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Review

TRICARBONYLIRON METHOXYCYCLOHEXADIENE AND DIENYL COMPLEXES: PREPARATION, PROPERTIES AND APPLICATIONS

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Section A. Introduction

The aim of this review is to anticipate questions about the title series: "How do I make a given structure efficiently?" "How do I confirm this structure?" "What are its probable reactions of use in synthetic organic chemistry, and what are the reaction conditions of choice?"

The importance of the series lies in that the members are either (i) synthetic organic equivalents [1] of: chiral 4-cyclohex-2-enone cations or similar anions as noted in Section F; specific cations equivalent to specifically protonated benzenes (which however react on carbon without deprotonation); specifically substituted benzenoid cations; or else (ii) are necessary precursors of these or other equivalents (see Section E).

Section B. General considerations in preparations of specifically substituted rings

(i) Specific structures. Conjugated cyclohexa-1,3-dienes from whatever source, e.g. [2], form $Fe(CO)_3$ complexes directly, under mild conditions, with the usual $Fe(CO)_4$ donors (see (d) below). However, because of the ready availability of substituted cyclohexa-1,4-dienes, from the Birch reduction of substituted benzenes [3], these form very convenient sources. They have the great advantage that the reduction mechanism dictates the unique double bond positions (including mono- and di-enol ethers) in all series except the *ortho*-substituted one, which provides some complications [4]. The complexes can be prepared following three sequences which yield different ratios of isomeric products. The sequences are (a) conjugation followed by mild complexation (b) more drastic direct complexation which is accompanied by formation of the complexes of conjugated dienes, but not through the free 1,3-dienes [5], (c) equilibration of the complexes themselves to form more stable isomers.

(a) Conjugation, of the 1-OMe-1,4-dienes which result from Birch reductions of anisoles, can be accomplished by base [6], by catalytic transition metal complexes such as Rh derivatives [7] or Cr derivatives [8], or by using charge transfer complexes e.g. with dichloromaleic anhydride [9]. The resulting equilibrium mixtures are

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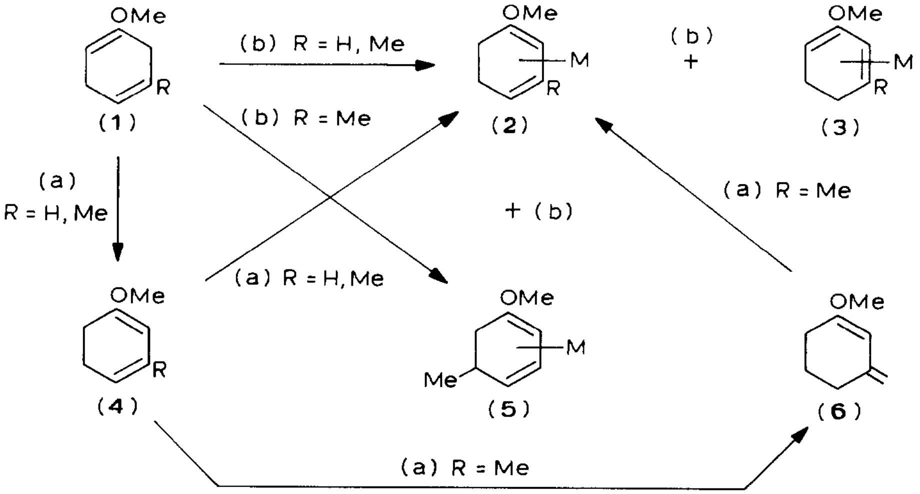
1,3-dienes (70–80%) and 1,4-dienes (20–30%). A predominantly *cisoid* mixture can undergo complexation of the 1,3-diene present under mild conditions, which accordingly defines the structure of the complex. When stable *transoid* dienes result from the conjugation process [7,9] they can be converted into complexes of *cisoid* dienes, sometimes with advantage in structural definition of a specific product, not readily available from the initial 1,4-diene.

(b) Direct complexation of the 1,4-diene, can have advantages or disadvantages. Initial π-complexation, probably with $Fe(CO)_4$, occurs before conjugation so that the products are not defined by the stabilities of the uncomplexed dienes. Also because H moves on the face occupied by the metal, any allylic alkyl group is specifically α-(*exo*) to the metal-occupied face. Isomers therefore result which are not obtainable by the first sequence, but usually in a more complex mixture, which may present separation problems. Examples are shown in Scheme 1 (M = $Fe(CO)_3$).

SCHEME 1

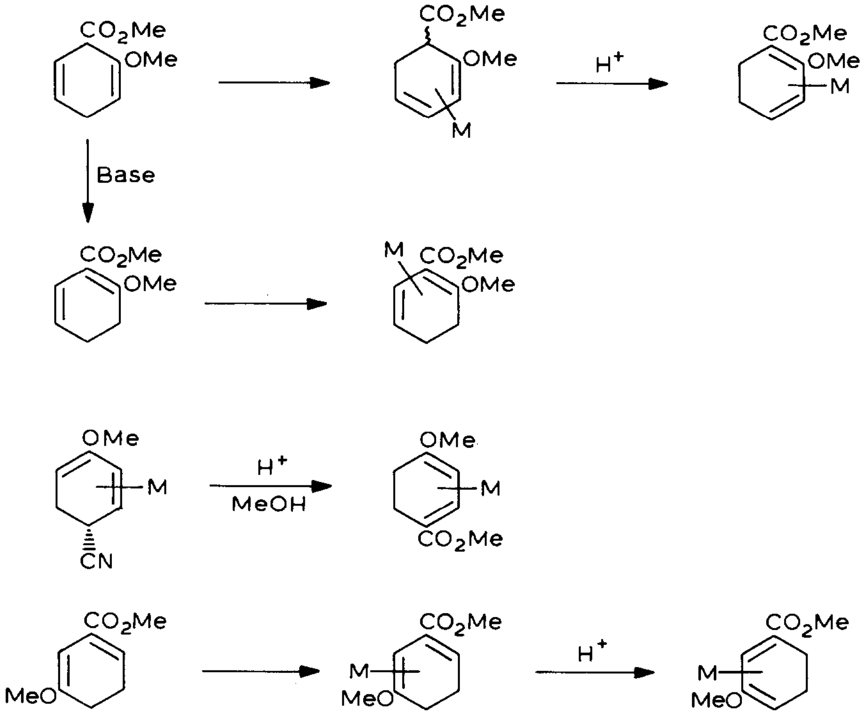


By sequence (a), **1** (R = H) gives predominantly **2** (R = H) corresponding to the stable [10] diene **4** (R = H), whereas direct complexation by contrast gives comparable mixtures of **2** (R = H) and **3** (R = H), separable by chromatography [11]. This is a useful way to make **3** (R = H) in reasonable yield for further manipulation (Section D). With **1** (R = Me) direct complexation gives a mixture of **2** (R = Me), **3** (R = Me) and **5**, which are more difficult to separate by chromatography, a process which readily distinguishes the 1-OMe from 2-OMe series, but is less successful with isomers due to Me. In this substituted diene series (and similar 3-alkyl derivatives [6]) the *cisoid* dienes such as **4** (R = Me) are subordinate at equilibria to *transoid* dienes such as **6** which can, however, readily be complexed [12] to yield mainly **2** (R = Me).

(c) The complexes may be equilibrated [13] by acids, or Lewis acids, or partially by heating, to thermodynamic mixtures of isomeric complexes, not corresponding to equilibrium mixtures of free dienes. For example, the stable conjugated uncomplexed diene in the dihydroanisole series is **4** (R = H), but the complexes **2** (R = H) or **3**, (R = H) are both equilibrated to a mixture in the ratio of about 7/4 respectively [14]. Similarly **2**, (R = Me) is converted into **3** (R = Me) [13].

Illustrative sequences [15] are shown by Scheme 2 involving OMe, CO_2Me derivatives.

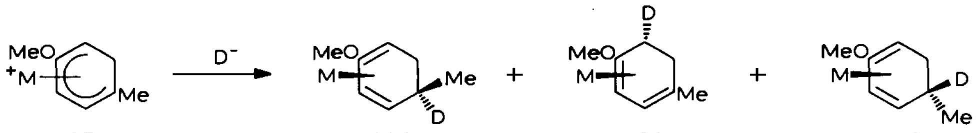
SCHEME 2



Conditions are important for equilibration of OMe complexes, since alternative processes involving OMe loss can occur (Section E).

Various other methods of converting available complexes into others can be deduced from their chemical reactions, as discussed in later sections. Notably, for example, alkylation of a cation (e.g. by LiR) introduces an allylic α(*exo*)-R, this stereoisomer being susceptible to further acid-catalysed isomerisation.

Separations of isomers can be indirect as well as direct, noting in the latter category the use of silver "doped" silica gel for some stereoisomers [16]. Indirect separation usually involves the removal of one or more components of a mixture by conversion into a cation (Section D) by specific removal of hydride by trityl cation [17]. A substituent on the face subject to abstraction tends to prevent this. For example, of the isomers **8**, **9** and **10** obtained by sterically unspecific borodeuteride reduction [18] of the cation **7** only the first two undergo deuteride abstraction, leaving the readily separable unchanged **10** required in Section E.



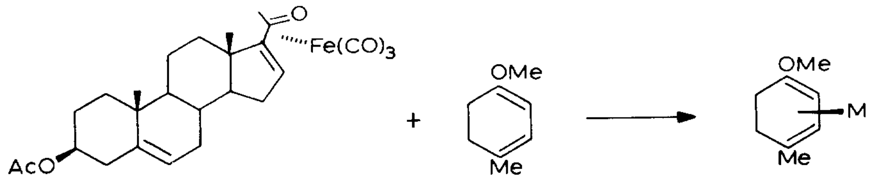
(7) (8) (9) (10)

(d) The source of $Fe(CO)_4$ for initial addition to the π-system of a double bond may be through thermal or photochemical treatment with $Fe(CO)_5$, $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$. The first carbonyl is a cheap commercial one, but is a volatile toxic liquid. It is less reactive than the other two, but under the right conditions it is a cheap and efficient source of complexes, particularly from the cyclohexa-1,4-dienes. The procedure of Cais, in boiling di-n-butyl ether [19] is basically the superior one, but requires modification in detail to obtain the best yields, and this has been described [20] for 1-methoxycyclohexa-1,4-diene. The other reagents are worth consideration, particularly for mild direct addition to *cisoid* 1,3-dienes. There is evidence [21] that reagents of the type $R_3NFe(CO)_4$ obtained by the action of amine oxides on $Fe(CO)_5$ or Fe_2CO_9 may be superior mild reagents for conjugated dienes, but further generalisation is needed.

Under correctly adjusted conditions, yields of 70–90% of total complexed product may usually be expected.

The benzylidene acetone-$Fe(CO)_3$ complex can be used to transfer $Fe(CO)_3$ [22]. It can be adapted to direct chiral donation of $Fe(CO)_3$ to a diene which has many attractions in view of the importance of chirality (Section G, H). $Fe(CO)_3$ adducts of *cisoid* α,β-unsaturated ketones [23], notably 16-dehydropregnenolone acetate react directly with 1-OMe cyclohexa-1,3-dienes to yield partially resolved complexes, but the maximum e.e. of 40–45% so far attained is unsatisfactory, and further investigation is needed to realise the full potential as part of "inorganic enzyme" [24] mediated synthesis.

A characteristic example of such a preparation is below (absolute configuration shown):



(−) (**11**)

Section C. Manipulations and physical characteristics

(a) Manipulations

The complexed group is stable to most standard organic reagents (most hydride donors; mild acids; bases; even Li, NH_3). This stability of the nucleus permits classical chemical manipulations by most standard procedures of attached functional groups. Oxidizing agents however tend to remove Fe (e.g. CrO_3, Fe^{3+}, Ce^{4+}) and may also alter the organic product. The best, mild, way to remove $Fe(CO)_3$ is with Me_3NO [25], which permits, in the 2-OMe series, isolation of a 2-methoxycyclohexa-1,3-diene, in contrast to an acidic medium, such as $FeCl_3$ in water, which produces hydrolysis to a cyclohex-2-enone.

(b) Physical characteristics

The data are of importance in defining substitution patterns, including stereochemistry (this section includes dienyl cations, see Section D).

IR: CO stretching frequencies for neutral $(OC)_3Fe(diene)$ complexes are typically found in the regions of 2070–2050 and 1990–1960 cm^{-1}; dienyl cations show $\nu(CO)$

at 2110–2090 and 2070–2040 cm^{-1}. 2-OMe complexes have a characteristic absorption at 1485 cm^{-1} [26].

UV: These spectra are not of a diagnostically useful kind in the present context. The neutral complexes exhibit λ_{max} in the region 230–240 nm, suggestive of partial de-conjugation, while the complexed dienones absorb in the range 225–240, similar to an α,β-unsaturated ketone [27].

^1H NMR: Typical ^1H NMR spectra of neutral methoxycyclohexadienetricarbonyliron are analysed in terms of (a) the position of the OMe resonance (1-OMe, ca. δ 3.4 ppm; 2-OMe ca. δ 3.6 ppm), (b) the position, number and multiplicity of "inner" diene protons (ca. δ 5.0 ppm, often first order couplings) and "outer" diene protons (ca. δ 2.8–3.4 ppm). The particular splitting patterns observed for methylene protons in 5- or 6-substituted complexes can often determine the steric orientation of that substituent [28].

First order spectra are usually observed for dienyl-$Fe(CO)_3$ cation complexes. For instance the spectrum of the unsubstituted complex shows resonances at δ 7.4 (t, H(3)); 5.9 (t, H(2,4)); 4.2 (t, H(1,5)); 3.16 (dt, H(6β)), 2.2 ppm (d, H(6α)). A methoxy in the 3-position of a cation complex is observed usually around δ 4.3, and at 3.9 ppm when in the 2-position.

^{13}C NMR: A study of substituent effects in dienyl-$Fe(CO)_3$ cation salts has been published [29]. In the neutral methoxy substituted complexes an OMe resonance is found around δ 55 ppm, but the diene-carbon resonance positions are more varied. A typical Fe–(CO) carbon resonance is around δ 210 ppm.

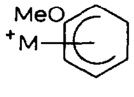
MS: Electron impact mass spectra of the neutral diene-$Fe(CO)_3$ complexes show stepwise loss of each carbonyl group followed by aromatisation. This latter process is restricted, by a factor of about 100, to loss of the β(*endo*) hydrogens (or deuteriums), so that the method can be successfully applied to the determination of levels of α(*exo*) versus β(*endo*) deuterium [30,13,18]. Mass spectra of the less volatile dienyl-$Fe(CO)_3$ cation salts has been little studied. New techniques may alter this situation.

X-ray structures have in some instances defined exact bond lengths [31].

Section D. Tricarbonylcyclohexadienyliron cations

Formations and synthetic reactions

The uncharged complexes undergo some direct reactions with a limited range of nucleophiles [32]. Electrophiles react much more readily, importantly in the context H^+ or D^+, discussed in Section G. The most important synthetic intermediates are, however, tricarbonylcyclohexadienyliron cations used as the BF_4 or PF_6 salts. Such compounds are available directly or indirectly from the OMe substituted uncharged complexes. The important synthetic organic equivalents of the 2-OMe (**12**) and 3-OMe (**13**, R = H) series are discussed in Section H. The 1-OMe cation series is unstable to hydroxylic solvents, notably water, and is converted into the cyclohexadienone series (**14**), itself of considerable synthetic importance as an equivalent of an aryl cation (**15**) [33] or by borohydride reduction or reaction with LiR, followed by acid, as indicated, as another source of substituted cations [34].



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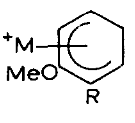

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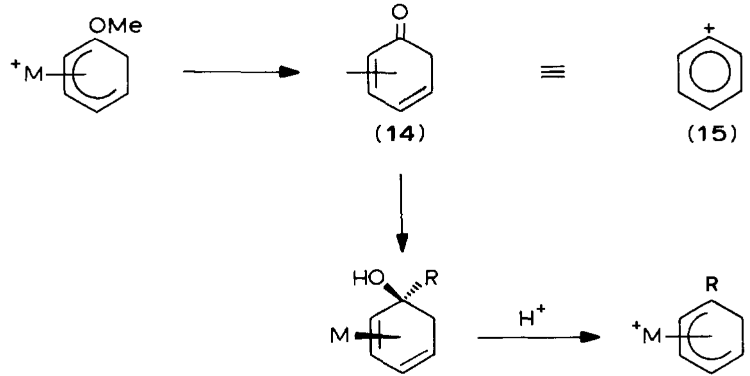


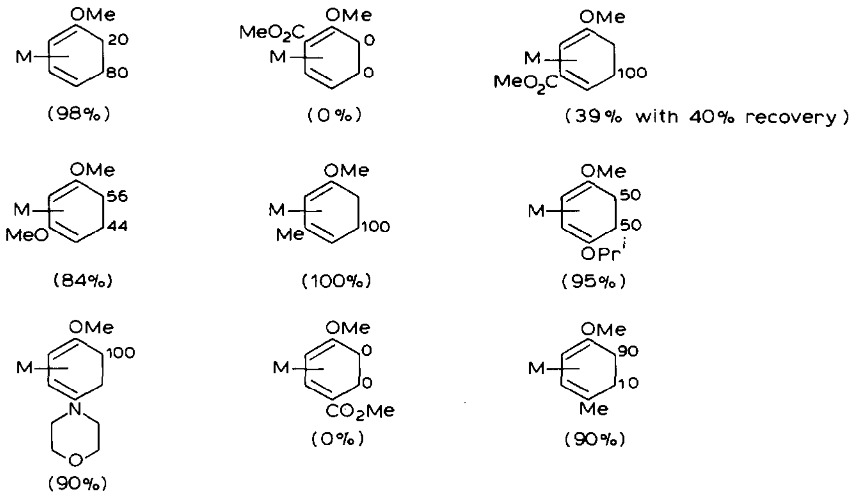
(14) (15)

Hydride abstractions

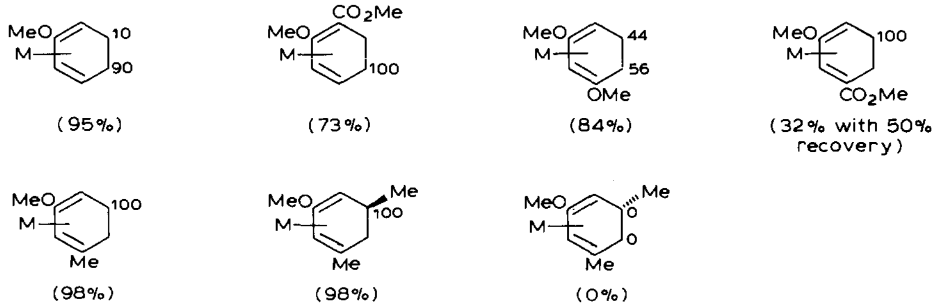
Reaction of uncharged complexes with Ph_3C^+ leads, in favourable structures, to α(*exo*)-stereospecific abstraction of hydride [11,17]. The positions of abstraction, in a OMe series, is controlled in a manner which cannot be at present fully rationalised, although both steric and electronic effects must be involved [35]. Some key results are [11,15,36]:

α-Hydride abstractions from some methoxy complexes. Relative amounts of hydride loss at alternative positions are indicated; total yields are given in parentheses.

1-OMe



2-OMe



Considerable position specificity with the 1-OMe and 2-OMe cases tends to show that in the absence of major steric factors the predominant product is the more stable one (1-OMe and 2-OMe cation, respectively). Likewise, in competition between OMe and NR_2, the latter forms the terminus of the cationic.system. The transition state may therefore resemble the product. The electron-attracting CO_2Me is inhibitory, although the 1-CO_2Me diene complex undergoes abstraction from the 5-position [37]. Because of the bulky nature of the trityl cation steric hindrance is frequently observed: any α(*exo*) substituent adjacent to a position from which hydride needs to be removed tends to inhibit this (see however ref. 38). The steric specificity has advantages in selectivity in some instances, but severe drawbacks also in preventing formation of some desired cations. Other equivalent reagents are needed with less steric demand. Tl^{3+} gives cations via electrophilic attack, then rearrangement and replacement with solvent OMe. Acid treatment then gives the cation. MnO_2 (which probably oxidises through the Fe[39]) and also $FeCl_3$ under some conditions [40] on some 5-functionalised complexes leads to products which can be converted into some cations [41].

Since acids, including HBF_4, may isomerise neutral complexes, cations resulting in its presence may not correspond structurally to the initial neutral complex. To avoid this, the fresh trityl salt (BF_4^- or PF_6^-) in CH_2Cl_2 should be shaken with anhydrous potassium carbonate and filtered before use. It is also advisable to check product structure by ^1H NMR.

Although the 1-OMe and 2-OMe complexes each undergo rather selective abstraction, to optimise the yield of a desired 2-OMe cation salt, separation of the mixture obtained from the 1,4-diene is not desirable. If worked-up in the presence of water, the alternative 1-OMe salt in the mixed product is hydrolysed to the uncharged cyclohexadienone complex, which is completely separable with ease from the salt [20].

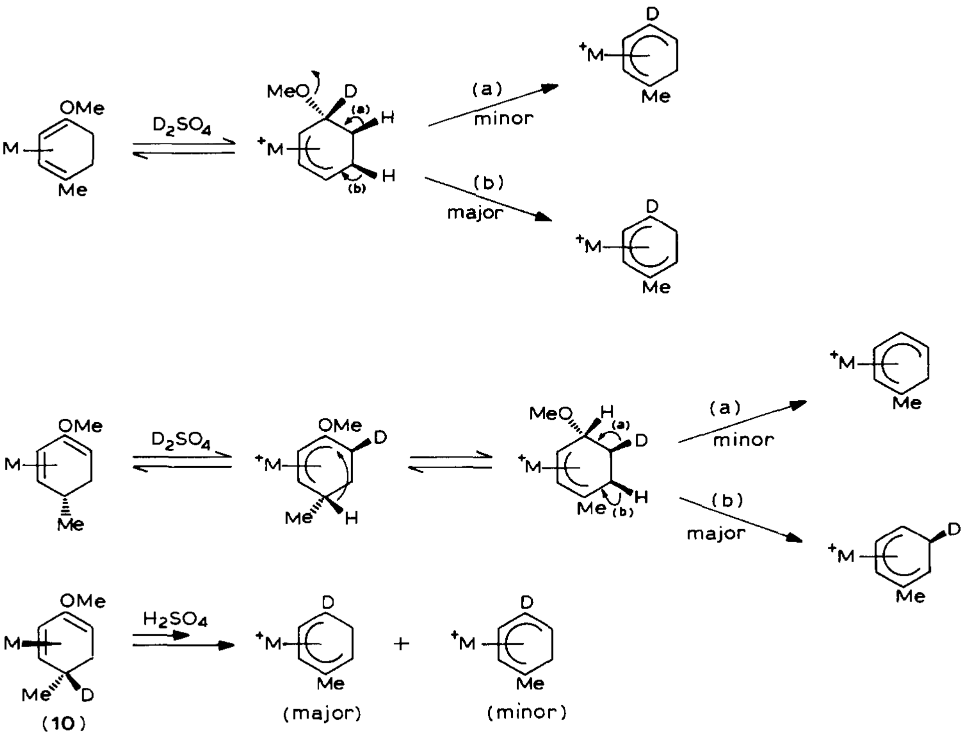
Section E. Removal of OMe or similar groups

Alternative method of cation formation

Uncharged complexes undergo completely stereospecific β(*endo*) reaction with protons, which can be demonstrated by the use of D^+ [42], accompanied by migration of the complexed system to give the most stable isomer [43]. Such isomerisations can be demonstrated in the MeO series as noted (Section B) under mild conditions, including deuterations. With H_2SO_4 (conc.) or TFA the protonation processes culminate in OMe loss to generate a cationic complex. Initially [43] it was thought that with H_2SO_4 only one cation results from the 1-OMe or 2-OMe series, the mesomeric complexed carbon system in the product terminating on the carbon initially carrying OMe. Later [13] it was found that a minor component with H_2SO_4 as reagent has this sytem terminating at a carbon adjacent to the original OMe position. Using D_2SO_4 or H_2SO_4 on a deuterated precursor to elucidate the course of additions, the following sequences are suggested (Scheme 3).

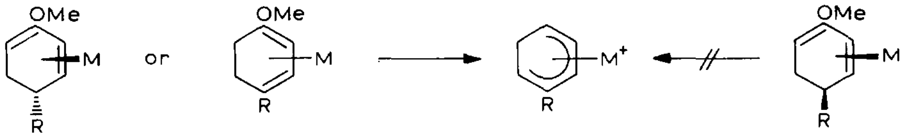
Later work [13,36], with TFA, gave a much more uniform cationic product in the simple OMe cases than with H_2SO_4, but the processes still need further examination over a range of structures. It is clear from the D-labelling results, for example, that equilibration occurs only to a minor extent with H_2SO_4, but is likely to be a major factor with TFA. The cation may then correspond to the more stable uncharged

SCHEME 3

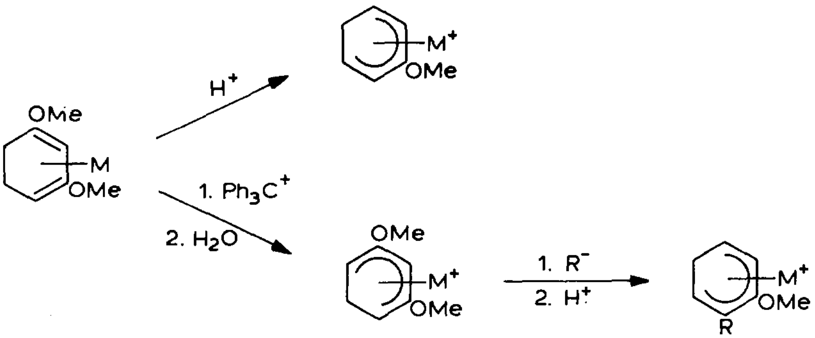


isomer, rather than to the actual starting complex used, a matter of importance when other substituents are unsymmetrically placed relative to OMe. The process does not work if there is a *β*(*endo*) alkyl group which blocks the necessary migration of H in the complexed system (see below).

With many complexes the 1-OMe and 2-OMe give the same product (except with deutero-acid) so that separation of the isomers from complexation is not necessary, e.g.:

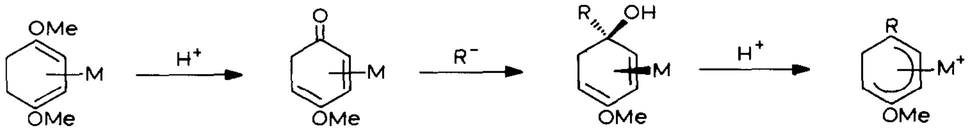


With 1,3-dimethoxy complexes, the resulting cations contain one OMe, and this is a good route to their formation in some cases [36]. It is necessary to carry out conjugation of the 1,3-dimethoxy-1,4-dihydrobenzene before complexing, otherwise OMe is largely lost during reaction with $Fe(CO)_5$. Examples of preparation of potentially useful [36,44] cations are:



The 1,4-dimethoxy-series also requires preliminary conjugation, but the complex behaves differently, acid giving the methoxydienone **15** [13,36] also of interest as a potential source of methoxy substituted cations as shown.

Other methods of cation formation, such as protonation of an exocyclic double bond in a complexed triene [45], or migration of a cationic charge from a side-chain [46], have potential applicability, but have not been fully examined in the OMe series.



(15)

Section F

(a) Nucleophilic reactions of the complexed cations

Reactions of the cations occur with a virtually unlimited range of nucleophiles, e.g. borohydride [47], amines [11,27,48], various oxygen and sulphur anions [11,27,49], phosphorus derivatives [49,50], enol silyl ethers [51] and a range of carbanions like those from LiR [52], alkyl-cadmium and -zinc compounds [53], $NaCH(CO_2Me)_2$ [27,54] etc. Direct reaction occurs with ketones through in situ enolisation [11]. This wide range contrasts favourably with a number of other useful organometallic reagents in which reactivity is conferred by a laterally attached complexed metal atom, such as the uncharged aryl-chromiums and the diene-$Fe(CO)_3$ complexes, where reactions are limited to anionoid reagents which are strong bases. A drawback in the present series is, however, the ease of removal of the nucleophile in some instances, to regenerate the cation even with breakage of a C–C bond [11].

Exact experimental conditions are notably important for good yields, including the presence of antioxidants [34] and the use of CH_2Cl_2 as solvent for alkylations [52].

Reaction occurs only at the termini of the carbon system, in contrast to similar complexes of some other metals [55], regiospecificity being determined by the nature of the substitution: 2-OMe, 2-Me and 1-CO_2Me react predominantly at position 5. Substitution affects rates [56], qualitatively in an additive manner with several substituents. Relative to the unsubstituted the rates are: 2-OMe, 0.1; 2,4-$(OMe)_2$, 0.01; 1-CO_2Me, 12; 1-CO_2Me-2-OMe, 1.6.

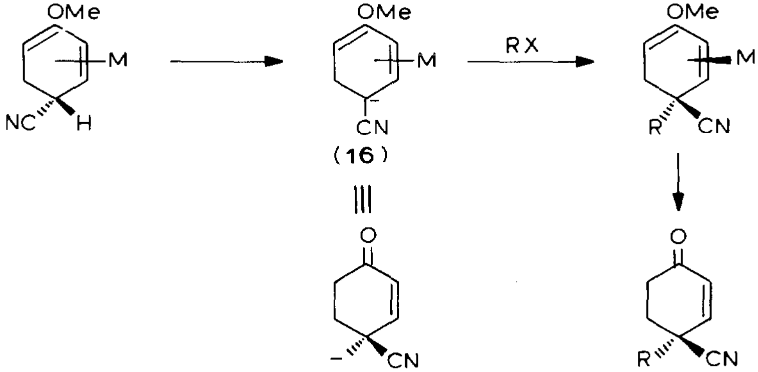
The nature of the nucleophile has an effect on regiospecificity which cannot be primarily steric, since ᵗBuLi [52] reacts to some 40% in the 1-position of the 2-OMe cation adjacent to the substituent, in contrast to MeLi where only the remote C(5) is attacked. More work is needed on methods for control of regiospecificity, notably in the 2-alkyl series [18].

(b) Related electrophilic reactions

One method of attaining regiospecificity is to make use of that of a very regiospecific anion such as CN^-. Formation of **16** can then be utilised [57] as shown to introduce regiospecifically other substituents, at the same time extending the range of synthetic capabilities by (i) reversal of the polarity of the C–C bond-forming reaction compared with the cation and (ii) leading readily to the formation of a quaternary carbon atom. The effects of $Fe(CO)_3$ on stereochemistry and chirality are identical with those in the cation series.

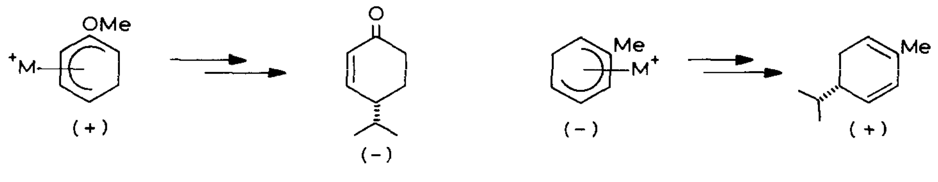
The anion **16** is synthetically equivalent to the chiral cyclohex-2-enone 4-anion, of which the absolute configuration can be defined by that of the initial carbenium complex. The functions of the CN can be performed by groups such as SO_2Ar or CO_2Me [57] (Scheme 4).

SCHEME 4

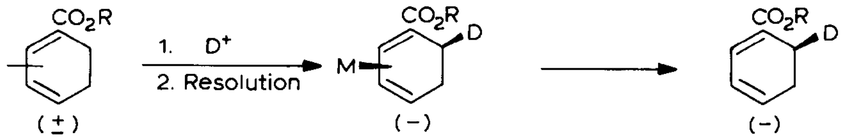


Section G. Optically active complexes

Kinetic resolution of the 2-OMe cation by partial reaction with a chiral nucleophile provided the first [51], but not very useful example. Other kinetic resolutions have been reported [58]. Resolved cations can be obtained from chiral neutral complexes. The cationic reactivity represents a useful functional group, and a practical resolution of the 2-OMe series can be achieved by separation of the diastereomers resulting from reaction with (−)-menthol [59]. Crystallisation of a partially resolved salt may give fully resolved material [60]. Absolute configurations are determined by stereospecific conversion into a compound with a configurationally known carbon centre [23].



Enantiospecific deuterations can be achieved either on the β(*endo*)-face by stereospecific incorporation through D^+ in a resolvable uncharged complex [61], or on the α(*exo*)-face by BD_4^- reduction of cations. Examples of optical activity due to D versus H (full resolution, known absolute configuration) are:

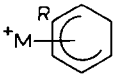
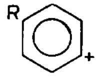
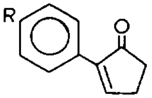
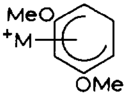
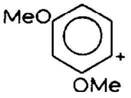
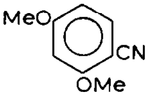
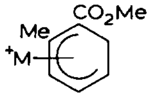
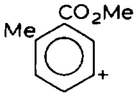
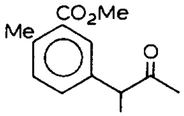
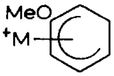
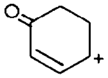
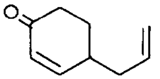
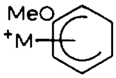
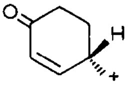
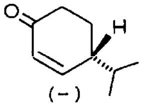
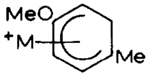
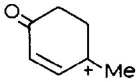
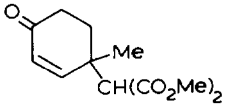
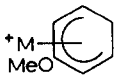
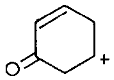
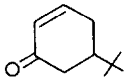
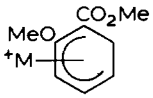
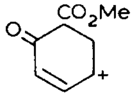
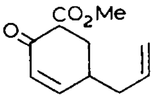
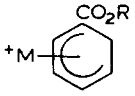
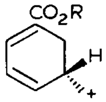
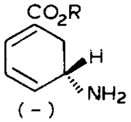
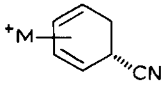
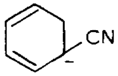
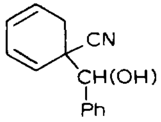


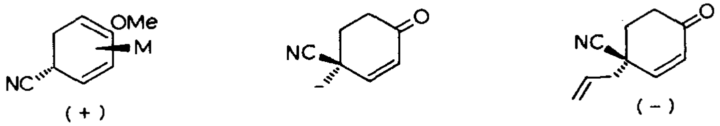
Section H. Synthetic applications

The availability of specifically substituted benzenoid compounds, and the complexation sequences outlined make available a wide range of neutral and cationic complexes. The usefulness of these can be expressed in the form of synthetic organic equivalents [1]. The metal atom confers steric and enantiomeric control (any unsymmetrical olefin gives a chiral complex) and superimposes new forms of reactivity (e.g. carbocations). The $Fe(CO)_3$ can be removed under mild neutral to basic conditions with Me_3NO. Lateral control of bond-formation processes confers the advantage that organic structures can be related more directly to those desired in the final structure, not principally to those needed to produce new bonds. Included in this is an ability to form quaternary carbons, regio- and enantio-specifically. The complexation also "stores" reactive structures (e.g. cyclohex-2-enone) while classical reactions are carried out elsewhere in the molecule. The structural remnant of the removal of the metal is typically unsaturation, which may be desirable or can be dealt with. The range of nucleophiles capable of reacting with the cations seems virtually unlimited.

Some present disadvantages relate to problems connected with making some specifically substituted complexes (particularly at an advanced stage of a synthesis when losses are not acceptable), some lack of complete regiospecificity in some 2-substituted cations with some nucleophiles, and occasional unwelcome competing reactions, e.g. proton elimination from a 1-alkyl cation instead of addition of a nucleophile.

The formulae below indicate a few important organic synthetic equivalents, but for growing applications the literature needs to be consulted [62]. We note that the broad principles examined, for instance the conferral of asymmetry to an unsymmetrical olefin, apply through a wide field of organometallic complexes, and a major aim of the present work has been to exemplify the benefits of the idea of lateral control [1] in bond-formations for organic synthetic purposes.

Complex	Equivalent	Example	Reference
(a) Cations			
 (R = H, Me, MeO)			63
			36
			51
			51
 (+)		 (−)	16, 59
			62
			64
			44
 (−)		 (−)	61
(b) Anions			
			44



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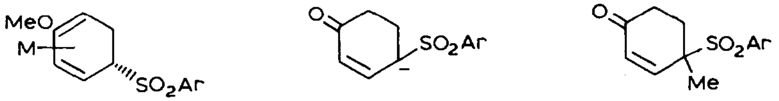

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