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G. R. Stephenson, R. P. Alexander, C. Morley and P. W. Howard

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π-Complexes with planar chirality: control centres for stereoselective synthesis

By G. R. Stephenson, R. P. Alexander, C. Morley and P. W. Howard
School of Chemical Sciences, University of East Anglia, Norwich, Norfolk NR4 7TJ, U.K.

Organometallic π-complexes are defined as the synthetic equivalents of cationic synthons for use in organic synthesis. When complexes of this type are employed, activation and stereocontrol effects (which arise from properties of the metal), and regiocontrol effects and functional group locations (resulting from substitution pattern), are separated from one another. The consequences of this distinction for synthesis design are discussed by using two examples, an approach for the synthesis of tridachiapyrones based on a 'linear' synthetic sequence, and an alternative method for double alkylations employing an 'iterative' strategy. Access to resolved compounds for enantiomer synthesis is described.

Introduction

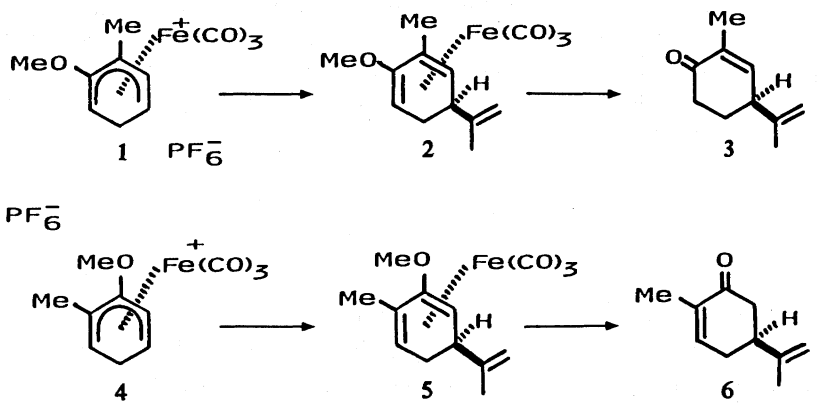
Transition metal π-complexes with planar chirality possess a number of properties that make them unusually well suited for development as intermediates in asymmetric and enantioselective synthesis (Palotai *et al.* 1987). Although frequently stable and non-hydroscopic, cationic examples are potent electrophiles, and can undergo synthetically useful alkylation reactions with a wide range of nucleophilic reagents (Birch & Kelly 1985). Our aim is to approach enantioselective synthesis by a series of alkylation reactions of resolved π-complexes that apply to the full the profound stereodirecting influence exerted by the metal over nucleophile approach. A number of observations that can be made about such reactions have implications in the design of organic syntheses in which π-complexes figure as key electrophilic intermediates. In fact, organic synthesis is planned in rather a different way in these circumstances, and one objective of our work at Norwich is to stimulate new developments in synthesis design by the investigation of methods of this type. In this paper I hope to convey an impression of the way in which these differences in planning methods arise, and to illustrate this with one example drawn from target-orientated synthetic work and a discussion of several distinct approaches to multiple alkylation sequences. Finally a method will be described that gives convenient access to resolved intermediates for enantioselective applications.

Control of reactivity

The formation of **2** from the cation **1** (Stephenson 1982*a*, *b*) provides a simple example that indicates some important and general points. As in the many cases described by Professor Pearson, nucleophile addition to **1** proceeds with complete stereocontrol, forming a new carbon–carbon bond exclusively on the face of the π-ligand opposite to that bound to the metal. This complete control of stereochemistry is particularly relevant to our requirement to employ the same metal centre to direct the formation of a series of new chiral centres. The profound

control influence of the metal is needed in these circumstances to overcome any stereodirecting effect of chirality at carbon at centres formed earlier in the synthetic sequence. Because it is required in the target molecule, chirality at other centres cannot be chosen to enforce a desirable direction of nucleophile approach as occurs. The effect of additional chirality on optical yields can be quite pronounced, as is seen, for example, in approaches to stereocontrol based on double stereodifferentiation (Masamune *et al.* 1985).

In the formation of **2**, the nucleophile reacts with the complexed π-system at the terminus that is more distant from the OMe substituent. In the cation **4**, on the other hand, the OMe group is placed at the centre of the dienyl system; nucleophile addition is now controlled by the methyl group, a less efficient control group. When assessing new situations, it is important to consider which substituents will be responsible for regiocontrol at each stage.



SCHEME 1

The diene complexes **2** and **5** can be converted into organic products **3** and **6** by oxidation and hydrolysis of the enol ether (Stephenson 1982*a*, *b*) in the usual way (scheme 1). The substituents on the organic ligands in the π-complexes are the sources of the functionality in the product, in this case, for example, the ketone groups. The reactivity properties apparent in these sequences can be conveniently summarized by the now widely used device of defining synthetic equivalents (Birch & Stephenson 1981 and references therein). The chiral 2-methylcyclohexenone cation synthon **8** has, as its equivalent, the cation **4**. Similarly, the cation **1** is the equivalent of **7**. Thus C-5 and C-4 cation synthons are available for use in identical reaction sequences. These relations are shown in figure 1. Normally one would need natural and 'umpolung' reagents for this purpose, but with organometallic π-complexes such considerations are not necessary in the design of the electrophile. The same activating and stereodirecting group can serve in either series, an advantage that leads to considerable flexibility when the metal is to be employed in series of alkylation steps. This situation arises because, although fundamental activation for nucleophile addition originates from the metal, functional group position in the product is determined by substitution patterns on the ligand. The normal relation between activation and functional group position is broken when organometallic π-complexes are used.

One final consequence of substitution pattern must be emphasized in the context of enantioselective applications. Because symmetrical intermediates must clearly be avoided, both

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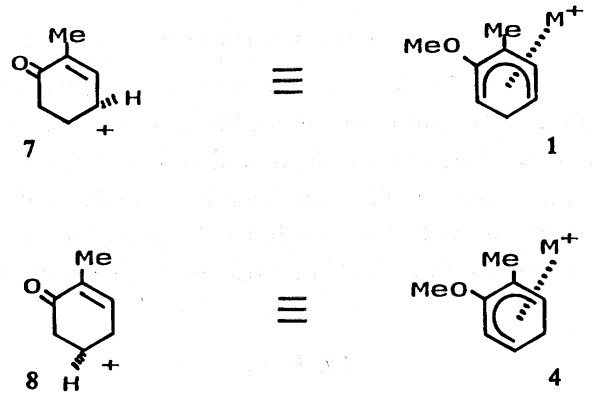
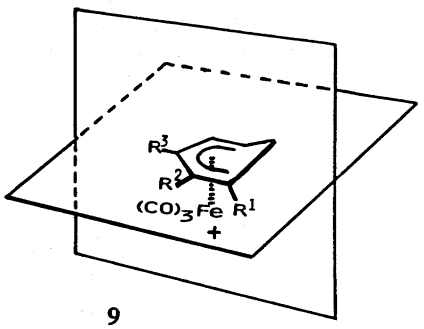


FIGURE 1

the substitution of the ligand and the location of the π-system must be appropriate throughout the synthesis. This is necessary in the intermediates themselves and also in any transient species that might be formed during reactions. Indeed, transient species, even when not participating in the main flow of the reaction, can still be significant, being responsible, if symmetrical, for gradual racemization of intermediates (Birch & Stephenson 1981). We have recently described (Palotai *et al.* 1987) the resolution of complexes chosen to illustrate the way that particular substitution patterns can be chosen to preclude the formation of symmetrical intermediates.

In overview, it is helpful to consider the division between the metal and the substituents, of responsibilities for the control of reactivity. In the general η^5 structure **9**, the metal, which sits directly below the dienyl system, distinguishes the upper and lower sides of the horizontal plane through the molecule. The metal converts prochiral ligands into chiral π-complexes and endows them with activation and stereocontrol. The substituents fulfil a quite different role. Either of the substituents R^1 and R^2 can distinguish the left- and right-hand sides of a vertical plane through the centre of the π-system. The substituents provide regiocontrol, are the sources of functional groups, and can be chosen to preclude symmetrical intermediates.

Although introduced with examples of η^5-dienyl complexes, this analysis in general to a range of π-complexes from η^2 to η^7. The benefits in synthetic applications, discussed above, will be available in all such cases, provided metal–ligand systems are able to confer chemical and optical stability. The situation is summarized in figure 2.



role of the metal
activation for bond formation
control of stereochemistry

role of the substituents
directing groups for regiocontrol
sources of functional groups
preclude symmetrical intermediates

FIGURE 2. Division of roles between the metal and substituents in electrophilic metal π-complexes from η^2 to η^7.

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Synthesis design: a worked example

Conventional synthesis design is based on an analysis of functional group position and consequent possibilities for bond-forming reactions. Because organometallic π-complexes sever the link between functionality and activation, new design criteria are more helpful when a synthetic application is contemplated. The true issue is an analysis of regiochemistry and the identification of η values for intermediates to facilitate the provision of regiocontrol throughout an extended sequence of reactions. Our work on synthetic routes to tridachiapyrones illustrates this process.

The target

The antibiotic tridachione **10**, (Faulkener 1978; Ireland *et al.* 1978) and the antileukaemic tridachiapyrones (Ksebati & Schmitz 1985), for example **11**, have a suitable degree of complexity to test our methods in their present state of development. Of particular significance is the common feature of the *cis* relative stereochemistry between two major groups, the vinyl group and the pyrone ring, located at adjacent positions on the six-membered cycloalkene ring. Our intention, by the use of transition metal complexes, is to ensure this *cis* relation by the introduction of both groups through metal-mediated alkylation reactions that use the same metal control centre. Because the metal should dominate stereocontrol in both reactions, the sequence of alkylations, if successful, would guarantee the attachment of both groups exclusively to the same face of the ring.

The analysis of regiocontrol and η^n values

This paper will examine routes to **10** and **11** via the prospective intermediate enone **12** in order to focus attention on the introduction of the two key groups, the task in this synthesis that is currently our highest priority. Introduction of part of the pyrone ring as a nucleophilic reagent requires the C-4 enone cation synthon **13**. Vinyl addition, for example by a vinyl Grignard or cuprate reagent, would require the C-5 synthon **14**. These synthons **13** and **14** are of the same general type as **7** and **8** discussed earlier, and would bear OMe groups destined to become the ketone in **12** (figure 3).

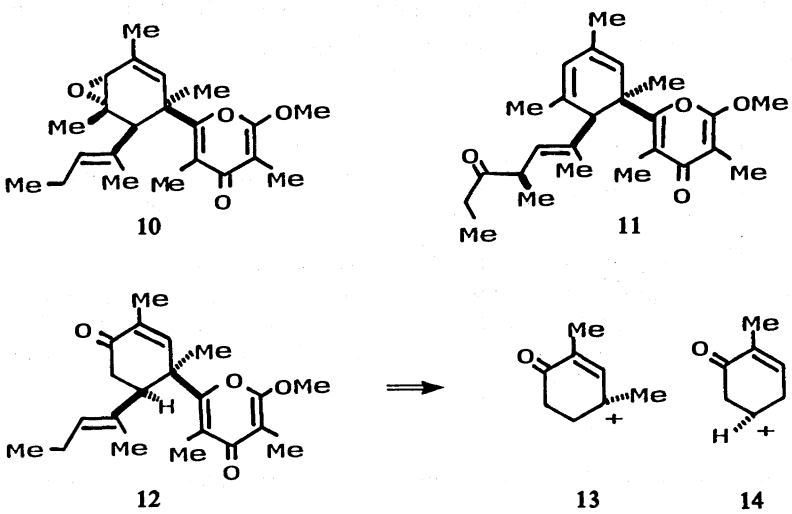

Figure 3

The complexes **15–19** (figure 4) indicate some of the possibilities for synthetic equivalents in the range η^6–η^2. The complexes **18** and **19** lack sufficiently extensive π-systems to offer direct access to enone products. Consideration of **15**, **16**, its isomer **20**, and **17**, however, makes clear the importance of the analysis of regiocontrol in the reaction sequence as a whole.

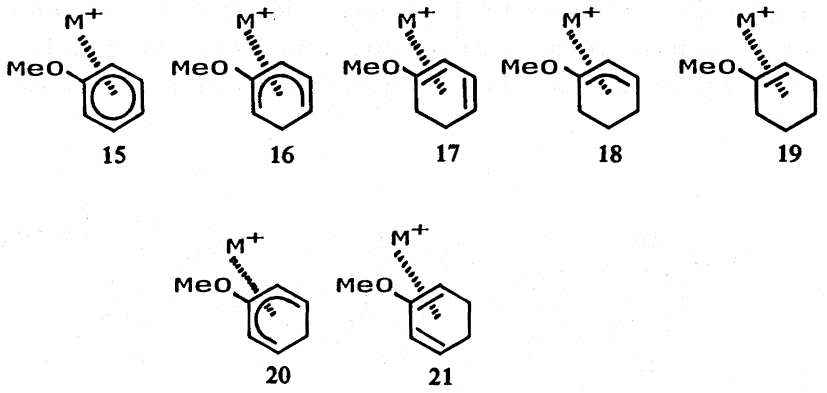

FIGURE 4

The C-5 synthon **14** demands a 1,3 relation between the OMe directing group and the site of alkylation. The arene complex **15** would provide this; anisole complexes are well known (Pauson & Segal 1975; Chung *et al.* 1982) to undergo *meta* alkylation by nucleophiles. As seen in the example of complex **4**, the 3-methoxy dienyl complex **20** would also give the 1,3 relation between oxygenation and alkylation. For access to **12** the directing group for the vinyl addition in this case would be a C-2 methyl substituent, a weak directing group.

For the C-4 synthon **14**, a 1,4 relation is required. The η^4 candidate **17** can be ruled out on regiocontrol grounds. The 1-methoxy substituent can be expected (Green *et al.* 1985) to promote *ipso* substitution. In the η^5 complex **16**, the 2-methoxy substituent will direct the nucleophile to the far terminus of the dienyl system, as was seen in the alkylation of **1**, offering a good prospect for a 1,4 product. However, 1,2-addition is possible for complexes of type **16** if steric blocking dominates at the far end of the π-system (Pearson 1978), an effect we are employing for other synthetic targets. The proposed equivalent for **13**, on the other hand, closely resembles the η^5-2-methoxy-5-methylcyclohexadienyl complex **22**, which has been extensively studied by Pearson (1977*a*, *b*) who found useful reactions with many nucleophiles, including cyanide (see below), at C-5.

There is not time, in this paper, to make a comprehensive analysis. The η^4 complex **21**, for example, could give 1,3 alkylation, although the isomer **17** was inappropriate for the 1,4 process. At this stage it is possible to identify one reasonable approach (there are others) for the use of electrophilic π-complexes to gain access to tridachiapyrones. By giving heavy emphasis to the design process, attention has been drawn to the differences between this and a more conventional organic approach. The conclusion arising from an examination of requirements for regiocontrol is that, for the construction of **12**, one appropriate sequence of reactions is C-5 alkylation followed by C-4 alkylation, effected first by the use of an η^6 electrophile and then an η^5 electrophile. In the next section some model studies are presented that probe these possibilities. Although the full reaction sequence has not yet been completed, both the required types of reaction have been achieved with substitution patterns indicated in the synthons **13** and **14**.

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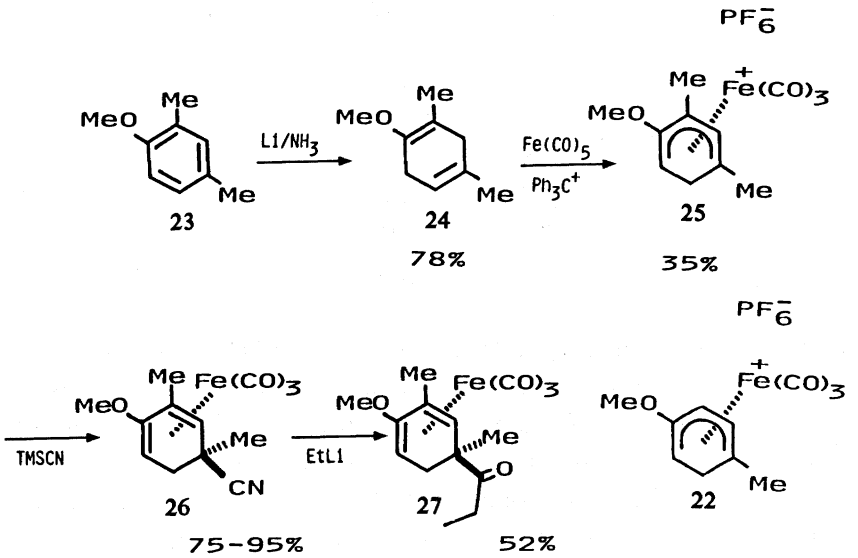
The synthetic equivalents

An organoiron complex required for **13** was prepared from 2,4-dimethylanisole **23** by Birch reduction, direct complexation with $Fe(CO)_5$, and hydride abstraction. Direct complexation of the 1,4-diene **24** ensures access to **25** without need for chromatography (Curtis *et al.* 1985); we currently prepare **25** in 15 g batches. By isomerization of **24** by the iron to form η^4-1,3-diene complexes, any isomers produced with methyl groups at sp^3 centres will have substituents directed away from the metal. This will block hydride abstraction in such cases (scheme 2).



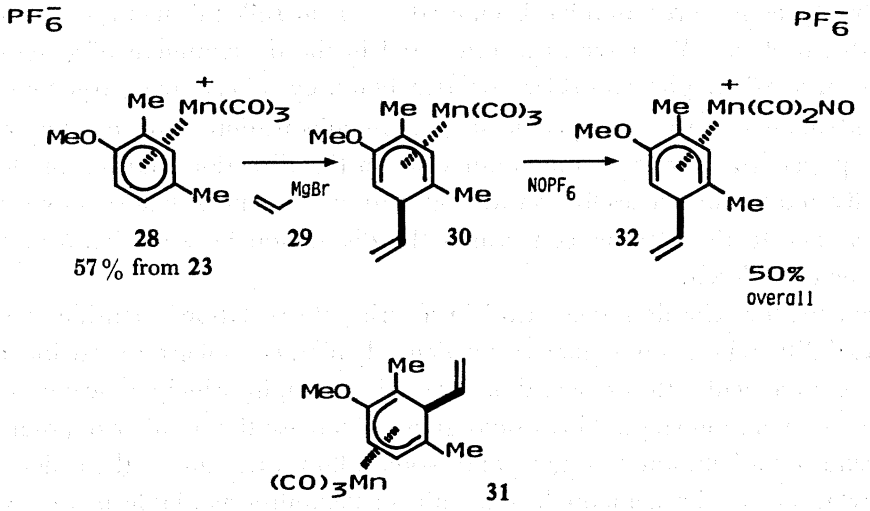
Scheme 2

Introduction of cyanide to **25** required the use of timethylsilyl cyanide (Alexander *et al.* 1987). The nitrile **26** was converted to the ethyl ketone **27**, which contains the oxygen and three of the carbon atoms for the dimethylpyrone ring.

A tricarbonylmanganese complex was chosen for the η^6 equivalent of **14**. Complexation of **23** with the general procedure of Pauson gave the new π-complex **28**, for which reaction with Grignard reagents was expected to occur at the less hindered of the carbons *meta* to the OMe group. In the event, a 4:1 mixture of **30** and **31** was produced by use of the Grignard reagent **29**. The major product **30** was purified by chromatography and converted by standard methods to the η^5 cation **32** (scheme 3) (Alexander & Stephenson 1986). We are currently investigating the elaboration of **32** into the manganese analogue of **27** that would bear both C-6 and C-5 substituents. At the present stage, however, we have successfully demonstrated both of the types of reactions required, although not yet in the same series of complexes.

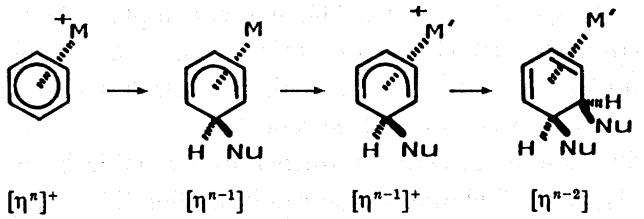
Linear and iterative routes

The approach described above will proceed from an η^6 complex to an η^4 product, forming two new chiral centres in the process. Such a sequence reduces the extent of the π-complex at each alkylation and so is clearly finite in scope (quite apart from obvious practical considerations) because eventually π-bonding to the metal will be completely consumed. This can be termed a linear reaction sequence, and is depicted in general terms in scheme 4 for



SCHEME 3

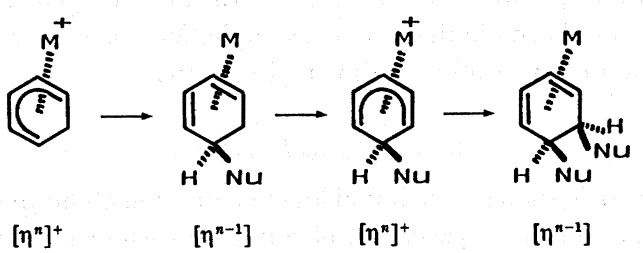
$n = 6$. Processes of this type require changes in the metal–ligand system (conversion of M to M′), for example by changing ligands as in the formation of **32**, in order to proceed from neutral to cationic complexes with the same η number. This currently imposes a severe constraint on the number of consecutive alkylation reactions that can be contemplated.



SCHEME 4. Linear reaction sequence for an η^6 complex.

An interesting alternative is available in the iterative sequence illustrated for $n = 5$ in scheme 5. Here the extent of bonding to the metal oscillates between η^n for cations and η^{n-1} for neutral complexes. This can be achieved by hydride abstraction after the alkylation step.

Examples of iterative procedures have been described, but for the extensively studied tricarbonyl(cyclohexadiene)iron complexes, hydride abstraction by triphenylcarbenium reagents is blocked once a substituent occupies the face of the ligand opposite to the metal. An



SCHEME 5. Iterative reaction sequence for an η^5 complex.

intramolecular oxygenation reaction has been used (Pearson 1980; Pearson & Chandler 1980) to overcome this problem. We have been interested in the development of general iterative sequences (Alexander & Stephenson 1987) for tricarbonyl(cyclohexadiene)iron complexes that are not dependent in this way on specific side-chain substitution patterns. The concluding sections of the paper will describe some of our work in this direction that has made available simple, optically active, complexes for iterative alkylation sequences. Before moving on to this point, however, one further matter concerning the distinction between iterative and linear routes should be considered.

The requirement for reliable regiocontrol in a series of alkylations identifies a substantial demand for flexibility in reaction sequences, particularly if functional groups are inconveniently located in a target molecule. Iterative and linear sections can, in principle, be combined in the same sequence of alkylation steps. This would greatly increase the number of potential routes through the required alkylation reactions, and would allow variation of the order of steps by which the alkylations are implemented. The gain in flexibility available in this way should greatly improve the prospects for the development of practical routes. Future work will be directed to the development of methods to link iterative and linear sequences.

Tricarbonyl(cyclohexadiene)iron complexes for iterative double alkylations

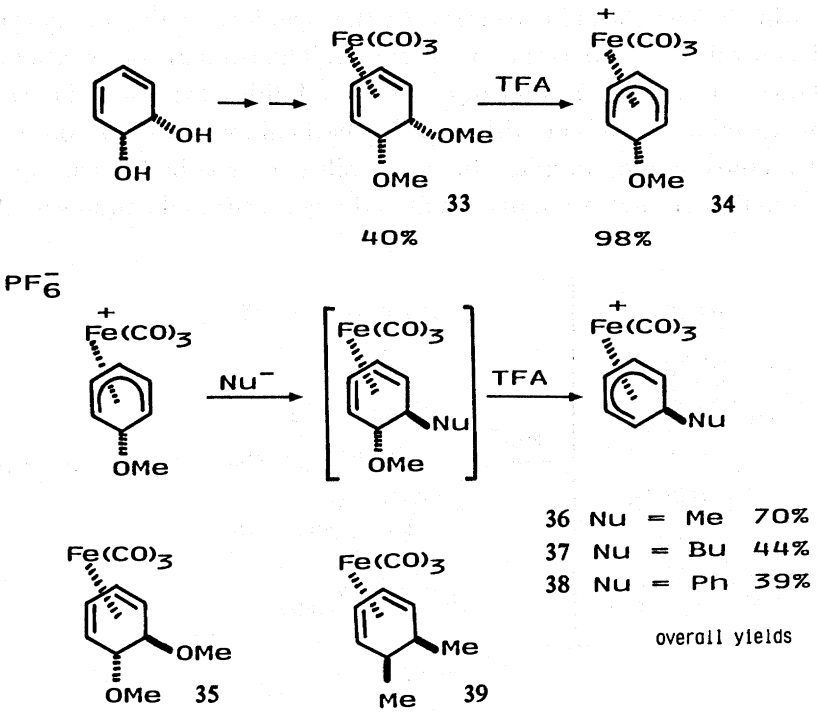
Because hydride abstraction is blocked when substituents hinder the approach of the triphenylcarbonium reagent to the allylic methylene groups, our search for iterative methods has concentrated on the use of reactions that are centred elsewhere in the molecule, and so should not be subject to the same constraints. The diether complex **33** provides a good example of this strategy. Electrophilic attack at an OMe group should effect demethoxylation, converting the η^4 complex to an η^5 cation. With two OMe groups in the molecule it is reasonable to expect that this process could be repeated.

Starting materials for these investigations are readily available by microbial oxidation of benzene (Ley *et al.* 1987) and alkylation of the resulting diol. The complex **33** was obtained by thermal complexation with $Fe_2(CO)_9$. Protonation with TFA gave the anticipated 6-methoxy complex **34** (Howard *et al.* 1988), which was precipitated from water by addition of NH_4PF_6. The stereochemistry of **34** has been determined by addition of methoxide, a reaction known (Reddy *et al.* 1980 and references therein) to proceed *trans* to the metal, to produce a new dimethoxy complex **35**. Two different OMe groups were apparent in the NMR spectrum of **35**, whereas for **34**, the OMe groups were equivalent, giving rise to a single resonance. This points to a *trans* substitution pattern in **35**, and, because the new OMe group was introduced opposite to the metal, substitution in **34** must be *endo*.

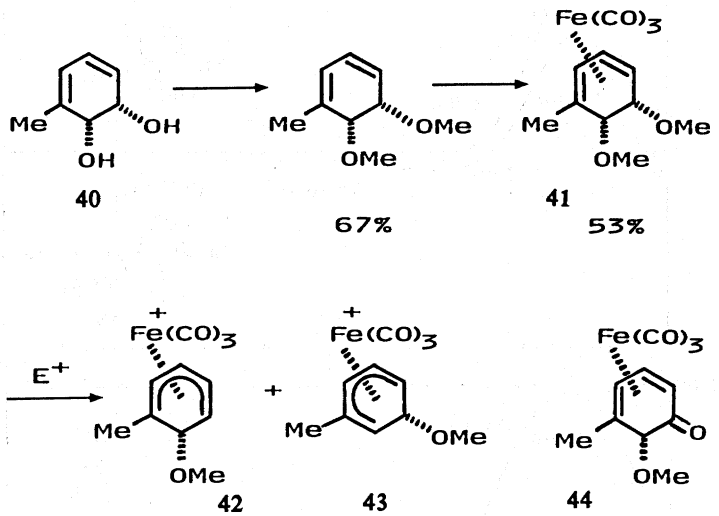
Alkylation of **34** with a range of cuprate reagents has been examined and the products were converted directly to the η^5 cations **36**, **37** and **38**. In this way (scheme 6) a series of 6-*exo* substituted complexes has been obtained. One example, **36**, has been converted in low yield to the double alkylation product **39** with dimethyl cuprate.

Access to resolved complexes

The use of microbial oxidation for the initial functionalisation of the arene offers the prospect of asymmetric induction in the oxygenation of suitable unsymmetrically substituted arenes. This has been extensively examined, for example by Gibson (Kobal *et al.* 1973) and by Ribbons



SCHEME 6

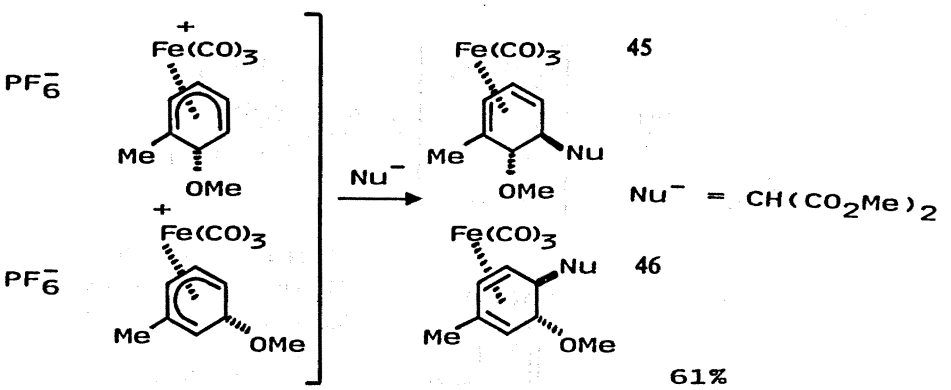


SCHEME 7

(Rossiter *et al.* 1987; Taylor *et al.* 1987), and at ICI (S. C. Taylor & A. Herbert, unpublished results).

Oxygenation of toluene affords the diol **40** ($[\alpha]_D + 73.4°$) which was converted to the dimethylether ($[\alpha]_D + 19.1°$) and complexed as before. Again, a single stereoisomer ($[\alpha]_D + 142.9°$) was produced, assigned the structure (+)-**41** on the basis of known relative

stereochemistries in the cyclohexadiene series. In the reactions of the methylcyclohexadiene complexes, regiocontrol is an important consideration. The comparison of reactions with two electrophiles shown in scheme 7 indicates that possibilities exist for the control of the demethoxylation reaction. Reaction with triphenylcarbenium tetrafluoroborate resulted in predominant demethoxylation, despite the availability of *exo* hydrogens for abstraction, although the production of small amounts of a dimethoxy substituted cation was also observed.



SCHEME 8

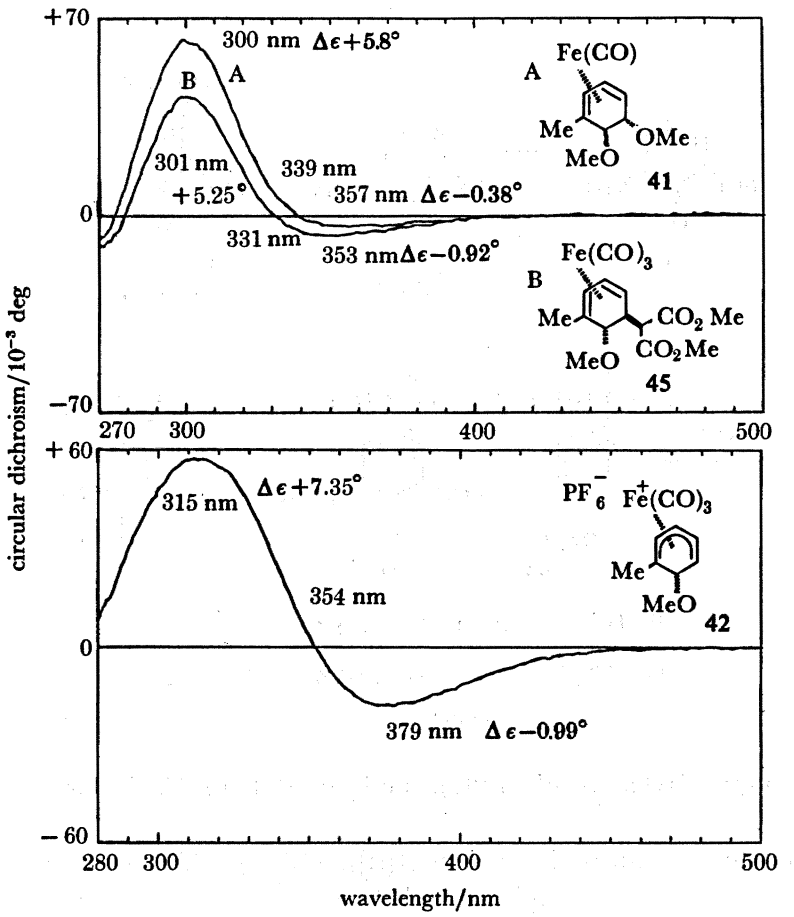
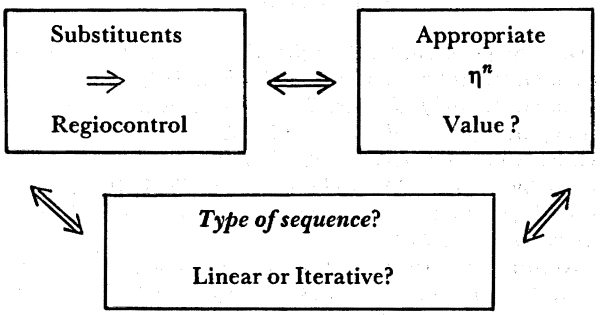


FIGURE 5. Circular dichroism spectra of some neutral and cationic organoiron complexes.

This latter complex was identified by conversion to the dienone **44** by hydrolysis. A sample of the 1-methyl cation (+)-**42** ($[\alpha]_D$ +37.8°) was obtained in *ca.* 97% purity by deprotonation with triethylamine, chromatography, and reprecipitation by protonation with TFA. This optically active cation bears a 6-*endo*-OMe substituent required for simple reformation of the η^5-cation following nucleophile addition, as demonstrated in the series of complexes derived from benzene. In this way, a suitable type of intermediate has been prepared for use in an iterative enantioselective synthesis of resolved *cis*-5,6-disubstituted cyclohexa-1,3-dienes.

Alkylation of the mixture of **42** and **43** with the sodium enolate of dimethylmalonate produced the two adducts **45** and **46**, which were separated by chromatography (scheme 8). Examination of the NMR spectrum of (−)-**45** ($[\alpha]_D$ −47.1°) in the presence of the chiral shift reagent, a general method (Stephenson 1982*a*, *b*) for measurement of optical purity of malonate derivatives of tricarbonyliron complexes, indicated that the (−)-enantiomer of **45** was present in very substantial excess. Circular dichroism spectra of (+)-**41**, (+)-**42**, and (−)-**45** are shown in figure 5. The use of microbially derived diene-diethers has, in these studies, made available simply substituted, optically pure, tricarbonyliron complexes by a transfer of chirality in the complexation process.



SCHEME 9. The choice of intermediate π-complexes.

CONCLUSION

In this paper, methods for both linear and iterative double alkylation systems have been discussed. The use of stoichiometric complexes, rather than catalytic processes, is important in this work. Catalytic reactions offer the most attractive enantioselective approach to the control of individual chiral centres, because only a catalytic quantity of a chiral auxiliary is required. With stoichiometric organometallic intermediates, however, the metal can be retained in the molecule through a series of steps. This is advantageous when control is required at several chiral centres. The complete stereocontrol of alkylation ensured by the metal control centre, is available at each stage if stoichiometric complexes are used, and should dominate stereoselectivity in the synthesis. In these circumstances, stoichiometric methods can be superior to catalytic systems, provided relatively inexpensive metals are used.

Our efforts are directed towards the fulfilment of two requirements that will allow an approach of this type to achieve its full potential. First, versatile and regiocontrolled methods are needed to develop and combine linear and iterative processes into a flexible general methodology.

Secondly, a new approach must be developed for synthesis design, and a more general

understanding of regiocontrol in alkylation reactions must be achieved. Synthetic applications of organometallic π-complexes require the identification of suitable bonding modes (η^n) and type of reaction sequence (see scheme 9) to ensure appropriate regiocontrol throughout a series of alkylations. In this way the flexibility of design, inherent in the use of electrophilic organometallic π-complexes in which the normal link between activation and functional group position is broken, can be employed in enantiomer synthesis in the most efficient way.

This paper has described some aspects of our recent work towards these objectives, which point the way for the future developments in this area, at least in our own research effort.

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