sed *si* face at C-4′ of PLP–substrate imines and the similarity of conformational changes upon substrate binding document the relatedness of these proteins but offer no obvious catalytic advantage. Examination of the cryptic stereochemistry of their reactions has given a conformational picture of the PLP–substrate complexes in the active sites and provided insight into mechanistic aspects, especially intramolecular proton transfers. With the exception of racemases,[64] PLP enzymes generally force retention modes of operation at the α and β carbons of substrates for processes as diverse as transamination, decarboxylation, retroaldolization, β replacement, α,β elimination, and β,γ elimination.[65] This allows in many cases the mediation of multiple proton transfers in a catalytic cycle by a single base; internal proton recycling can then reduce the number of diffusion-controlled steps. This bias favors similar conformations for the bound coenzyme–substrate complexes in the active sites of many of these enzymes. Predominantly, reactions seem to occur on only one side of the enzyme-bound substrate–cofactor complex. Work is already in progress in several laboratories to determine how α-racemases, ω-aminotransferases,[66] enzymes operating on D-amino acids, and the "anomalous" reactions of serine transhydroxymethylase fit into this concept and the single progenitor hypothesis.

Work from our laboratories was supported by the U.S. Public Health Service (NIH Research Grant GM 18852) and by the Natural Sciences and Engineering Council of Canada (NSERC A0845). We especially wish to thank our enthusiastic and capable co-workers whose names appear in the references.

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Tricarbonyl(diene)iron Complexes: Synthetically Useful Properties

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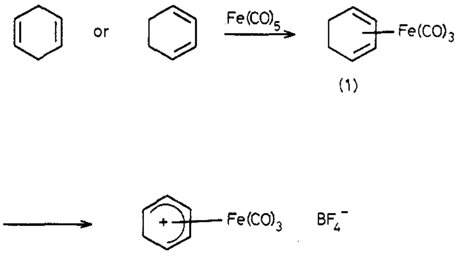
Synthetic application of organometallic complexes is both an exciting and a challenging area of research: exciting because of the enormous areas of chemistry still awaiting exploration, and challenging because, to a large extent, the behavior of such complexes has still to be put on a firm mechanistic basis. While not forgetting some of the earlier pioneering work of Pettit, Lillya, Whitesides, Lewis,[1] and Birch (references) this account mainly concentrates on our own efforts to develop reactions of tricarbonyl(diene)iron complexes which may be applied to the synthesis of fairly complex natural products. Although most of our targets are still far from being realized, we hope to convey the considerable potential of these compounds.

Synthesis of Tricarbonylcyclohexadienyliron Salts

Reaction of either cyclohexa-1,4-diene or cyclohexa-1,3-diene with pentacarbonyliron gives tricarbonyl(cyclohexa-1,3-diene)iron (1) in moderate yield.[2] This complex undergoes hydride abstraction by treatment with triphenylmethyl (trityl) tetrafluoroborate in dichloromethane to give tricarbonylcyclohexadienyliron tetrafluoroborate (2), precipitated quantitatively by addition of diethyl ether.[3] Birch et al. have studied complex formation between pentacarbonyliron and substituted cyclohexa-1,4-dienes, readily available by metal–ammonia reduction of aromatic compounds.



(2)

Predictably, this reaction results in the formation of mixtures, since the 1,4-diene can be conjugated in two or more ways. Examples which concern us are the complexes (3 and 4) derived from 2,5-dihydroanisole, and (5 and 6) from 4-methyl-2,5-dihydroanisole.[4]

Anthony J. Pearson is currently recipient of a Science Research Council Advanced Fellowship at the University of Cambridge. After undergraduate studies at Leeds University and postgraduate research at Aston University, he spent 3 postdoctoral years with A. J. Birch in Canberra.

(1) See, for example: J. E. Mahler and R. Pettit, *J. Am. Chem. Soc.*, **85**, 3955 (1963); G. F. Emerson, L. Watts and R. Pettit, *ibid.*, **87**, 131 (1965); G. F. Emerson and R. Pettit, *ibid.*, **84**, 4591 (1962); G. F. Emerson, J. E. Mahler, and R. Pettit, *Chem. Ind.* (*London*), 836 (1964); R. Pettit and J. Henery, *Org. Synth.*, **50**, 21 (1970); R. Pettit, J. C. Barborak, and L. Watts, *J. Am. Chem. Soc.*, **88**, 1328 (1966); C. P. Lillya and R. A. Sahatjian, *J. Organometal. Chem.*, **32**, 371 (1971); R. E. Graf and C. P. Lillya, *J. Am. Chem. Soc.*, **94**, 8282 (1972); *J. Organometal. Chem.*, **47**, 413 (1973); *J. Chem. Soc., Chem. Commun.*, 271 (1973); *J. Organometal. Chem.*, **122**, 377 (1976); T. H. Whitesides and R. W. Arhart, *J. Am. Chem. Soc.*, **93**, 5296 (1971); T. H. Whitesides, R. W. Arhart, and R. W. Slaven, *ibid.*, **95**, 5792 (1973); T. H. Whitesides and J. P. Neilan, *ibid.*, **95**, 5811 (1973); **98**, 63 (1976); T. H. Whitesides and R. W. Slaven, *J. Organometal. Chem.*, **67**, 99 (1974); B. F. G. Johnson, K. D. Karlin, and J. Lewis, *ibid.*, **145**, C23 (1978); and references cited therein.
(2) B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 642 (1958).
(3) E. O. Fischer and R. D. Fischer, *Angew. Chem.*, **72**, 919 (1960).
(4) (a) A. J. Birch, P. E. Cross, J. Lewis, and D. A. White, *Chem. Ind.* (*London*), 838 (1964); (b) A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc. A*, 332 (1968); (c) A. J. Birch, K. B. Chamberlain, M. A. Haas, and D. J. Thompson, *J. Chem. Soc., Perkin Trans. 1*, 1882 (1973).

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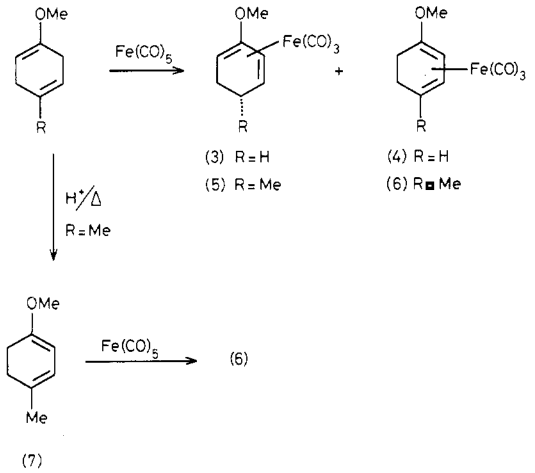
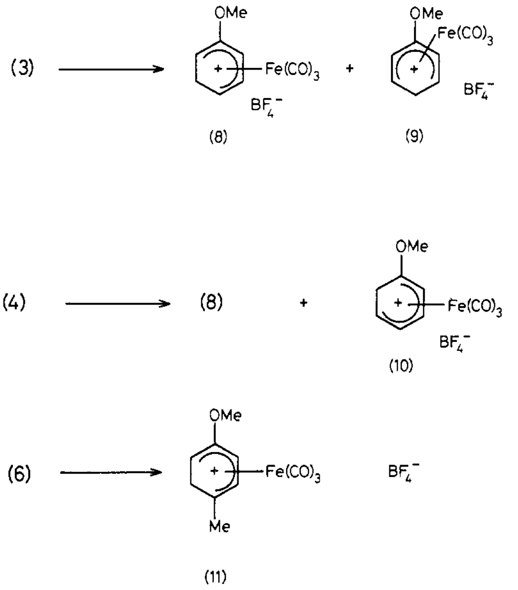
Scheme I

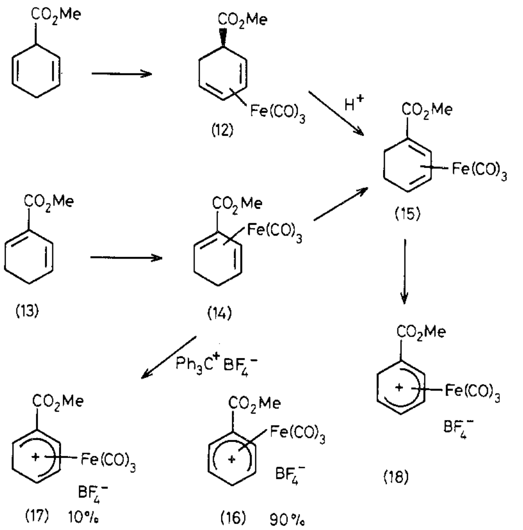


These pairs of complexes can be separated by chromatography, but this is inconvenient on the scale which we are currently preparing **6**. Preconjugation of the 1,4-diene to give **7**, with either a catalytic amount of *p*-toluenesulfonic acid at elevated temperature or base at room temperature, followed by reaction with pentacarbonyliron at 140 °C, results in formation of only **6** in yields of up to 80%[5] (Scheme I).

Complex **3** undergoes hydride abstraction to give mainly **8** and small amounts of **9**,[4,6] while **5** is untouched by trityl fluoroborate. This is a common feature of complexes which carry a substituent M-exo at C-5 or C-6, undoubtedly due to steric hindrance.[4c] The isomeric compound **4** gives mainly **10**, with some **8**, while hydride abstraction from **6** results in greater than 90% yield of **11**.[4,7] The factors controlling direction of hydride abstraction from **3** and **4** are not well understood, but the predominant complexes appear to have dienyl systems with lowest energy LUMO's and highest energy HOMO's, as expected from the well-known synergic interaction between ligand and metal.



Scheme II

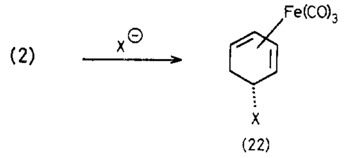


The ester group in carbomethoxy-substituted complexes provides another means of obtaining specifically substituted complexes. Reaction of methyl 1,4-dihydrobenzoate with pentacarbonyliron gives complex **12** in which the ester remains on an sp^3-hybridized carbon atom.[8] It has been reported (in a footnote) that the ester group is M-endo as shown here.[9] Base treatment of dihydrobenzoic acid followed by esterification affords the conjugated diene **13** which on treatment in the above manner leads to the complex **14**. Treatment of **12** or **14** with refluxing methanolic sulfuric acid results in isomerization to give **15** (Scheme II). Similar results are obtained with all complexes derivable from *o*-, *m*-, and *p*-anisic acids.[10]

Hydride abstraction from **14** results in **16** as the major salt, with a small amount of **17**, while **15** gives **18** as the only isolatable product.[8] This indicates the value of the methoxycarbonyl group in dictating the structures of dienyl systems obtainable by this method. Specifically methylated cyclohexadienyl cations **19**, **20**, and **21** can be produced by treatment of appropriate complexes with strong acid. Illustreated in Scheme III, this demonstrates a useful alternative to treatment with trityl fluoroborate for obtaining these types of complex, though it has so far only been applied to relatively simple examples.[11]

Reactions of Cyclohexadienyl Complexes

These complexes react readily with nucleophiles. Such reaction for the parent complex **2** results in regio- and stereospecific addition to give the complexes **22**. A very large number of simple nucleophiles have been studied,[4,6,12] although it was found impossible to achieve



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(5) A. J. Pearson, M. Chandler, and C. W. Ong. unpublished results.

(6) R. E. Ireland, G. G. Brown, Jr., R. H. Stanford, Jr., and T. C. McKenzie, *J. Org. Chem.*, **39**, 51 (1974).

(7) (a) A. J. Pearson, *J. Chem. Soc., Perkin Trans. 1*, 2069 (1977); (b) A. J. Pearson, *J. Chem. Soc., Chem. Commun.*, 339 (1977).

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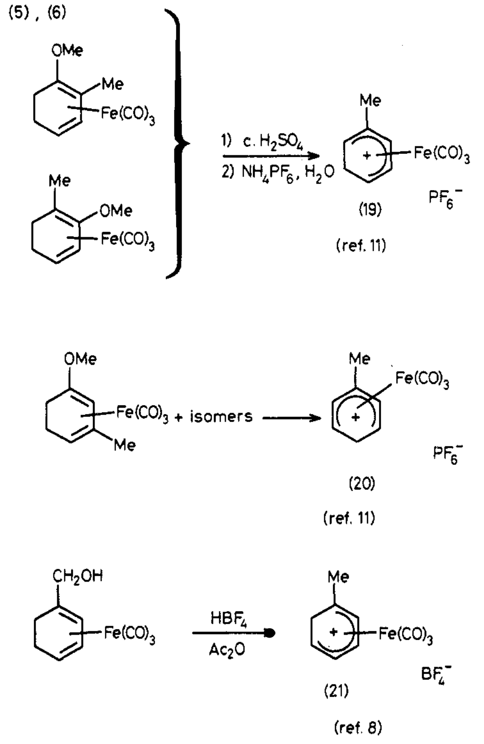
(9) T. H. Whitesides, R. W. Slaven, and J. C. Calabrese, *Inorg. Chem.*, **13**, 1895 (1974).

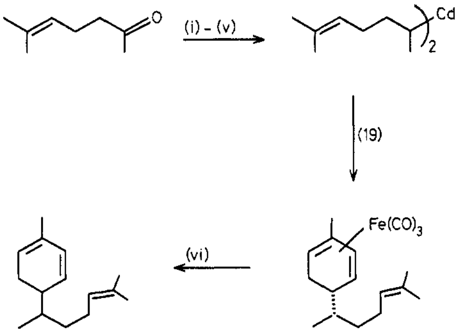
(10) A. J. Birch and A. J. Pearson, *J. Chem. Soc., Perkin Trans 1*, 638 (1978).

(11) A. J. Birch and M. A. Haas, *J. Chem. Soc. C*, 2465 (1971).

Scheme III



Scheme IV[a]

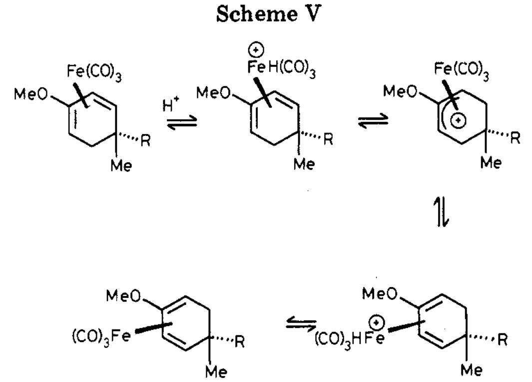


[a] Reagents: (i) NaBH$_4$, (ii) TsCl/pyr, (III) LiBr, acetone reflux, (iv) Mg, THF, (v) CdCl$_2$, THF, (vi) CuCl$_2$, EtOH.

direct alkylation in good yield with Grignard or alkyllithium reagents.[4b] (Note added in proof: Recently it has been shown that organolithium reagents give clean alkylation in dichloromethane at −78 °C.[48]) However, use of organozinc or -cadmium reagents results in clean alkylation in good yield.[13,14] This has been applied successfully to a synthesis of zingiberene[15] (Scheme IV).

Dimethylzinc and dimethylcadmium do not react with cyclohexadienyl complexes, but direct methylation is readily achieved with lithium dimethylcuprate,[16] and general alkylation may also be achieved by using mixed alkylcuprate reagents.[17]

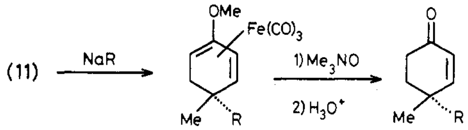
Scheme V



Most of the reactions so far studied have been trivial in that they are not necessarily superior to traditional methods. There is, however, an important property of certain types of dienyl complex which has great synthetic potential, namely, that in complexes of structure **8** and **11**, the methoxy group exerts a directing effect such that nucleophiles add to the para terminus. We shall now consider the implications of this in more detail.

Complexes Equivalent to a Cyclohexenone γ-Cation

It has long been known that tricarbonyl(2-methoxycyclohexadienyl)iron tetrafluoroborate (**8**) reacts with nucleophiles at the terminus remote from the methoxyl. This behavior is due to electronic deactivation of the α position, as reflected in the ^{13}C NMR spectrum of **8**, where C-1 is found at much higher field (43.8 ppm) than C-5 (65.3 ppm).[18] Birch et al.[4c] had treated the disubstituted complex **11** with borohydride, which gave equal addition of H$^-$ at both termini, and morpholine and hydroxide, which both added mainly to the methylated terminus. It therefore seemed an obvious step to us to examine the reactions of **11** with carbon nucleophiles to determine where carbon–carbon bond formation would occur. The results were indeed gratifying: all nucleophiles examined at that time reacting exclusively, and in very high yield, at the methylated terminus.[7] Removal of Fe(CO)$_3$ was achieved in good yield by using Shvo and Hazum's trimethylamine *N*-oxide method;[19] this resulted, after enol ether hydrolysis, in the formation of 4,4-disubstituted cyclohexenones (**24**). We have more recently found[20,21] that reaction even with cyclic keto ester enolates also occurs regiospecifically in excellent yield. The results are summarized in Table I. At first sight, the formation of diastereoisomers, e.g., **25** and **26**, might seem a disadvantage. However, these are very readily separated by crystallization, and their stereochemistries can be assigned from their proton NMR spectra. Pure diastereoisomers can be reconverted to the mixture by



(23) (24)

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(12) L. A. P. Kane-Maguire and C. A. Mansfield, *J. Chem. Soc., Chem. Commun.*, 540 (1973); C. A. Mansfield, K. M. Al-Kathumi, and L. A. P. Kane-Maguire, *J. Organometal. Chem.*, 71, C11 (1974); J. E. Mahler and R. Pettit, *J. Am. Chem. Soc.*, **85**, 3955 (1963).

(13) A. J. Birch and A. J. Pearson, *Tetrahedron Lett.*, 3617 (1975).

(14) A. J. Birch and A. J. Pearson, *J. Chem. Soc., Perkin Trans. 1*, 954 (1976).

(15) A. J. Birch and A. J. Pearson, unpublished work, 1976.

(16) A. J. Pearson, *Aust. J. Chem.*, **29**, 1101 (1976).

(17) A. J. Pearson, *Aust. J. Chem.*, **30**, 345 (1977).

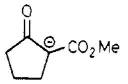
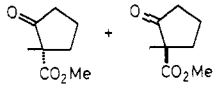
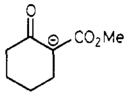
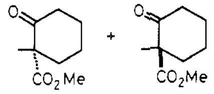
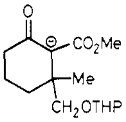
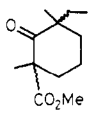
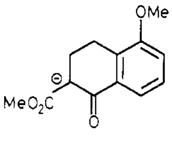
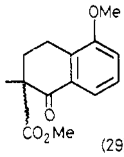
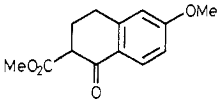
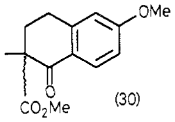
(18) A. J. Birch, P. W. Westerman, and A. J. Pearson, *Aust. J. Chem.*, *29*, 1671 (1976).

(19) Y. Shvo and E. Hazum, *J. Chem. Soc., Chem. Commun.*, 336 (1974).

(20) A. J. Pearson and P. R. Raithby, *J. Chem. Soc., Perkin Trans 1*, 395 (1980).

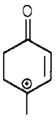
(21) A. J. Pearson, E. Mincione, M. Chandler, and P. R. Raithby, *J. Chem. Soc., Perkin Trans. 1*, in press.

Table I
Nucleophile Additions to Complex 11

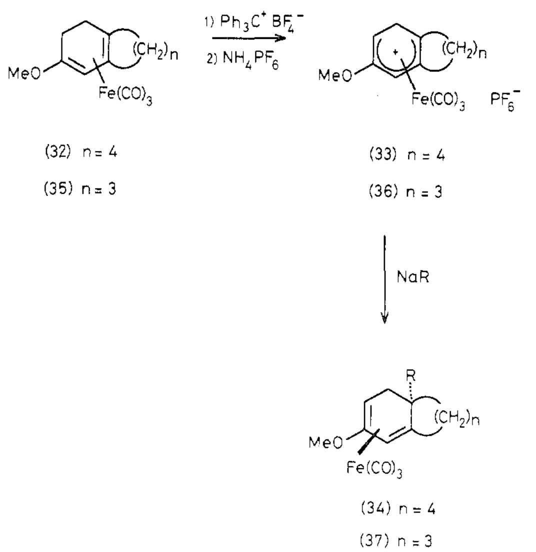
nucleophile	products 23 R =	yield, %	ref
CN^-	CN	52	7b
$^-CH(CO_2Et)_2$	$CH(CO_2Et)_2$	89	7a
$^-CMe(CO_2Et)_2$	$CMe(CO_2Et)_2$	85	7a
$^-CH(CO_2Et)COMe$	$CH(CO_2Et)COMe$	79	7a
$^-CH(CO_2Bu\text{-}t)COMe$	$CH(CO_2Bu\text{-}t)COMe$	71	7a
	 (25) (26)	100	20
	 (27) (28)	97	21
	 stereoisomer mixture	85	21
	 (29)	98	21
	 (30)	96	21

treatment with *p*-toluenesulfonic acid in dichloromethane, thereby making either diastereoisomer available in better yield. This is a property of the diene–$Fe(CO)_3$ group and occurs as shown[22] in Scheme V.

We are currently studying the conversion of **25** and related compounds to trichothecane derivatives and the conversion of **29** and related compounds to steroid derivatives. In the language of synthons, we can regard the complex **11** as an equivalent of the cyclohexenone cation **31**.

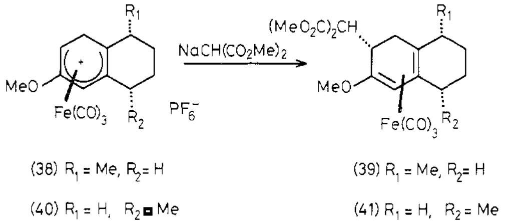


(31)

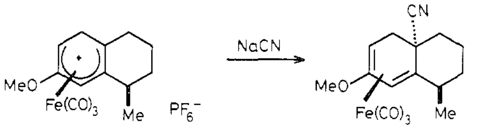


(32) n = 4 (33) n = 4
(35) n = 3 (36) n = 3
(34) n = 4
(37) n = 3

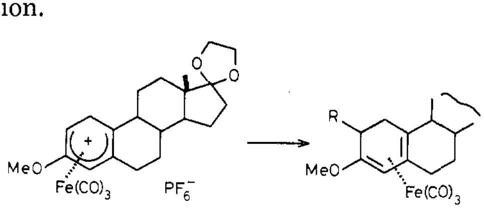
When we first discovered this behavior, it seemed appropriate to examine simple analogous bicyclic systems, attempting to introduce a functionalized substituent at the angle. With the simple derivatives **33** and **36**, this was achieved with spectacular success[7a] and the complexes **34** and **37** were produced in very high yield. However, introduction of methyl substituents into the noncomplexed ring resulted in changes of regioselectivity, examples being the reactions of **38** and **40**. If the substituent is remote from the angular dienyl terminus and is M-endo, then reaction at the angle is allowed, e.g., **42** → **43**.[23] This behavior made us reluctant to attempt introduction of a 19-angular substituent in a steroidal system, and the later observations by Birch et al.[24] that reaction of complex **44** with nucleophiles results in formation only of **45** confirms our suspicion.



(38) R_1 = Me, R_2 = H (39) R_1 = Me, R_2 = H
(40) R_1 = H, R_2 = Me (41) R_1 = H, R_2 = Me



(42) (43)



(44) (45)

Application to the Synthesis of Spirocyclic Compounds

The ability to create a quaternary center in a six-membered ring where one of the substituents is methyl is for the most part a relatively easy process in organic chemistry.[25] However, formation of a quaternary carbon atom with remote functionality is a more dif-

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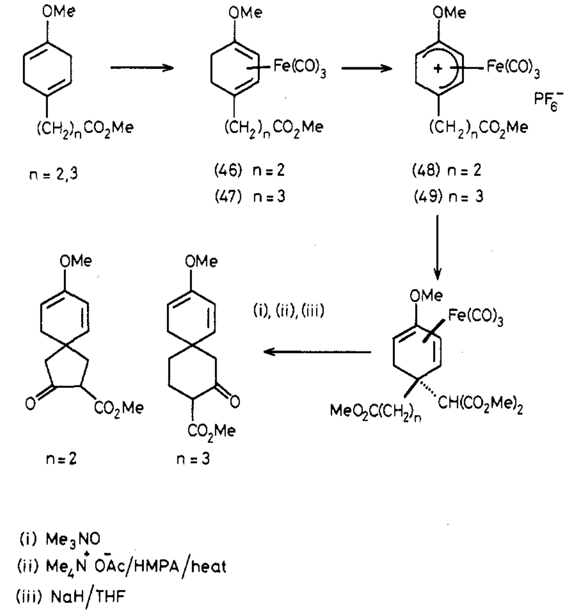
[22] H. Alper, P. C. LePort, and S. Wolfe, *J. Am. Chem. Soc.*, **91**, 7553 (1969); Whitesides and Neilan, 1; C. P. Casey and C. R. Cyr, *J. Am. Chem. Soc.*, **93**, 1280 (1971); **95**, 2240, 2248 (1973).

[23] A. J. Pearson, *J. Chem. Soc. Perkin Trans. 1*, 495 (1978).

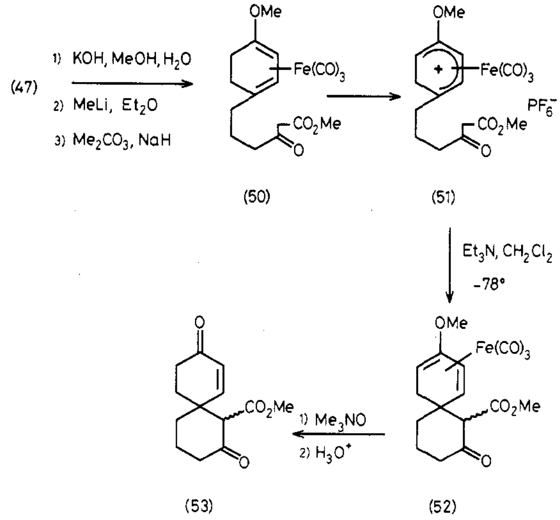
[24] A. J. Birch and W. D. Raverty, personal communication.

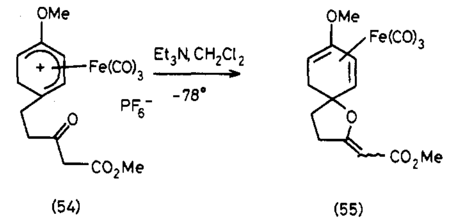
[25] H. O. House, "Modern Synthetic Reactions," 2nd ed., W. A. Benjamin, New York 1972.

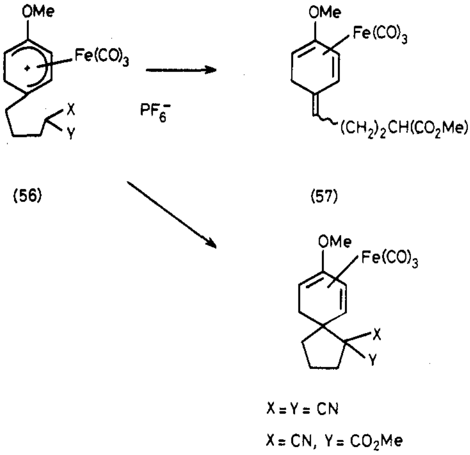
ficult operation,[26] and we hoped to achieve this by using the new method. We were interested in the first instance in spirocyclic compounds since the spiro[4.5]-decane[27] and spiro[5.5]undecane[28] systems are found in a number of natural products. Accordingly, the preparation of complexes **46** and **47** was undertaken, and, as it turned out, the reaction (by $Fe(CO)_5$) produced only these isomers. The dienyl complexes **48** and **49**, obtained by regiospecific hydride abstraction, showed greater than 80% selectivity for the substituted dienyl terminus on reaction with dimethylsodiomalonate, and we were able to convert the products into the desired spirocycles as shown.[29a]



After completion of this work we became interested in examining an alternative approach to the same ring systems, viz., intramolecular addition of a carbon nucleophile to the complexed cyclohexadienyl cation. Synthesis of the appropriate complex **51** containing a keto ester group was readily achieved, indicating also that many standard organic transformations are possible in the presence of the $Fe(CO)_3$ group. Treatment of **51** with 1 equiv of triethylamine at −78 °C gave almost instantaneous reaction, producing the crystalline spiro[5.5]undecane derivative **52** in 90% yield,[29b] readily converted to the enone **53**. Similarly, **54** could be synthesized, though this underwent cyclization on oxygen to give **55**, as anticipated from similar reactions.[30] An attempt to overcome this difficulty in synthesizing the spiro[4.5]decane carbocyclic system by using the gem diester **56** resulted only in deprotonation *α* to the dienyl terminus to give **57**. The diester methine proton is insufficiently acidic, but we have recently found that use of a bisnitrile or cyano ester does lead to cyclization.[31]







Use of $Fe(CO)_3$ as Protection for the Diene and Enol Ether Groups

It has long been known that the diene–$Fe(CO)_3$ group moderates the reactivity of double bonds. For example, the 22, 23 double bond of ergosteryl acetate can be selectively hydrogenated by $Fe(CO)_3$ protection of the ring B diene (**58**).[32] The complex withstands hydroxylation using osmium tetroxide, allowing formation of the 22,23-diol from **58**.[33] Tricarbonyl(myrcene)iron (**59**) can be acetylated under mild Friedel–Crafts conditions to the monoacetyl derivative **60**,[34] even though acetylation Friedel–Crafts diene–$Fe(CO)_3$ complexes can be achieved fairly readily.[35] This behavior can be

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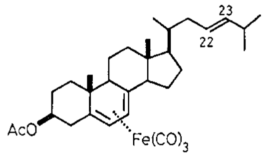

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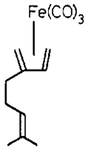

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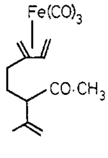

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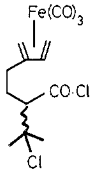

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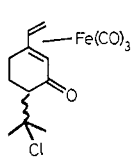

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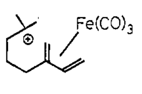

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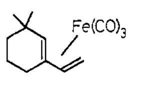

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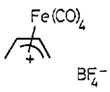

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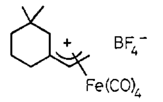
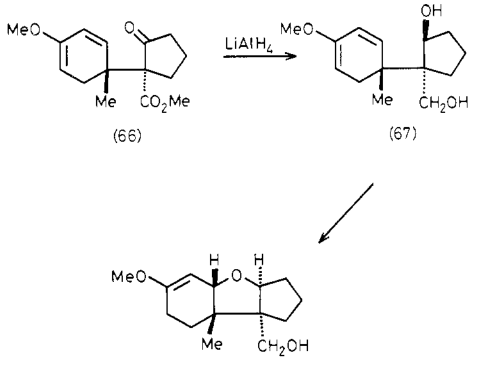


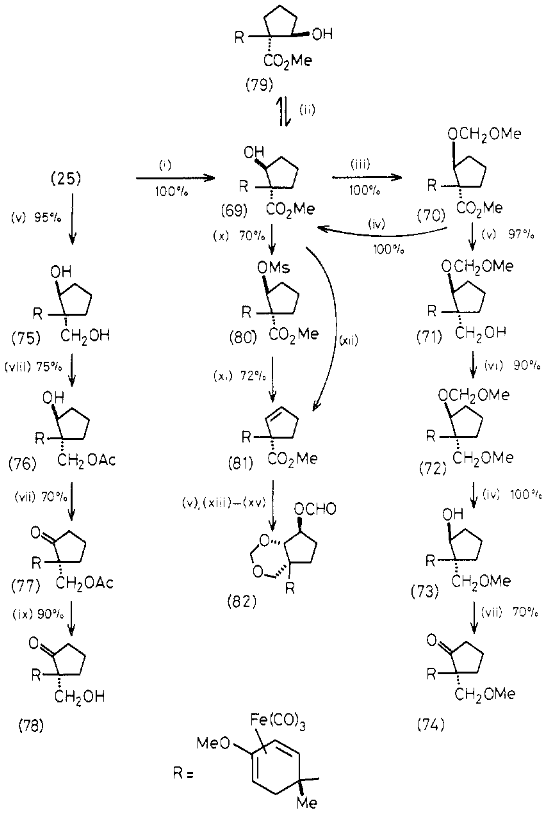
(66)

extrapolated to a double acylation using oxalyl chloride–AlCl$_3$, to give the cyclic complex **62**,[34] presumably via **61**.[36] Treatment of **59** with a catalytic amount of anhydrous tetrafluoroboric acid gives **64**, via the cation **63**,[37] even though (butadiene)tricarbonyliron protonates readily under carbon monoxide atmosphere to give the allyl complex **65**.[38] Treatment of either **59** or **64** with 1 equiv of anhydrous tetrafluoroboric acid under carbon monoxide gives almost quantitative yield of **66**.[37]

In connection with our recent entry into trichothecane synthesis via the complex **25**, we have studied in more detail the conversions of a number of functional groups using **25** and **26** as examples. This was necessary since we found that attempted reduction of the keto ester groups on the uncomplexed molecule **66** gave **67** which underwent irreversible cyclization to **68** extremely readily.[20] We therefore investigated methods of reduction, oxidation, and protection/deprotection in the presence of the Fe(CO)$_3$ group,[39] (Scheme VI). Attempted reductions of ester to alcohol with lithium aluminum hydride result in considerable decomposition of the complex and very poor yields. However, diisobutylaluminum hydride reacts smoothly to give **71** or **75** almost quantitatively. Note the usefulness of the Fe(CO)$_3$ group for protecting the dienol ether, which now withstands conditions for removal of the methoxymethyl ether protecting group (**72** → **73**). Treatment of either pure hydroxy ester **69** or **79** with *p*-toluenesulfonic acid in dichloromethane at room temperature gives back the 1:1 mixture of these complexes. Whereas the initial synthesis of **25** gave a mixture, high yields of either diastereoisomer are now accessible (see above). It is noteworthy that the secondary alcohol group in **73** and **76** can be oxidized to ketone in **74** and **77** by Collins' reagent without affecting the Fe(CO)$_3$ group.[40] Also noteworthy is the relatively straightforward dehydration of **69** to the olefin **81** and subsequent conversion to **82**, which is now an advanced intermediate for trichothecane synthesis.[41]



Scheme VI
Some Useful Functional Group Transformations in the Presence of a Diene-Fe(CO)$_3$ Group[a]



[a] Reagents: (i) NaBH$_4$, MeOH, 0 °C. (iii) *p*-CH$_3$C$_6$H$_4$SO$_3$H, CH$_2$Cl$_2$, 25 °C, 16 h. (iii) ClCH$_2$OMe, *i*-Pr$_2$NEt, CH$_2$Cl$_2$, 25 °C, 16 h. (iv) *p*-CH$_3$C$_6$H$_4$SO$_3$H, MeOH, 55 °C, 5 h. (v) *i*-Bu$_2$AlH, THF, −78 °C → 25 °C, 16 h. (vi) MeI, NaH, THF, 25 °C, 14 h. (vii) CrO$_3$·2C$_5$H$_5$N, CH$_2$Cl$_2$, −20 °C, 3 min. (viii) Ac$_2$O, pyr, 0 °C, 14 h. (ix) K$_2$CO$_3$, MeOH, 25 °C, 3 h. (x) CH$_3$SO$_2$Cl, (6 equiv), pyr, 0 °C, 36 h (not optimized). (xi) Activated Al$_2$O$_3$, CH$_2$Cl$_2$, 25 °C, 60 min (not optimized). (xii) *t*-BuOOH, VO(acac)$_2$, benzene, reflux. (xiv) ClCH$_2$OMe, *i*-Pr$_2$NEt, CH$_2$Cl$_2$, reflux. (xv) HCO$_2$Na, HCO$_2$H, 25 °C.

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Acc. Chem. Res. 1980, 13, 469–476

Summary

We have evolved a useful and apparently general method of creating a quaternary carbon atom in a six-membered ring, surrounded by functionalized groups. The appearance of such a system in a large and diverse number of natural products or their synthetic precursors, such as steroids, tetracyclic diterpenoids, trichothecanes,[42] compounds related to pentalenolactone,[43] picrotoxin,[44] the erythromycins,[45] spirocycles,[27,28] aspidosperma alkaloids,[46] and many others,[26] makes this a very exciting discovery indeed. We are currently involved in applying our new methodology to the synthesis of a number of these targets.[47]

I am grateful to Professor A. J. Birch for introduction to this interesting area of chemistry and to the Science Research Council and Cancer Research Campaign for financial support.

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Synthesis, Molecular Dynamics, and Reactivity of Mixed-Metal Clusters

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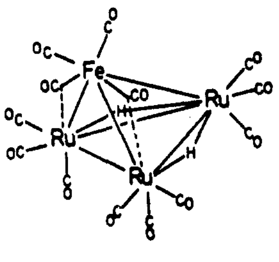
Transition-metal cluster compounds are currently under intense scrutiny, largely due to their numerous potential applications in catalysis. Clusters can function as homogeneous catalysts in which special reactivity features may occur as a result of adjacent metals[1–3] or may serve as "storehouses" for the release of catalytically active fragments. Clusters are also being employed to model substrate bonding and the reactions of substrates on metal surfaces.[4–6] Furthermore, they are useful precursors for the preparation of novel heterogeneous catalysts; they are absorbed onto a catalytic support and then decomposed to yield small metal crystallites.[7,8]

Mixed-metal clusters such as $H_2FeRu_3(CO)_{13}$ (1) and $H_3CoRu_3(CO)_{12}$ (2) are especially interesting in these regards.[9] Mixed-metal clusters have been successfully employed for the preparation of bimetallic heterogeneous catalysts.[7] From a chemical viewpoint, mixed-metal dimers and clusters should show unique reactivity features as a result of combining the different reactivity properties of the constituent metals. For example, dimers and clusters which have early–late transition-metal combinations (e.g., Zr with Rh) are expected to be able to polarize and activate substrates such as CO. From a mechanistic viewpoint, the low symmetry which mixed-metal clusters inherently possess can allow a differentiation of specific sites of reactivity and can provide important insight into mechanistic detail. Mixed-metal clusters are also ideally suited for studies of fluxional processes in which the carbonyls, hydrides, and even the metals themselves undergo rearrangement. In such clusters, the majority of ligands are in chemically nonequivalent positions and are thus distinguishable by NMR spectroscopy.



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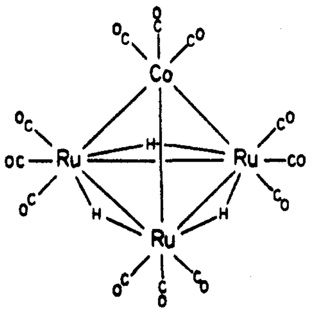

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Mixed-metal carbonyl clusters have been under study in this laboratory from several viewpoints. We have been interested in developing better methods for the synthesis of mixed-metal clusters and have more recently been evaluating features of their reactivity with a variety of substrates. We have chosen to concentrate our reactivity studies on one particular cluster, $H_2FeRu_3(CO)_{13}$ (1) and to examine its reactivity in as much detail as possible. It has been our aim to fully understand the kinds of chemical reactions which this cluster

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