcyclohexadienyliron cation with acetylacetone under standard[25] conditions (40° ± 0.1°) in homogeneous solution in MeCN (or $MeNO_2$ in instances noted) have been examined under pseudo first order conditions by quantitative disappearance of the infrared peak at $\nu = 2110\,cm^{-1}$ due to $Fe(CO)_3^{\oplus}$. Previous preparative work, confirmed by tlc with the products here, indicates only one product from the unsymmetrical cations, representing addition to the 5-position. The rates relative to the unsubstituted cation **2**, 1.00 (MeCN) or 1.10 ($MeNO_2$) are: symmetrical: 3-Me (**12**, R = Me) 0.83; 3-OMe (**12**, R = OMe) 1.24 ($MeNO_2$); 3-OMe-1,5-Me_2, (**14**), 0.006 ($MeNO_2$), unsymmetrical: 1-CO_2Me, (**10**, R = CO_2Me) 12.13 or



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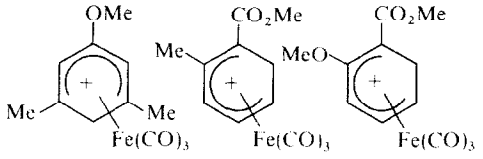


14 15 16

10.55 ($MeNO_2$); 1-CO_2Me-2-Me, (**15**), 6.59 or 7.31 ($MeNO_2$); 1-CO_2Me-2-OMe, (**16**), 1.62; 2-OMe, (**11**, R = OMe) 0.09; 2-Me, (**11**, R = Me) 0.38.[26]

A comparison between symmetrical and unsymmetrical cations requires recognition of the existence of two possible reactive positions in the first series and one in the second. The rates can be qualitatively explained partly by probable electronic effects of substituents: donation stabilising the cation and slowing reaction rates (2- or 3-Me, and particularly 2-OMe) (which must affect the 1-position much more than the 5-position) and electron withdrawal (1-CO_2Me) increasing rates. The 3-OMe marginally increases rates possibly through its inductive effect. In the disubstituted cases, expected effects of competition are seen. Steric effects must also be involved, particularly in the slow rate of the 1,5-Me_2-3-OMe (**14**) cation where addition must take place in a substituted position if it occurs at all. Because of the low rate the product could not be identified: it might be that of deprotonation. Whatever the product, the presence of the terminal Me is highly inhibitory of addition. Such steric effects have already been qualitatively noted.[27] Comparison of rates MeCN:$MeNO_2$ are not representative of a reproducible trend, but the difference, at maximum, is about 10%.

Stereochemistry

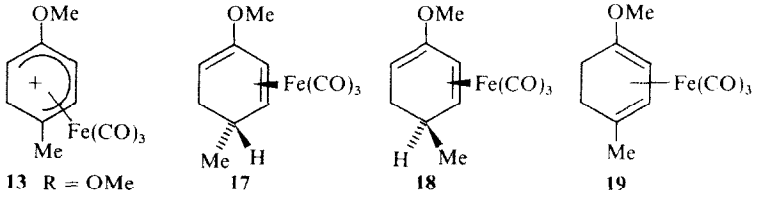
There is evidence[10,28] for reversible interaction of $Fe(CO)_3^{\oplus}$ with $RO^{\ominus}$, but no indication of direct transfer to the carbon system. The first evidence of substantial kinetic β-attack on a cation was the formation of some **17** by borohydride reduction of **13** (R = OMe), together with the expected **18** and **19**. A possible explanation[18] is partial attack on carbonyl to give a formyl complex, with transfer of hydride direct to the carbon system. To see to what extent the result depends on the reagent this was changed using the symmetrical cation **14**. With $NaBH_4$ the α:β ratio (**20**, **21**) is 88:12; $LiBH_4$ 79:21; K(*s*-Bu)$_3$BH 56:44; $LiEt_3BH$ 24:76 [all in THF:MeCN (2:1, 0)]. The result agrees with observations[18] that trialkylborohydrides favour attack of metal carbonyls on the CO.

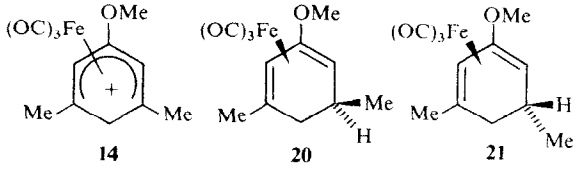
Steric control

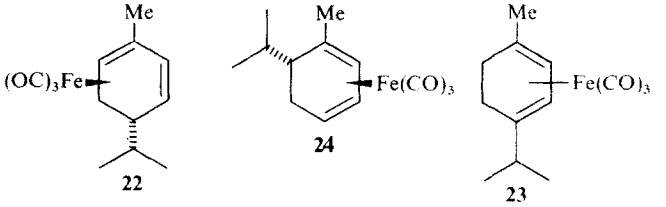
X-Ray studies of products in several key cases[29] confirm that kinetic α-attack occurs on the carbon system of cations. Expectation that this is general is extended to other cases on the basis of usual formation of only one product in C–C forming reactions, and of the internal consistency with results from this assumption in explaining other reactions of the products requiring proton migrations (on the β-face),[3] and attack of $Ph_3C^{\cdot}$ to remove hydride (on the experimentally supported assumption that this is on the α-face and is inhibited by adjacent α-substituents).[12] Furthermore, production of the known α-isomer **22** of the phellandrene complex, by an alkylation of the cation **11** (R = Me) is unaccompanied by any formation of the known β-complex which could have been readily detected. Acid-catalysed isomerisation of **22** yields **23** by β-face shift of hydrogen.[4,9]

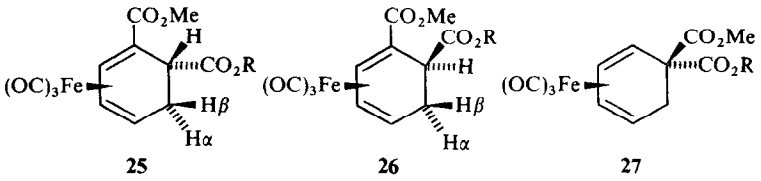
The course of hydride addition is more complex and is discussed in more detail below, but in the unsubstituted case[30] the deuterium introduced by $BD_4^{\cdot}$ is selectively removed by the trityl cation and is therefore on the α-face.

In any case it is very important in relation to potential applications to define whether a neutral



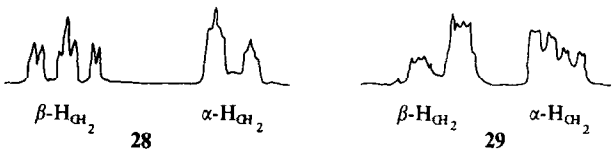






CH_2-splitting patterns

α-substituted complex (25) β-substituted complex (26)



with Eu(fod-d_9)$_3$

complex has an α- or a β-substituent. This may be reasonably definable on the basis of expectations: for example since rearrangements involve H-migration on the β-face, a centre bearing a substituent should be generated with this on the α-face. However, in cases such as esters where competing directive factors are involved,[4] it is particularly important to have clear evidence, and in the examples **25** (R = Me) and **26** this was provided by X-ray crystallography. Rapid spectral methods are clearly more desirable.

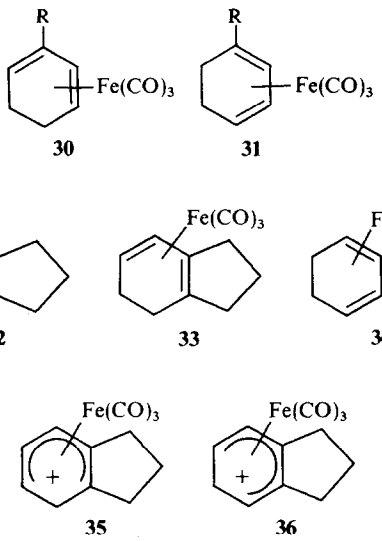
^{1}H NMR spectroscopy can be used to distinguish an α- from a β-substituent, particularly if an isomeric pair is available. Protons on a β-face resonate at lower field than the corresponding α-protons.[10,31] If only one isomer is available its steric configuration can often be assigned by examining the splitting pattern of an adjacent CH_2.[32] The types of pattern observed for CH_2 splitting are illustrated by those of the isomeric diesters **25** and **26**, the structures of which have been defined by X-ray.[33] In some cases it is necessary to add lanthanide shift reagents to resolve the pattern: in the case of **26** Eu(fod-d_9)$_3$ is present.

A range of complexes with groups such as NR_2, OR, SR, SeR, phenyl and CN have been examined by NMR[34] and the splitting patterns obtained for CH_2 enable the stereochemical assignment of the substituent in 5-position.

Lateral control of the structure of a complexed system

Lateral attachment of a complexed metal atom has several consequences in permitting control of the nature of the complexed diene. If the complex results from olefinic migration processes, e.g. based on 1,4-dihydrobenzenes, the nature of the kinetic product depends on the mechanism of the migration process, including the β-migration of H which results in any sp^3-substituent being α. The nature of the C-metal bonding requires a cisoid unsaturated system. The ability to bring about acid-catalysed equilibration between isomeric substituted complexes further can lead to a new dominant product. A series of defined dienes can thus be made available through the complexes.

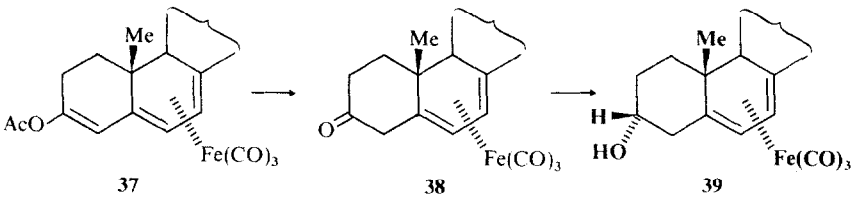
The thermodynamic stability, as related to substitution, is not the same for the complex as for the diene. With alkyl complexes the group is found predominantly in the 2-position **30**,[35] and with



CO_2Me in the 1-position (**31**, R = CO_2Me).[13,36] Also, attempts to equilibrate free cyclohexadienes result often in dehydrogenation, disproportionation or formation of transoid dienes. For example, attempts to make the uncomplexed hydrocarbon of **33** from the readily available **32** failed.[37] Reaction of the latter with $Fe(CO)_5$ under controlled conditions gave exclusively **33** from which $Fe(CO)_3$ can be removed to yield the required diene for further use in a diterpene synthesis.[37] Acid-catalysed isomerisation of **33** led to **34**. Removal of hydride from **33** gave **35** and from **34** the isomeric **36**.[38] These conversions are one example of a set of processes leading controllably to isomeric complexes, dienes and cations.

Lateral control of classical reactivities

Attachment of $Fe(CO)_3$ to a diene can usefully alter the classical reactions of organic groups carried on the system towards conventional reagents both in rate and stereochemistry. An example of the latter is the conversion of the less hindered α-side of the ergosterol nucleus into the more hindered side, enabling hydride attack of a 3-carbonyl from the β-side. We described this work at the Chemical Society Anniversary Meeting in April 1976, and shortly afterwards the same



result was published by another group.[39] We merely note here (Experimental) that the use of the enol acetate of ergosterone (**37**) is superior to the published method, since the required 3-carbonyl (**38**) can be recovered by mild hydrolysis rather than oxidation of 3-OH, a procedure to be avoided where possible with $Fe(CO)_3$ complexes susceptible to oxidation. Hindered hydride reduction then occurs mainly from the β-face (**39**).

The classical way to alter the rate of hydrolysis of CO_2R is to alter the nature of the alkyl group. Lateral control in appropriate cases can alter, reversibly, the nature of the acid portion instead. In particular a 1-CO_2Me of a cyclohexa-1,3-diene $Fe(CO)_3$ complex is found to be very resistant to alkaline hydrolysis, and an adjacent β-CO_2Me (**26**) is apparently highly hindered, although the situation is complicated by base-catalysed isomerisation to α-CO_2Me, which is then hydrolysed to **25** (R = H).

The half hydrolyses formulated above **26** (R = Me) to **25** (R = H) and **27** (R = Me) to **27** (R = H) are readily accomplished in excellent yields without taking any particular precautions related to conditions.[40] In the ^1H NMR of **27** (R = H) it is the high-field Me of **27** (R = Me) which has disappeared and which correlates with the steric configuration.[40]

Lateral protection

Lateral complexing of olefins, by altering the properties of the unsaturated system can act either as reversible protection to inhibit classical reactivities, or to induce alternative reactivities. An example is provided by thebaine, which readily yields a diene–$Fe(CO)_3$ complex[41] in which the characteristic reactions of the diene are abolished; for example N-demethylation can be brought about, to give, after removal of $Fe(CO)_3$ N-desmethylthebaine.[42] Otherwise unknown rearrangements of the skeleton can result from the complexing.[41]

Synthetic equivalents

The concept of synthetic equivalents[43] is inherent in the known reactivities of molecules, but in practice its expression is a graphic way to bring to the attention of the synthetic chemist the potentialities of a defined sequence based on a particular type of structure. The equivalence formulae are particularly useful in demonstrating the potentials of lateral control, since this is imposed on the classical anionoid and cationoid reactivities of substituents, in terms of which the synthetic chemist usually thinks, in a way which renders these modifying rather than central to reactivity, and therefore a new way of expressing the equivalent reactivity is desirable.

If extended too far the notation would lose much of its usefulness, and we have arbitrarily confined it to sequences of not more than three steps, excluding removal of the complexing group. The discussion is here limited to η^5 cations in the $Fe(CO)_3$ series, and the related dienones below, but it could be extended not only to neutral complexes, but to other metal complexes including the η^2–η^3 series. The (+)-charges (Tables 1 and 2) mark the actual positions of reactivity, and also have the designated steric consequence, which may be of significance after removal of the iron, dependent on the symmetry of the organic part.

The "equivalent" depends on the sequence of reactions, so the same starting material (e.g. **11**, R = OMe) can be regarded as several alternative equivalents. The sequences here are shown as (A) and (B): (A) reaction with an anionoid reagent (nucleophile) to give **40** followed by dehydrogenation with $Fe(CO)_3$ removal results in the equivalent of an aryl cation **41** (Table 1); and (B) removal of $Fe(CO)_3$ leads from **40** to a cyclohexadiene which in the OMe series is the equivalent of a cyclohex-2-enone (**42**) into which it is convertible by acid hydrolysis (Table 2). The equivalence of **43** can be extended further to **44** on the basis of classical organic reactions of nucleophilic

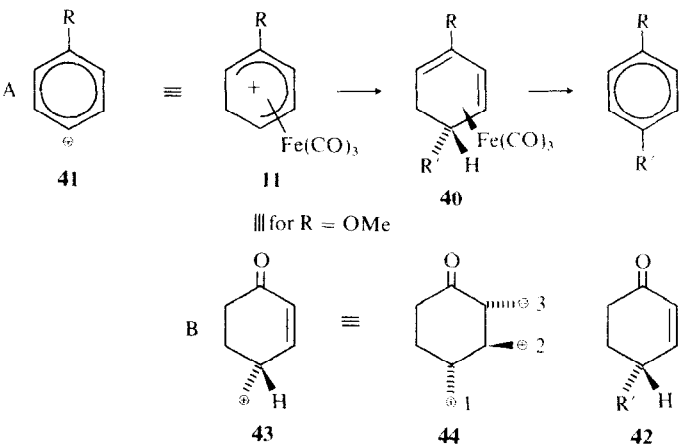
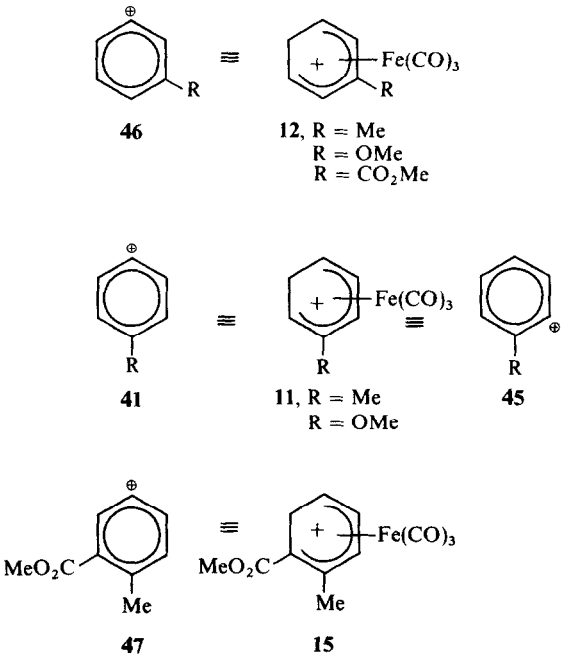


Table 1. Examples of aryl cation equivalents



46 | 12, R = Me, R = OMe, R = CO_2Me

41 | 11, R = Me, R = OMe | 45

47 | 15

addition to the first produced enone and subsequent regiospecific electrophilic reaction with the resulting anion. This equivalent would also be expected to have the dominant stereochemistry indicated (**44**). It is necessary in such equivalence formulae to conduct reactions in the numbered sequence.

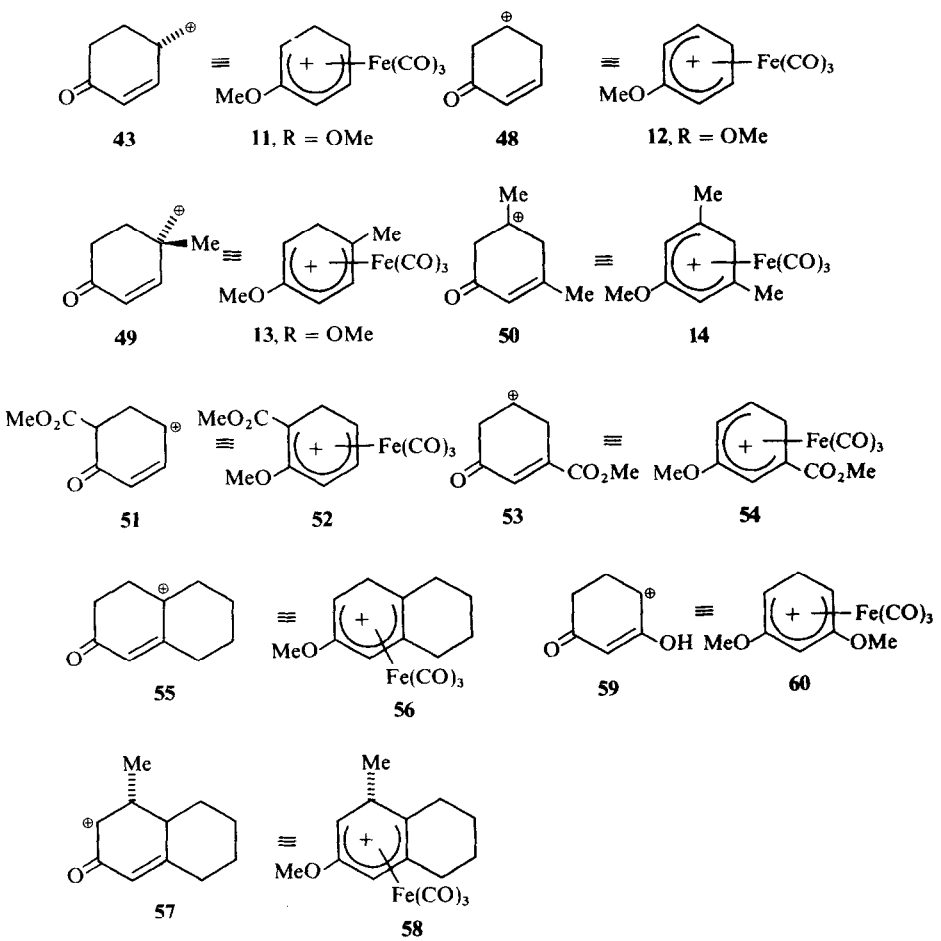
One example of the designated steric significance of the positive charge is that optical activity of the cation will lead to production of the unsaturated ketone product as one defined enantiomer, of known absolute configuration if that of the cation is known.

In some cases the notion of equivalence can usefully be extended back by one stage to the neutral precursors of cations, e.g. **17** or **19** can be regarded as **11** (R = Me) and hence as **45** or **41** (R = Me).

Deuterium can also be considered as a substituent of similar equivalents in conjunction with specific methods[3] for its introduction.

Another set of direct aromatic equivalents is defined by the substituted cyclohexadienone complexes of type **61**. These can be reacted in the carbonyl form with $BrZnCH_2CO_2Et$,[44] or with LiR under defined experimental conditions. Removal of $Fe(CO)_3$ then results in a substituted benzene by dehydration. For example, the cyclohexadienone complex itself with n-BuLi yields n-butylbenzene.[45] For reactivity purposes

Table 2. Examples of cyclohexenone cation equivalents



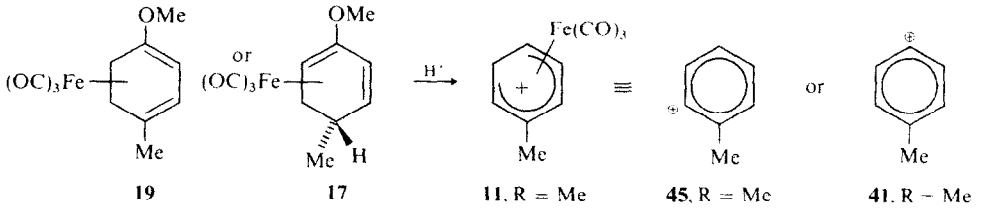
43 | 11, R = OMe | 48 | 12, R = OMe

49 | 13, R = OMe | 50 | 14

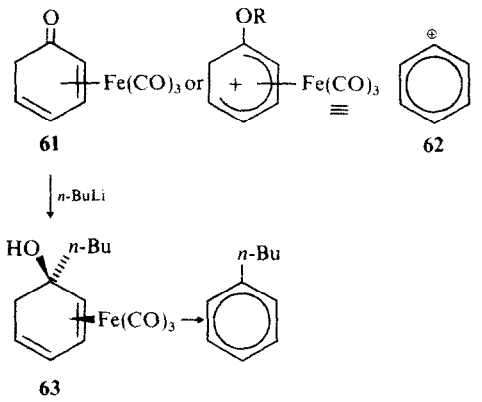
51 | 52 | 53 | 54

55 | 56 | 59 | 60

57 | 58



19 17 11, R = Me 45, R = Me 41, R = Me



61 62 63

they behave as ketonic tautomers of phenols, although carbonyl reactions are sluggish.

Reversal of classical polarities

The ability to formulate equivalents in the 2-OMe series as a cation in the 2- or 4-position to a CO reverses the classical activation associated with a CO group or a OMe group. 2-Enolate anions are well known; the classical electron-donating effect of OMe in a diene leads in Diels–Alder processes to the equivalent of a 4-anion of cyclohex-2-enone (**64**).[2] The equivalence notation shows very clearly in this case the difference induced by complexing. The notation also clearly indicates what cation equivalents are at present missing from the series (e.g. a pure equivalent of a cyclohexenone 6-cation).

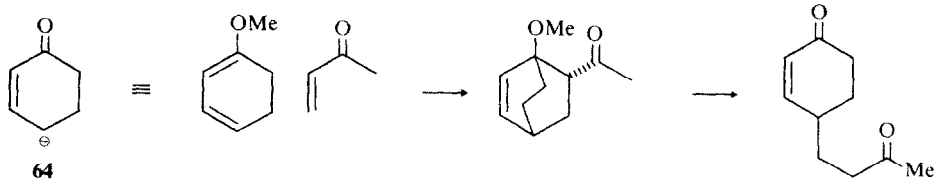
C–C forming reactions

The naked nature of the cations confers a wide ability to form C–X (X = N, O, S, C etc) under very mild experimental conditions. The outcomes most interesting for synthetic purposes are new methods of forming C–C. Hitherto, the laboratory use of the equivalents in synthetic action has been necessarily mainly confined to examining the basic features of the processes they undergo, but the topic is now at a point where it should be possible to participate in complex syntheses, with the increasing definitions of ways to make specifically substituted pure complexes, and the increasing understanding of the reactions. We have recently reported experimental advances which convert what were to some extent paper processes into practical ones. These involve the expansion of the range of participating anionoid (nucleophilic) reagents and the use of advantageous experimental techniques discussed below.

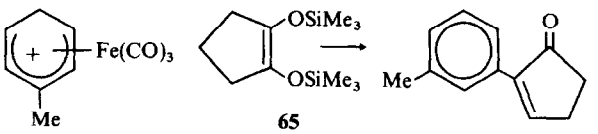
Previous work has already noted reactions with anions such as cyanide, malonate, β-diketone enolates, or even with the conjugate acids of such enols, including ketones, which seem to react as the stable enol.[3] Enamines have been shown to react as expected,[46] but recently TMS enol ethers, which can result from either kinetic or thermodynamic enolisation have been found to react with retention of regiospecificity.[47] Such enol ethers can be derived from ketones, aldehydes, esters, or lactones and if treated with aryl cation equivalents, efficient arylations in the 2-position of such CO precursors can be achieved.[48]

Initial difficulties with attempted alkylations using lithium alkyls, when decomposition resulted in ether solvents,[49] have been overcome. Alkylations of cations in CH_2Cl_2 at low temperature give yields >80%, including t-BuLi.[20] It seems no longer necessary to use Zn or Cd reagents.[49]

The reactions of TMS enol ethers are rapid and require no catalyst. One example below is that of a model reaction being developed for aromatic analogues of prostaglandins. The 3-Me cation PF_6 **12** (R = Me) reacts with the bis-TMS ether (**65**), required in excess, followed by acid treatment, dehydrogenation with removal of $Fe(CO)_3$ to give **66**. This novel approach to 2-arylcyclopentenones, which effectively defines an equivalent of a cyclopent-2-enone 2-anion,



64



12, R = Me 65 66

depends also on the unusual ease of the dehydration possibly due to enolisation and oxyallyl cation formation.[50]

Allylsilanes or allyltin reagents also react readily, notably involving only the initial double bond terminus.[21,51]

Substitutions of a number of aromatic rings occur when these are sufficiently reactive,[52] including anilines.[23,53] This can be used as a carbazole synthesis,[23] e.g. alkylation of the unsubstituted salt **2** with *p*-toluidine gives a mixture of **67** and **68**. 3-Methylcarbazole (**69**) is obtained by oxidation of the major product (**67**).

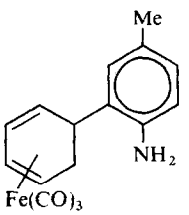
Difficulties connected with applications in synthesis

Some desirable, rather highly substituted, complexes are not readily available, either because available unconjugated dienes are isomerised to conjugated ones in unwanted directions during or before complexation, or because the required conjugated dienes themselves are not at present available. Formations of appropriately substituted cations also encounter structural limitations, for example the trityl cation does not abstract hydride from an α-alkylated position or one adjacent to it.[12,54] However, the range of methods available for cation formation includes acid-catalysed removal of α-CO_2H,[55] or of OR in consequence of migration.[35a]

Reactions do not always proceed as simple models would indicate, and effects of multiple substituents still require examination. Some obvious steric effects are observed; for example the 2-OMe cation (**11**, R = OMe) normally reacts in the 5- and not in the 1-position, but a 5-Me tends to inhibit reaction there relative to C-1 in borohydride reductions.[12] Deprotonation of an alkyl group at a terminal position of a cation is also sometimes dominant over addition,[56] yielding a conjugated triene complex.

Much further work is needed on the production, in pure form, of strategically substituted cation salts, including the use of other metals and complexing groups.

The importance of availability of optically active salts has been emphasised. These are often not readily available, but a classical resolution of the 1-CO_2H (**10**, R = CO_2H) has been achieved,[57] and presumably other acids could be resolved and the CO_2H used to lead to other substituted groups. Optically active natural dienes such as (−)phellandrene or (−)carvone can lead to optically active complexes by stereoselective isomerisations,[4] but appropriate dienes are rarely available. A very attractive method would be to have the ability to transfer $Fe(CO)_3$ chirally from an optically active donor, such as the complex of an α,β-unsaturated ketone,[58] to any unsymmetrically substituted diene, irrespective of the nature of its substituents. This method was found to be partially successful; for example the complexes of (+)-pulegone (**70**) yield an active complex (**5**)* when reacted with 1-methoxy-4-methyl-cyclohexa-1,3-diene (**4**), which has



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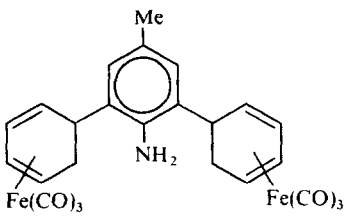

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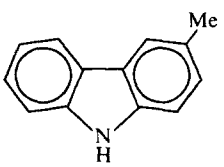

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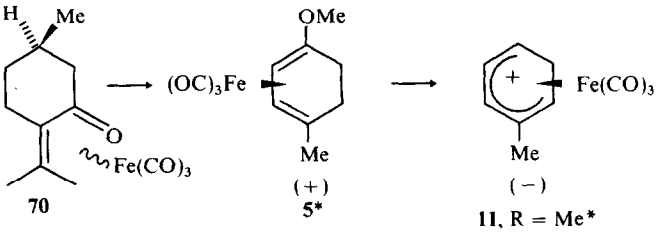

70 5* 11, R = Me*

however too low an enantiomeric excess (about 10%) to be synthetically useful, although it can be used to demonstrate absolute configurations[5] and the feasibility of enantiospecific processes. **5*** was converted to optically active 2-Me salt (**11**, R = Me)*. The $Fe(CO)_3$ complex of 16-dehydropregnenolone acetate, gives a higher excess (up to about 30%) and of the opposite absolute configuration.[58] Work is in progress to develop more specific donors.

Reactions of the optically active OMe complex with acid generate the expected[35a] cation by OMe loss, which have apparently an undiminished degree of resolution.[5]

EXPERIMENTAL

This section contains at the end some details related to the previous discussions, but its aim is chiefly to provide some characteristic experimental examples which can be more generally extrapolated. The conditions noted are good ones, without necessarily being optimal.

The examples given include the use of aromatic precursors through metal-ammonia reductions; complexation with or without isomerisation; the action of acid both as an isomerising agent and a generator of cations; the use of TMS enol ethers both in complexation and as reagents; asymmetric complexation; reactions of cations with some characteristic nucleophilic (anionoid) reagents including an aromatic amine, and the production of a *m*-substituted aryl cyclopentenone by an alkylation process.

M.p.s were determined on a Reichert hot stage apparatus and are uncorrected. IR spectra were recorded using a Pye-Unicam SP800 spectrophotometer. 100 MHz ^{1}H-NMR spectra were measured on Varian HA100 and JEOL Minimar spectrometers (Me_4Si as the internal standard). Mass spectra were measured on an A.E.I. MS902 mass spectrometer. $[\alpha]_D$ measurements were made on NPL Automatic Polarimeter 143C. Solvents used, unless otherwise stated, were reagent grade.

Metal ammonia reductions of aromatic precursors

The following is an example of the procedure which we routinely employ for reduction of a variety of aromatic substrates to yield precursors.

Anisole (216 g, 2 mol), t-BuOH (500 ml), diethyl ether (500 ml) were placed in a 5 l conical flask. About 2 l of liquid ammonia were transferred directly from an inverted cylinder into the reaction flask, which is swirled several times during the addition to mix the reactants. Li wire (*ca* 5 cm lengths) was added to the magnetically stirred mixture, as rapidly as the foaming allows, until a permanent blue colour was maintained for 30 min. About 5 g-atom of Li was usually required for the reduction. Towards the end of the reaction, the wall of the conical flask was washed with ether to return any unreacted material to the flask. MeOH (or solid NH_4Cl) was cautiously added to destroy the blue colour. The ammonia was allowed to evaporate overnight. Cold water (1 l) and petroleum ether (b.p. 30–40°, 1 l) were added to the remaining liquid. The organic phase was separated and washed with water (5 × 1 l) to remove t-BuOH and ammonia, followed by drying over anhyd. K_2CO_3. Evaporation of solvent, followed by distillation gave 1-methoxy-1,4-cyclohexadiene (176 g, 80%) b.p. 50°/35 mm (lit.[59] 40°/20 mm). Similarly 3-methyl-, 3-methoxy-, and 4-methoxyanisole gave 75–77% yields of the respective dihydroanisole derivatives.

Acid catalyzed isomerisation of kinetically to thermodynamically favoured complexes; synthesis of bicyclo-[4.3.0]nona-2,6(1)-diene

Bicyclo[4.3.0]*nona*-3,6(1)-*diene* (**32**). Indene (11.6 g, 0.10 mol) was reduced with Li (3 g, 0.43 mol) following the procedure described above to give the title product (10.9 g, 91%) as a colourless liquid b.p. 59–60°/14 mm (lit.[60] 59–59.5°/11 mm). IR (neat): 1650, 915, 660 cm^{-1}. NMR ($CDCl_3$): δ 1.67–2.53 (6 H, m, 7-H, 8-H, 9-H); 2.63 (4 H, s, 2-H, 5-H); 5.71 (2 H, s, 3-H and 4-H).

Tricarbonyl[(1,2,3,6-η)-*bicyclo*[4.3.0]*nona*-2,6(1)-*diene*]-*iron*(0) (**33**). The hydrocarbon **32** (5 g, 0.04 mol) and $Fe_2(CO)_9$ (18 g) were heated in refluxing acetone (50 ml) under N_2 for 3 hr. Cyclohexane was then added and the volume reduced to approximately 20 ml, by evaporation *in vacuo* at 25°. The residue was filtered through a short column of alumina and washed through with petroleum ether. After the solvent had been removed the residue was freed of uncomplexed material by heating to 50° at 0.1 mm for 30 min which gave pure complex **33** (3.6 g, 32%) as a yellow oil. IR (neat): 2045, 1955 cm^{-1}. NMR ($CDCl_3$): δ 1.4–2.8 (10 H, m, $-CH_2-$); 2.94 (1 H, m, 3-H); 5.27 (1 H, d, J = 7 Hz, 2-H). MS: 260 (M^+), 232, 204, 176, 174. (Found: 260.0138 (M^+). $C_{12}H_{12}FeO_3$ requires: M 260.0136.

Tricarbonyl[(1,2,5,6-η)-*bicyclo*[4.3.0]*nona*-1,5-*diene*] *iron* (0) (**34**). The complex **33** (300 mg, 1.2 mmol) was dissolved in conc H_2SO_4 (1 ml) and stirred under N_2 for 1.5 hr. A satd $NaHCO_3$aq was cautiously added to the mixture until effervescence ceased, the neutral soln was then extracted with hexane (3 × 10 ml), the extract dried over $MgSO_4$ and freed of solvent to give the complex (222 mg, 74%) as a yellow oil. IR (neat): 2040, 1955 cm^{-1}. NMR ($CDCl_3$): δ 1.36–2.92 (10 H, m, $-CH_2-$); 3.30 (2 H, broad s, 2-H, 5-H). MS: 260 (M^+), 232, 204, 176, 174. (Found: 260.0141 (M^+). $C_{12}H_{12}FeO_3$ requires: M 260.0136).

Bicyclo[4.3.0]*nona*-2,6(1)-*diene*. The Fe-complex **33** (100 mg) was added dropwise to $FeCl_3 \cdot 6H_2O$ (2 g) in acetone (5 ml) at 0° and the soln stirred for 30 min. The soln was then partitioned between ether and water, the ether phase washed with water, dried and freed of solvent to yield 37 mg (80%) of pure product. IR (neat): 3030, 2920, 2870, 2820, 1442, 1008 and 758 cm^{-1}. NMR ($CDCl_3$): δ 1.90 (2 H, tt, J = 6 Hz, 8-H); 2.08–2.56 (8 H, m, 9-H, 7-H, 5-H, 4-H); 5.59 (1 H, dt, J = 3 Hz, 10 Hz, 3-H); 5.89 (1 H, d, J = 10 Hz, 2-H). UV(hexane): λ_{max} 294 (ε 680 sh), 277 (2000 sh), 274 (2100 sh), 269 (2200 sh) and 260 nm (2000 sh). (Found: C, 89.7 H, 10.1. C_9H_{12} requires: C, 89.9 H, 10.1).

Conjugation of a 1,4- *to a* 1,3-*diene prior to complexation; an improved procedure for the synthesis of tricarbonyl* [(2,3,4,5-η)-2,4-*cyclohexadien*-1-*one*]*iron* (**61**).

1,4-Dimethoxy-1,4-cyclohexadiene (11 g) was stirred in degassed refluent $CHCl_3$ (EtOH-free, 100 ml) containing Wilkinson's catalyst (0.12 g) during 2 hr. The cooled soln was filtered through alumina and the solvent removed to leave a colourless oil (11 g) which was shown to consist of the conjugated and non-conjugated 1,4-dimethoxycyclohexadienes (ratio 3:1 respectively) together with some aromatic material (< 10%). NMR for the conjugated isomer in the mixture ($CDCl_3$): δ 2.40 (4 H, br s, 5-H, 6-H); 3.60 (6 H, s, OMe); 4.90 (2 H, s, 2-H, 3-H).

This mixture (11 g) was heated in the presence of filtered $Fe(CO)_5$ (25 ml) and di-n-butyl ether (freshly filtered through basic alumina) at a bath temp of 135–145° for 18 hr. After cooling, the soln was filtered through Celite and solvent removed, together with excess $Fe(CO)_5$, under aspirator pressure (12 mm, 70°). Chromatography on silica with petroleum ether gave a single band which was collected and distilled to give tricarbonyl[(1,2,3,4-η)-1,4-dimethoxy-1,3-cyclohexadiene]iron b.p. 90°/10^{-3} mm as a low melting solid (7.13 g, 48% based on conjugated diene). IR (CCl_4): 2055, 1960 cm^{-1}. NMR (CCl_4): δ 1.70–2.35 (4 H, m, 5-H, 6-H); 3.40 (6 H, s, OMe); 5.02 (2 H, s, 2-H, 3-H). MS: 280 (M^+) 252, 224, 196. (Found: C, 47.29 H, 4.28. Calc for $C_{11}H_{12}FeO_5$: C, 47.18 H, 4.32%).

Conc H_2SO_4 (4 ml) was poured onto the foregoing complex (1.5 g) at *ca* 0° and the resulting slurry was stirred for 1 hr. Addition of dry ether caused a gum to separate which was triturated with ether until the washings were colourless. The gum was then dissolved in water and gently warmed (50°, 0.5 hr) to hydrolyse any 1-MeO salt. Extraction with ether

followed by usual work-up gave **61** (1.2 g, 80%) identified by comparison of its spectral properties with those of the known compound.[11] Addition of NH_4PF_6 (1 g) to the aqueous washings caused a yellow solid to precipitate which was collected and readily identified as the known[59] 2-MeO cation **11** (R = OMe) (0.17 g, 8%).

Preparation of tricarbonylcyclohexadienyliron salts from unsaturated ketones via trimethylsiloxydienes; complexation and acid cleavage

Trimethylsiloxy-1,3-cyclohexadienes. These were prepared according to the procedure reported in the literature[61] except that the solvent system used was 1:1 ether/THF.

2-*Trimethylsiloxy*-1,3-*cyclohexadiene* was prepared from commercially available 2-cyclohexen-1-one in 67% yield; b.p. 55–56°/0.9 mm (lit.[61] 56–58°/6.0 mm). NMR ($CDCl_3$): δ 0.20 (9 H, s, $OSiMe_3$); 2.1–2.3 (4 H, m, $-(CH_2)_2-$); 4.8–5.0 (1 H, m, 1-H); 5.6–6.1 (2 H, m, 3-H and 4-H).

1-*Trimethylsiloxy*-1,3-*cyclohexadiene* was prepared from 3-cyclohexen-1-one[62] in 66% yield; b.p. 54–56°/0.70 mm. NMR ($CDCl_3$): δ 0.24 (9 H, s, $OSiMe_3$); 2.29 (4 H, m, $-(CH_2)_2-$); 5.15 (1 H, d, J = 5 Hz, 2-H); 5.3–5.6 (1 H, m, 4-H); 5.8–6.0 (1 H, m, 3-H). (Found: 168.0972 (M^+). $C_9H_{16}OSi$ requires: M 168.0970).

1-*Methyl*-3-*trimethylsiloxy*-1,3-*cyclohexadiene* was prepared from commercially available 3-methyl-2-cyclohexen-1-one in 80% yield; b.p. 57–59°/0.60 mm (lit.[61] 51–53°/1.0 mm). NMR ($CDCl_3$): δ 0.19 (9 H, s, $OSiMe_3$); 1.85 (3 H, s, Me); 2.0–2.4 (4 H, m, $-(CH_2)_2-$); 4.76 (1 H, m, 4-H); 5.47 (1 H, t, 2-H).

2-*Methyl*-3-*trimethylsiloxy*-1,3-*cyclohexadiene* was prepared from 2-methyl-2-cyclohexen-1-one[63] in 74% yield; b.p. 62–64°/0.74 mm. NMR ($CDCl_3$): δ 0.22 (9 H, s, $OSiMe_3$); 1.76 (3 H, broad s, Me); 2.14 (4 H, m, $-(CH_2)_2-$); 4.94 (1 H, t, J = 4 Hz, 4-H); 5.63 (1 H, m, 1-H). (Found: 182.1128 (M^+). $C_{10}H_{18}OSi$ requires: M 181.1127).

Complexation of trimethylsiloxy-1,3-cyclohexadienes. 2-Trimethylsiloxy-1,3-cyclohexadiene (2.0 g, 12 mmol) was refluxed with $Fe(CO)_5$, (3.1 ml, 24 mmol, filtered through cotton wool) in 20 ml di-n-butyl ether at 140° under argon atmosphere for 12 hr. The mixture was allowed to cool to room temp before it was filtered under argon through a pad of Celite, which was washed with ether. The very air-sensitive green to yellow solution obtained was placed under vacuum (not water aspirator) to remove the solvent. The residual greenish yellow to brown liquid was distilled to give tricarbonyl[(1,2,3,4-η)-2-trimethylsiloxy-1,3-cyclohexadiene]-iron (2.83 g, 77%); b.p. 49–52°/0.007 mm. IR (neat): 1965, 2050 cm^{-1}. NMR ($CDCl_3$): δ 0.31 (9 H, s, $OSiMe_3$); 1.3–2.1 (4 H, m, $-(CH_2)_2-$); 2.74 (1 H, dt, 4-H); 3.37 (1 H, q, 1-H); 5.22 (1 H, dd, $J_{1,3}$ = 2 Hz, $J_{3,4}$ = 7 Hz, 3-H). (Found: 308.0140 (M^+). $C_{12}H_{16}FeO_4Si$ requires: M 308.0167).

The other complexes in the series, all very air-sensitive, were prepared using the same procedure. *Tricarbonyl*-[(1,2,3,4-η)-1-*trimethylsiloxy*-1,3-*cyclohexadiene*]*iron*, yield 52%; b.p. 74–76°/0.05 mm. IR (neat): 1960, 2040 cm^{-1}. NMR ($CDCl_3$): δ 0.21 (9 H, s, $OSiMe_3$); 1.3–2.3 (4 H, m, $-(CH_2)_2-$); 2.6–3.0 (1 H, m, 4-H); 4.8–5.3 (2 H, m, 2-H and 3-H). (Found: 308.0167 (M^+). $C_{12}H_{16}FeO_4Si$ requires: M 308.0167).

Tricarbonyl[(1,2,3,4-η)-1-*methyl*-3-*trimethylsiloxy*-1,3-*cyclohexadiene*]*iron*, yield 41%; b.p. 57–59°/0.007 mm. NMR ($CDCl_3$): δ 0.20 (9 H, s, $OSiMe_3$); 1.5–2.0 (4 H, m, $-(CH_2)_2-$); 2.07 (3 H, s, Me); 2.88 (1 H, q, 4-H); 5.13 (1 H, d, 2-H). (Found: 322.0326 (M^+). $C_{13}H_{18}FeO_4Si$ requires: M 322.0323).

Tricarbonyl[(1,2,3,4-η)-2-*methyl*-3-*trimethylsioxy*-1,3-*cyclohexadiene*]*iron*, yield 28%; b.p. 55–58°/0.01 mm. NMR ($CDCl_3$): δ 0.29 (9 H, s, $OSiMe_3$); 1.3–1.7 (4 H, m, $-(CH_2)_2-$); 2.11 (3 H, s, Me); 2.69 (1 H, t, 1-H or 4-H); 3.05 (1 H, t, 1-H or 4-H). MS: 322 (M^+), 294. (Found: 294.0373 (M^+-CO). $C_{12}H_{18}FeO_3Si$ requires: M 294.0374).

Acid cleavage of tricarbonyl(trimethylsiloxycyclohexadiene)-iron complexes to form cations. The procedure used was that described below for tricarbonyl(methoxycyclohexadiene)-iron complexes. The cationic complexes, isolated as the PF_6 salts, were readily identified by their characteristic proton NMR spectra.

Tricarbonyl(2-trimethylsiloxy-1,3-cyclohexadiene)iron and tricarbonyl(1-trimethylsiloxy-1,3-cyclohexadiene)iron both gave **2** (75% in each case). Tricarbonyl(1-methyl-3-trimethylsiloxy-1,3-cyclohexadiene)iron gave **12** (R = Me) (75%). Tricarbonyl(2-methyl-3-trimethylsiloxy-1,3-cyclohexadiene)iron gave **11** (R = Me) (70%).

Preparation of tricarbonylcyclohexadienyliron salts via demethoxylation of tricarbonyl 1- and 2-methoxycyclohexadieneiron

180 ml of conc H_2SO_4 in a round-bottom flask, equipped with a magnetic bar, was cooled to 0°. 1 ml of formic acid was added dropwise to the acid. To this slightly foaming acid mixture was then added the complex **30**/**31** (R = OMe[59]) (45 g, 0.18 mol) dropwise at a rate that maintained the reaction temp below 5°. The colour of the mixture was never permitted to be darker than amber. If the colour of the mixture became too dark, addition was stopped to allow it to return to a lighter colour. The addition usually took 60–90 min. The dropping funnel and other glassware used in the transfer of the complex were washed with nitromethane, and the washings added to the mixture. Stirring was continued for another 30 min. The amber liquid was then poured into a mixture of 1 kg of ice and 60 g of NH_4PF_6 in a 2 l beaker with vigorous stirring. The residual liquid in the reaction flask was washed into the beaker with water. The yellow ppt formed was filtered, washed several times with water followed by ether. The air-dried salt was dissolved in about 300 ml nitromethane. The resultant soln was filtered directly into 1.2 l of ether. The ppt **2**, after vacuum drying, amounted to 60–62 g (92–95%).

Addition of nucleophiles to cations

Reaction of a cation with an oxygen nucleophile: Tricarbonyl[(1,2,3,4-η)-2-*methyl*-5α-(2-*propoxy*)-1,3-*cyclohexadiene*]*iron* (0) (**40**), R = Me, R^1 = O-*i*-Pr). To a stirred suspension of tricarbonyl[(1,2,3,4,5-η)-2-methyl-2,4-cyclohexadien-1-yl]iron (1 +) PF_6 (1 −) **11** (R = Me)[35a] (500 mg, 1.32 mmol) and 2-propanol (0.5 ml) in dry CH_2Cl_2 (25 ml) was added ethyldiisopropylamine (200 mg) at room temp. When a clear yellow soln was observed (*ca* 15 min), the solvent was removed under reduced pressure. The residue was extracted with petroleum ether (b.p. 30–40°), and the concentrated soln was passed through a short column of basic alumina (act. 4). Removal of solvent gave a yellow oil (297 mg, 77%). IR (neat): 2035, 1965 cm^{-1}. NMR ($CDCl_3$): δ 1.07 (6 H, two d, J = 6 Hz, diastereotopic $CHMe_2$); 1.50 (1 H, m, J = 15 Hz, 6α-H); 2.12–2.28 (4 H, m, overlapped with the singlet at δ 2.12, 6β-H, 2-Me); 2.88 (2 H, m, 1-H, 4-H); 3.53 (1 H, hept, J = 6 Hz, $CHMe_2$; 3.92 (1 H, dt, J = 10.4 Hz, 5β-H); 5.33 (1 H, d, J = 6 Hz, 3-H). (Found: 292.0343 (M^+) $C_{13}H_{16}FeO_4$ requires: M 292.0398).

Alkylation of aromatic amines; carbazole formation

Tricarbonyl [(1,2,3,4-η)-5-(2′-*amino*-5′*methylphenyl*)1,3-*cyclohexadiene*]*iron* (0). A soln of PF_6 salt **2** (1.17 g, 3.2 mmol) in MeCN (50 ml) was added dropwise to a soln of *p*-toluidine (0.75 g, 7.0 mmol) in MeCN (20 ml) at reflux over a period of 30 min. After a further 30 min the solvent was evaporated and excess *p*-toluidine removed from the residue by sublimation (45°/0.5 mm). The brown residue was extracted with boiling hexane (4 × 20 ml). The title product was obtained from the combined extracts, after concentration, as yellow needles (0.6 g, 59%), m.p. 86–87°. IR (cyclohexane): 2055, 1983 cm^{-1}. NMR ($CDCl_3$): δ 1.44 (1 H, dm, 6α-H); 2.18 (3 H, s, Me); 2.30 (1 H, dq, 6β-H); 3.12 (2 H, m, 1-H, 4-H); 3.22 (2 H, broad, NH_2); 3.31 (1 H, dt, 5β-H); 5.45 (2 H, m, 2-H, 3-H); 6.32 (1 H, d, J = 8 Hz, 3′-H); 6.66 (1 H, dd, J = 8 Hz, 2 Hz, 4′-H); 6.71 (1 H, d, J = 2 Hz, 6′-H).

MS: 325 (M^+), 297, 269, 241. (Found: C, 59.46 H, 4.88 N, 4.23. $C_{16}H_{15}FeNO_3$ requires: C, 59.10 H, 4.65 N, 4.31%). The residue was separated by prep. tlc (silica, ether/hexane, 3:7) to give the title product (0.16 g, 15%) and the double alkylation product **68** (0.68 g, 9%), m.p. 165–167°. IR (cyclohexane): 2055, 1983 cm^{-1}. NMR ($CDCl_3$): δ 1.49 (2 H, d, 6α-H); 2.17 (3 H, s, Me); 2.30 (2 H, dq, 6β-H); 3.10 (4 H, m, 1-H, 4-H); 3.24 (2 H, broad, NH_2); 3.30 (2 H, dt, 5β-H); 5.46 (4 H, m, 2-H, 3-H); 6.65 (2 H, s, aromatic protons). MS: 543 (M^+), 515, 487, 459, 431, 403, 375. (Found: C, 55.39 H, 4.03 N, 2.90. $C_{25}H_{21}Fe_2NO_6$ requires: C, 55.28 H, 3.90 N, 2.58%).

3-Methylcarbazole (**69**). I_2 (0.35 g; 2.8 mmol) was added in one portion to a soln of **67** (0.25 g, 0.8 mmol) in pyridine (5 ml). Gas was evolved. The soln was warmed to 90° and heated for 1 hr. After addition of sodium dithionite (0.1 g) to the cooled soln the suspension was poured into aq. citric acid (50 ml; 10%) and extracted with ether (4 × 20 ml). The extracts were washed with sat NaCl (20 ml) and dried over $MgSO_4$. The title product was isolated by prep. tlc (silica, ether/hexane, 1:5) as colourless plates (0.1 g, 69%). IR (mull): 3400, 807, 753, 748, 729 cm^{-1}. A sample was recrystallised from CCl_4 and sublimed (100–120°/10^{-3} mm) as plates, m.p. 206–207° (lit.[64] 207–208°). MS: 181 (M^+). UV (EtOH): λ_{max} 236 nm. (Found: C, 86.16 H, 6.22 N, 7.75. $C_{13}H_{11}N$ requires: C, 86.15 H, 6.12 N, 7.73).

Alkylation with LiR; Reaction of t-butyl lithium with tricarbonyl[(1,2,3,4,5-η)-2-methoxy-2,4-cyclohexadien-1-yl]-iron(1+) PF_6(1−) **11** (R = OMe). To a suspension of **11** (R = OMe)[59] (2.0 g, 5.08 mmol), in CH_2Cl_2 (30 ml) at −78°, was added t-BuLi (4 ml of 1.52 M soln in pentane/hexane, 20% excess) dropwise. The mixture was stirred at this temp for 1 hr, after which the cooling bath was removed and 1 ml of 2 M HCl added with stirring. On reaching room temp, the mixture was washed with dil HClaq, water and $NaHCO_3$aq. After drying over K_2CO_3, the solvent was removed. The crude product was chromatographed on basic alumina (act. 4) with petroleum ether to give 1.25 g (80%) of a yellow liquid. The NMR is consistent with the presence of a 60:40 mixture of 2 isomeric compounds, (a) tricarbonyl[(1,2,3,4-η)-5-t-butyl-2-methoxy-1,3-cyclohexadiene]iron: NMR ($CDCl_3$): δ 0.73, (9 H, s, t-Bu); 3.30 (1 H, m, 1-H); 3.61 (3 H, s, OMe); 5.17 (1 H, dd, 3-H); (b) tricarbonyl[(1,2,3,4-η)-6-t-butyl-1-methoxy-1,3-cyclohexadiene]iron: NMR ($CDCl_3$): δ 0.83, (9 H, s, t-Bu); 3.40 (3 H, s, OMe); 4.98 (1 H, dd, 3-H); 5.56 (1 H, d, 2-H). The region δ 1.12–2.80 contains a series of multiplets which integrate for 4-H, 5-H and 6-H of the two isomers. MS: 306 (M^+), 278, 250, 248, 220. (Found: 306.0552 (M^+). $C_{14}H_{18}FeO_4$ requires: M 306.0554).

Alkylation with allylsilane

A stirred mixture containing **11** (R = Me)[35a] (0.5 g) and allyltrimethylsilane (2 ml) in dry CH_2Cl_2 was refluxed in an atmosphere of N_2 during 36 hr. The clear soln was evaporated and the resulting oil chromatographed on silica with petroleum ether. Distillation of the yellow oil offered tricarbonyl [2-methyl-5-(2-propenyl)-1,3-cyclohexadiene]-iron, which according to ^1H NMR was >95% of one regioisomer, b.p. 90°/10^{-3} mm (Kugelrohr). IR (CCl_4): 2050, 1975, 1640 cm^{-1}. NMR (CCl_4): δ 1.24 (1 H, m, H-6); 1.90 (3 H, m, H-6, CH_2=CH–C$\underline{H}_2$); 2.04 (1 H, m, H-5); 2.08 (3 H, s, Me); 2.90 (2 H, m, H-1, H-4); 5.16 (1 H, dd, J = 6, 2 Hz, H-3); 5.82–4.76 (3 H, m, CH_2=CH); MS: 274 (M^+), 246, 218, 190, 188. (Found: C, 56.82 H, 5.09. $C_{15}H_{14}O_3Fe$ requires C, 56.97 H, 5.15%).

Synthetic equivalents

Formation of a 5-substituted cyclohex-2-enone; alkylation of tricarbonyl-3-methoxycyclohexadienyliron (1+). The 3-MeO cation **12** (R = OMe)[21] (2 g) was heated at 80° in EtOH (25 ml) containing cyclopentanone (3 ml). After about 0.5 hr a homogeneous soln was obtained which was then cooled, poured into water and extracted with ether. The organic phase was collected, dried ($MgSO_4$) and evaporated to leave a yellow oil. Chromatography on silica (petroleum ether/ether, 9:1) gave tricarbonyl [(1,2,3,4-η)-2-methoxy-6-(2′-oxocyclopentyl)1,3-cyclohexadiene]iron as a yellow oil (1.5 g, 90%). IR (CCl_4): 2045, 1975, 1738 cm^{-1}. NMR (CCl_4): δ 1.90–2.50 (10 H, m, cyclohexanone ring protons, 5-H, 6-H); 2.60 (1 H, m, 4-H); 3.12 ($\frac{1}{2}$H, overlapping dd, J = 4 and 2 Hz, diastereomeric 1-H); 3.35 ($\frac{1}{2}$ H, overlapping dd, J = 4 and 2 Hz, diastereomeric 1-H); 3.55 (3 H, s, OMe); 5.06 (1 H, dd, J = 6, 2 Hz, 3-H). Irradiation at δ 5.06 caused the resonances at both 3.12 and 3.35 to collapse into doublets (J = 4 Hz). MS: 332 (M^+). (Found: C, 54.14 H, 4.96. $C_{15}H_{16}FeO_5$ requires: C, 54.24 H, 4.86%).

To a stirred soln of this complex (1.3 g) in acetone at 0° was added Jones' reagent dropwise until evolution of gas ceased. The soln was poured into water and extracted with ether. After drying, the organic phase was evaporated to leave a colourless oil which was chromatographed on silica (petroleum ether/ether, 1:1) to give pure 5-(2′-oxocyclopentyl)-cyclohex-2-en-1-one as an oil (0.5 g, 57%). IR (CCl_4): 1740, 1690 cm^{-1}. NMR ($CDCl_3$): δ 1.3–2.6 (12 H, m, remaining ring protons); 5.88 (1 H, d, J = 10 Hz, 2-H); 6.84 (1 H, m, 3-H). (Found: 178.0992 (M^+). $C_{11}H_{14}O_2$ requires: M 178.0994).

Alkylation involving formation of a m-substituted 2-arylcyclopentenone; 2-(3′-methylphenyl)-1-oxo-2-cyclopentene (**66**). Compound **65**[65] (1 ml; excess) was added to a stirred suspension of **12** (R = Me)[35a] (500 mg, 1.3 mmol) in dry MeCN (4 ml) at −25°. After 15 min the solvent was evaporated. The residue was dissolved in MeOH (10 ml); conc. HCl (5 drops) was added and the soln stirred at rt for 42 hr. The mixture was poured into water (50 ml) and extracted with ether (3 × 40 ml). The extracts were combined, washed with water (3 × 40 ml) and dried over $MgSO_4$. Evaporation gave a brown gum which was eluted through a short column of alumina with $CHCl_3$. This crude material was dissolved in toluene (40 ml) and heated at reflux with 10% Pd–C (200 mg) for 60 hr. Filtration, evaporation and tlc (silica, hexane/ether, 1:1) gave **66** (64 mg, 28% based on **12** (R = Me). Recrystallisation from MeOH gave needles, m.p. 51–53°. IR (mull): 1715 cm^{-1}. NMR ($CDCl_3$): δ 2.38 (3 H, s, Me); 2.64 (4 H, m, two CH_2); 7.1–7.6 (4 H, m, aromatic H); 7.78 (1 H, t, vinyl H). MS: 172 (M^+). (Found: C, 83.37 H, 6.96. $C_{12}H_{12}O$ requires: C, 83.69 H, 7.02%).

Optically active complexes

Preparation of optically active tricarbonyl[(1,2,3,4,5-η)-2-methyl-2,4-cyclohexadien-1-yl]iron(1+) hexafluorophosphate(1−) **11** (R = Me)**1-Methoxy-4-methyl-1,3-cyclohexadiene* (**4**). 1-methoxy-4-methyl-1,4-cyclohexadiene (17 g, 0.14 mol) was heated at reflux with Wilkinson's catalyst (30 mg) in EtOH–free $CHCl_3$ (150 ml) for 3 hr. After cooling and evaporation, the residue was filtered through basic alumina with benzene. Evaporation gave a 10:3 mixture of 1,3- and 1,4-dienes as a pale yellow oil. This material was used without further purification; in the following complexation with pulegone-$Fe(CO)_3$ (**70**) allowance was made for the presence of 1,4-diene in considering the weight of 1,3-diene used.

Asymmetric complexation of 1-methoxy-4-methyl-1,3-cyclohexadiene. (+)-Pulegone ($[\alpha]_D^{20}$ + 22°) (3.7 g, 24 mmol) was added to $Fe_2(CO)_9$ (10 g, 27 mmol) suspended in degassed petroleum ether (b.p. 40–60°; 150 ml). The mixture was warmed very gently to reflux, with efficient stirring. The reaction mixture darkened to a deep red and the $Fe_2(CO)_9$ was consumed. After 5 hr, **4** (4 g, 32 mmol) was added and heating at reflux continued for 11 days; the progress of the reaction was followed by tlc (silica, benzene/hexane, 1:1). The solvent was removed on a rotary evaporator and the volatile products were distilled from the residue (30–80°/10^{-3} mm, Kugelrohr). The distillate was chromatographed in two portions on silica (benzene/hexane) and the yellow fractions combined and distilled (60°/10^{-3} mm, Kugelrohr) to give **5*** (6.71 g, 78%). ($[\alpha]_D^{20}$ + 13°, c = 9, $CHCl_3$). (Found: C, 50.06 H, 4.58. $C_{11}H_{12}FeO_4$ requires: C, 50.03 H, 4.58%).

Treatment with conc. H_2SO_4. The product **5*** (3.36 g, 12.7 mmol) was stirred at 5° with conc H_2SO_4 (2 ml). After 20 min the resulting thick paste was triturated with dry ether

(4 × 20 ml) and then dissolved in water (20 ml). NH_4PF_6 (2.1 g, 12.9 mmol) was added and the yellow ppt was collected by filtration, washed with water and ether, and air-dried. Pure **11** (R = Me)* (4.22 g, 88%) ($[\alpha]_D^{20}$ − 2.5°, *c* = 9, MeCN), obtained by reprecipitation from MeCN by addition of dry ether, was dried over KOH pellets.

Alkylation with a Cd*-derivative; optically active* (−)-*tricarbonyl*[(1,2,3,4-η)-5α-*isopropyl*-2-*methyl*-1,3-*cyclohexadiene*]*iron*(0) (**22**)*. An excess of di-isopropyl cadmium in THF was added to a stirred soln of **11** (R = Me)* ($[\alpha]_D^{20}$ − 2.5°, *c* = 9, MeCN) (0.41 g) in MeCN (4 ml) at −24°. After 7 min NH_4Claq (5 ml, 10%) was added and the THF removed on a rotary evaporator. Water (20 ml) was added, and the product was extracted with pentane (4 × 30 ml), the combined organic phases dried, concentrated and eluted through a short column of silica with hexane. Removal of solvent gave 0.23 g (76%) of a 7:3 mixture of the isomers (**22*** and **24**) which was separated by chromatography on silica/$AgNO_3$ (15%) with hexane. **22*** eluted first and was isolated as a yellow oil ($[\alpha]_D^{20}$ − 1.4°, *c* = 7, $CHCl_3$). IR (cyclohexane): 2040, 1970, 1964 cm^{-1}. NMR ($CDCl_3$): δ 0.77 (3 H, d, J = 6 Hz, Me); 0.81 (3 H, d, J = 6 Hz, Me); 1.32 (2 H, m); 1.86 (2 H, m); 2.05 (3 H, s, Me); 2.86 (1 H, dd, J = 6.3 Hz, 4-H); 2.99 (1 H, m, 1-H); 5.20 (1 H, dd, J = 6.2 Hz, 3-H) MS: 276 (M^+), 248, 220, 218. (Found: C, 56.61 H, 5.64. $C_{13}H_{16}FeO_3$ requires: C, 56.55 H, 5.84%). Further elution gave **24**. IR (cyclohexane): 2038, 1969, 1963 cm^{-1}. NMR ($CDCl_3$): δ 0.57 (3 H, d, J = 6.5 Hz, Me); 0.82 (3 H, d, J = 6.5 Hz, Me); 1.36 (1 H, m, 1′-H); 1.50 (3 H, s, Me); 1.82 (1 H, dt); 1.95 (1 H, m); 2.24 (1 H, dt); 2.86 (1 H, m, 4-H); 5.07 (1 H, m, 3-H); 5.24 (1 H, m, 2-H).

Reductions

Reduction of tricarbonyl[(1,2,3,4,5-η)-1,5-*dimethyl*-3-*methoxy*-2,4-*cyclohexadien*-1-*yl*]*iron*(1+) PF_6 (1−) (**14**). General procedure. To a magnetically stirred soln of the **14**[12] (106 mg, 0.25 mmol) in 5 ml of 2:1 THF/MeCN, at 0° under N_2, was added, by syringe, 1.0 ml of a 1 M soln of lithium triethylborohydride in THF. The mixture was stirred at 0° for 30 min, quenched by the dropwise addition of 0.6 ml water and partitioned between ether and water. The ether phase was washed well with water, dried and evaporated. Filtration of the crude product through a small amount of alumina yielded 48 mg (65%) of a 76:24 mixture of **21**[12] and the corresponding **20**.

Pure **20** could be obtained from mixtures of **20** and **21** by selective demethoxylation of **21** (conc H_2SO_4, 0°) and subsequent purification of the ether soluble residue by tlc (silica). IR (cyclohexane): 1980, 1972 cm^{-1}. NMR ($CDCl_3$): δ 1.00 (3 H, d, 5-Me); 1.24–2.32 (3 H, m, 5-H, and 6-H); 1.62 (3 H, s, 1-Me); 3.16 (1 H, t, J = 1.5 Hz, 4-H); 3.59 (3 H, s, OMe); 4.98 (1 H, s, 2-H). MS: 278 (M^+), 250, 222, 220, 182, 178, 162. (Found: 278.0246 (M^+). $C_{12}H_{14}FeO_4$ requires: M 278.0241).

Temperature dependence of $NaBH_4$ *reduction of* **11** (R = Me).[35a] $NaBH_4$ (50 mg, excess) was added in one portion to a soln of the title salt[35a] (100 mg, 0.26 mmol) in dry MeCN (3 ml) at reflux, 25°, −5° or −40°. After 20 min the mixture was filtered, evaporated, and the residue was taken up in pentane (30 ml). The soln was filtered through a small pad of alumina, washed with water (2 × 10 ml), dried over $MgSO_4$ and evaporated to give the neutral complexes (33–34 mg, 50%) as a yellow oil. The ratio of **31** (R = Me)[11,35a] and **30** (R = Me)[11,35a] was determined by glc analysis (2% OV17 on Gas Chrome Q) at 60–120°. **30** (R = Me) elutes before **31** (R = Me). Each reduction was repeated twice, and each sample was analysed twice by glc. The mean of these four values (±2–3%) is given in the theoretical section.

Alteration of reactivity of a conjugated group.

Alkaline hydrolysis of tricarbonyl[(1,2,3,4-η)-1,6-*dimethoxycarbonyl*-1,3-*cyclohexadiene*]*iron* (0) **25**, (R = Me).[32] An ice-cooled methanolic soln (30 ml) of the title diester (100 mg, 0.3 mmol) and NaOHaq (15 ml, 20%) was stirred at 5–10° for 2 hr. Water (100 ml) was added and the resulting soln was washed with petroleum ether. The aqueous soln was acidified with ice-cooled HCl (20%) and extracted with ether (4 × 25 ml). The combined ether extract was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure to give a yellow solid residue (71 mg, 74%), (**26**, R = H) which was recrystallised from chloroform/petroleum ether (b.p. 40–60°), m.p. (dec >150°). IR ($CHCl_3$): 3500–2300 (br. CO_2H); 2035, 1987, 1700 (CO) cm^{-1}. NMR ($CDCl_3$): δ 1.91 (1 H, m, 5α-H); 2.40 (1 H, m, $J_{5\alpha,5\beta}$ = 15.5 Hz, 5α-H); 3.23 (1 H, m, $J_{2,4}$ = 1 Hz, $J_{4,5\alpha}$ = 2.8 Hz, $J_{4,5\beta}$ = 15.5 Hz, 4-H); 3.46 (1 H, dd, $J_{6,5\beta}$ = 12 Hz, $J_{6,5\alpha}$ = 3.7 Hz, 6-H); 3.67 (3 H, s, CO_2Me); 5.43 (1 H, dd, $J_{3,4}$ = 4.5 Hz, $J_{3,5}$ = 0.9 Hz, 3-H); 6.21 (1 H, d, $J_{2,3}$ = 4.5 Hz, 2-H); 10.21 (1 H, s, CO_2H). MS: 322 (M^+), 294, 266, 238. (Found: C, 44.58 H, 3.33. $C_{12}H_{10}FeO_7$ requires: C, 44.75 H, 3.13%).

Tricarbonyl[(1,2,3,4-η)-5α-*carboxy*-5β-*methoxycarbonyl*-1,3-*cyclohexadiene*]*iron* (0) (**27**, R = H). An analogous treatment of **27** (R = Me)[32] (300 mg, 0.89 mmol) gave **27** (R = H) (241 mg, 84%). The title compound was crystallised from $CHCl_3$ and petroleum ether (b.p. 40–60°) as unstable yellow crystals, m.p. 98–99°. IR ($CHCl_3$): 3400–2400 (br, CO_2H); 2045, 1980, 1720 cm^{-1} (CO). NMR ($CDCl_3$): δ 2.20–2.56 (2 H, m, 6-H); 3.20 (1 H, m, 1-H); 3.32 (1 H, dd, $J_{3,4}$ = 6 Hz, $J_{2,4}$ = 2 Hz, 4-H); 3.78 (3 H, s, CO_2Me); 5.38 (2 H, m, 2-H, 3-H); 11.2 (1 H, s, CO_2H). MS: 322 (M^+), 294, 266, 238. (Found: C, 44.74 H, 3.20. $C_{12}H_{10}FeO_7$ requires: C, 44.75 H, 3.13%).

Steric hindrance of a classical reduction in the ergosterol series

Tricarbonyl(*ergosta*-3,5,7,22-*tetraen*-3-*ol*-*acetate*)*iron* (**37**). To a soln of the ergosta-3,5,7,22-tetraen-3-ol-acetate[66] (0.872 g, 2 mmol) in anhydrous benzene (15 ml) was added $Fe_3(CO)_{12}$ (2.05 g, 4 mmol) and the mixture was stirred and heated at reflux under N_2 for 20 hr. After filtration through Celite and evaporation of the solvent, the residue was chromatographed on silica (30 g). Elution with benzene/petroleum ether (1:1) removed traces of unreacted $Fe_3(CO)_{12}$. The *tricarbonyl* (*ergosta*-3,5,7,22-*tetraen*-3-*ol*-*acetate*)*iron* (**37**) was eluted with benzene and recrystallised 6-H or 7-H, 22-H, 23-H); 5.37 (1 H, d, J = 2 Hz, 4-H). UV: λ_{max} 253 (ε 2200) and 207 nm (ε 27000). (Found: C, 69.2 H, 7.7. $C_{33}H_{44}FeO_5$ requires: C, 68.8 H, 7.7%).

Tricarbonyl(*ergosta*-5,7,22-*trien*-3-*one*)*iron* (**38**). A mixture of **37** (0.576 g, 1 mmol), $KHCO_3$ (0.2 g, 2 mmol) and MeOH (20 ml) was stirred and heated at reflux under N_2 for 0.5 hr. After cooling to room temp the product was collected, washed with water/MeOH (1:1), dried *in vacuo* and recrystallised from EtOH to give bright yellow needles (0.96 g, 83%), m.p. 148–150°. IR: 2025, 1960, 1940, 1750, 1660 cm^{-1}. NMR: δ 2.07 (3 H, s); 4.96 (1 H, d, J = 4 Hz, 6-H or 7-H); 5.14 (3 H, m, 6-H or 7-H, 22-H, 23-H); 5.37 (1 H, d, J = 2 Hz, 4-H). UV: λ_{max} 253 (ε 2200) and 207 nm (ε 27000). (Found: C, 69.2 H, 7.7. $C_{33}H_{44}FeO_5$ requires: C, 68.8 H, 7.7%).

carbonyl(ergosta-5,7,22-trien-3-one)iron (0.49 g, 92%), m.p. 181–182° (in a tube sealed *in vacuo*) (lit.[39] 145–147° dec). On a Kofler block in air these crystals begin to darken at approximately 145° but do not melt. IR: 2020, 1945, 1710 cm^{-1}. NMR: δ 4.84 (1 H, d, J = 4 Hz, 6-H or 7-H); 5.16 (3 H, m, 6-H or 7-H and 22-H, 23-H). MS: 534 (M^+). UV: 240 (18300) and 213 nm (ε 20200). No max at 252 nm in $CHCl_3$ [lit.[39] UV: ($CHCl_3$) 252 nm (ε 10800)]. (Found: C, 69.4 H, 7.8. Calc for $C_{31}H_{42}FeO_4$: C, 69.7 H, 7.9%).

Reduction of tricarbonyl(*ergosta*-5,7,22-*trien*-3-*one*)*iron* **38** *to* **39**. A stirred soln of the ketone complex **38** (0.25 g) in purified THF (15 ml) under N_2, was cooled in an ice bath and treated with lithium tri-t-butoxyaluminium hydride (0.5 g). After keeping the mixture at 5° overnight it was worked up by addition of $(NH_4)_2SO_4$aq and extraction with benzene. The benzene soln was filtered through silica and the product was recrystallised from MeOH to give **39** as yellow needles (0.21 g, 84%), m.p. 124–126° (lit.[39] 120°). IR: 3610, 3560, 2020, 1945 cm^{-1}. NMR: δ 4.04 (1 H, m, 3-H); 4.80 (1 H, d, J = 4 Hz, 6-H or 7-H); 5.16 (3 H, m, 6-H or 7-H and 22-H, 23-H). MS:

536 (M^+). UV: 239 (19800) and 209 nm (ε 23700). (Found: C, 69.2 H, 8.4. Calc for $C_{31}H_{44}FeO_4$: C, 69.4 H, 8.3%). Tlc and NMR of the total reduction mixture indicated the presence of only traces of the more polar 3β-OH epimer.

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