Stoichiometric applications of organotransition metal complexes in organic synthesis

JULIAN BLAGG

Pfizer Central Research, Sandwich, Kent, CT13 9NJ, UK

Reviewing the literature from 1 July 1992 to 31 August 1993

1 Introduction

This review covers the literature from 1 July 1992 to 31 August 1993 and is a selective account of recent developments in the applications of stoichiometric organotransition metal chemistry to organic synthesis. Particular attention has been given to work of general applicability to the practising synthetic organic chemist and to reactions which lead efficiently to otherwise elusive structural entities. Areas which have seen particularly notable advances in their synthetic applicability in the period covered include hydrozirconation reactions, the use of carbene complexes in organic synthesis, and transition metal mediated cycloadditions. Relevant reviews published during the period are cited in the text.

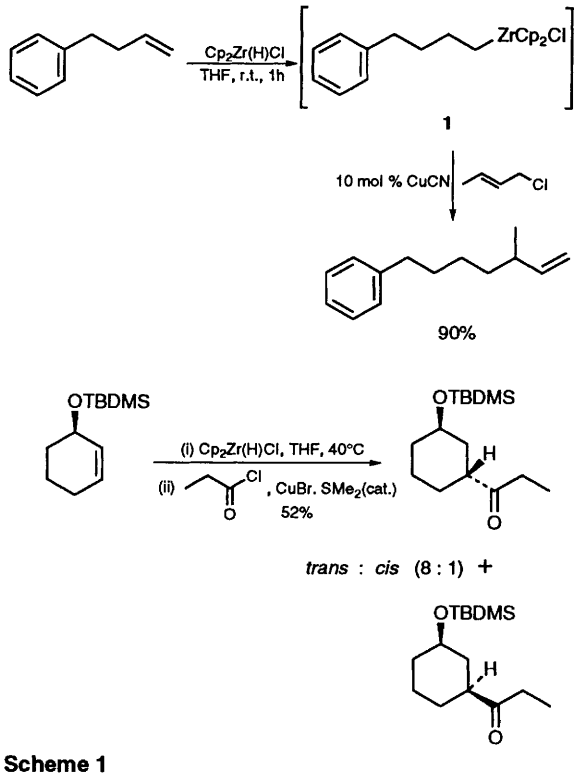
2 Transition metal alkyl, allyl, alkenyl, alkynyl, and acyl complexes in organic synthesis

2.1 Hydrozirconation methodology

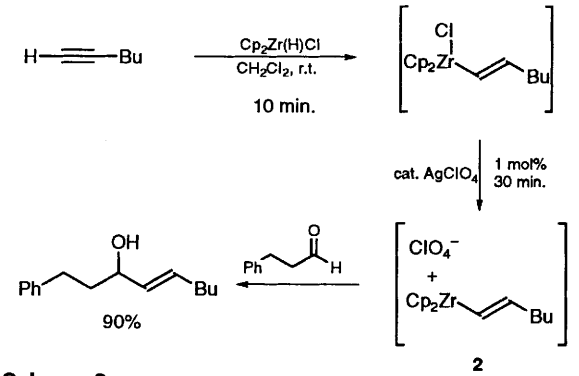
The utility of the classical hydrozirconation reaction originally developed by Schwartz[1] has been considerably expanded over the past year with much of the work having general applicability in organic synthesis. For example, regioselective hydrozirconations of alkenes followed by transmetallation of the resulting alkylzirconate **1** (**Scheme 1**) with catalytic CuCN (10mol%) gives alkyl cuprates which can subsequently be used in coupling reactions with allylic chlorides, bromides, or phosphonates. For unsymmetrically substituted allylic systems the predominant mode of attack is S_N2'. Unfortunately, couplings with monosubstituted epoxides, allylic acetates, and aryl or alkenyl halides were unsuccessful.[2] Transmetallation of alkyl and alkenyl zirconates with $CuBr.SMe_2$ (5–10mol%) in the presence of an acid chloride gives ketones in a one-pot reaction. In the absence of a copper catalyst this reaction is very slow for alkylzirconates and fails for alkenyl zirconates (**Scheme 1**).[3]

An alternative approach to enhancing the reactivity of alkyl and alkenyl zirconates avoids transmetallation but uses a catalytic amount of $AgClO_4$ (0.1–5mol%) to generate the cationic species **2**; reactions with aldehydes lead to a highly efficient C–C bond forming process (**Scheme 2**).[4] Epoxides have been shown to react in a similar manner *via in situ* generation of an activated aldehyde.[5]

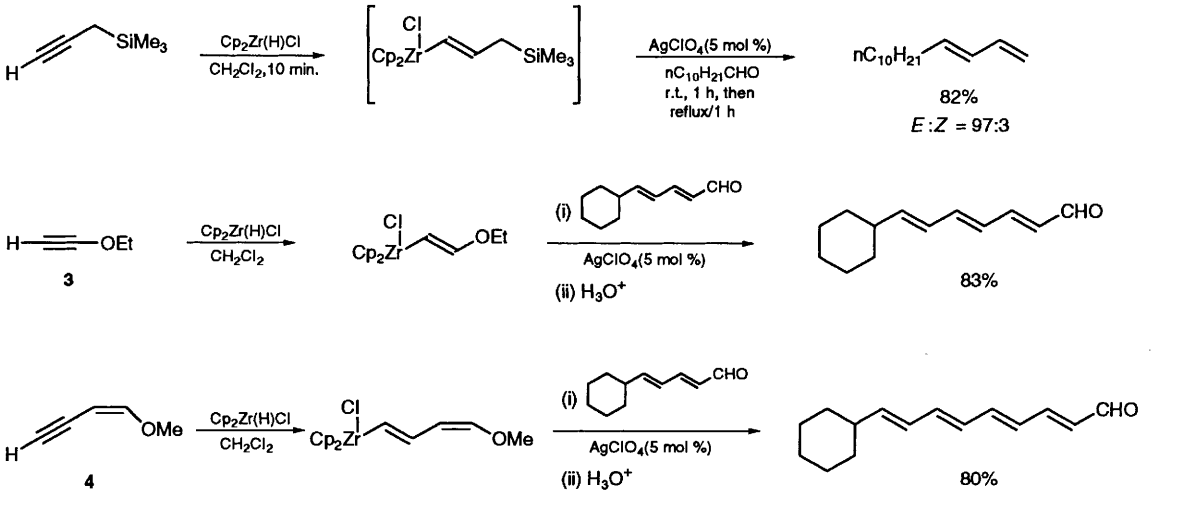
The Grignard-like reactivity of alkenyl zirconates in the presence of catalytic $AgClO_4$ has been applied to the highly *E*-selective synthesis of terminal 1,3-dienes *via* three-carbon homologation of an aldehyde



Scheme 1



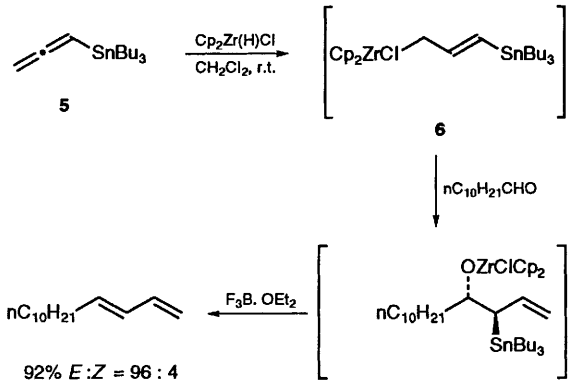
Scheme 2



Scheme 3

(**Scheme 3**).[6] Moreover, hydrozirconation of ethoxyethyne **3** or (*Z*)-1-methoxy-but-1-en-3-yne **4** followed by $AgClO_4$ catalysed reaction with aldehydes gives an efficient two-and-four-carbon homologation protocol respectively, leading to conjugated polyenals (**Scheme 3**).[7]

An interesting aspect of this chemistry is the hydrozirconation of the allenyl stannane **5** to give the allylzirconate **6** which undergoes smooth reaction with aldehydes and ketones in the absence of any catalyst. Subsequent $F_3B.OEt_2$ catalysed β-elimination affords an alternative approach to terminal *E*-dienes (**Scheme 4**).[8]

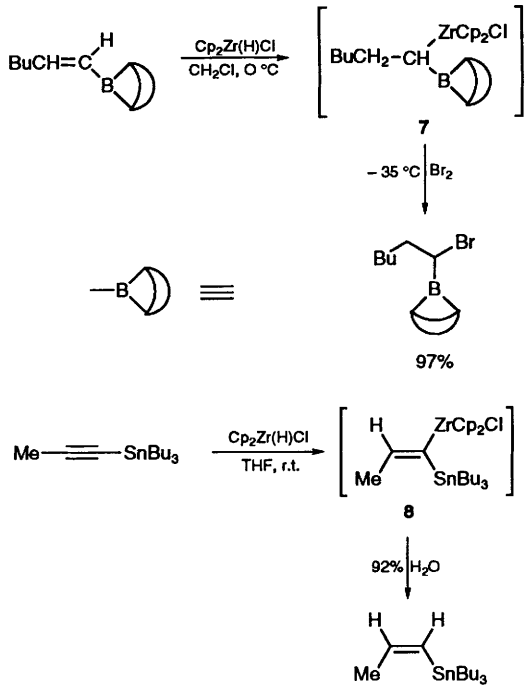


Scheme 4

Hydrozirconation products from acyclic alkenes[9] or alkynes[10] have also been shown to be useful precursors to alkyl or alkenyl boranes respectively *via* transmetallation with BCl_3, BBr_3, or chlorocatecholborane. Hydrozirconations of various vinyl-9-BBN derivatives give 1,1-dimetalloalkanes **7**; the C–Zr bond can be selectively cleaved with bromine to give α-bromoboranes (**Scheme 5**).[11]

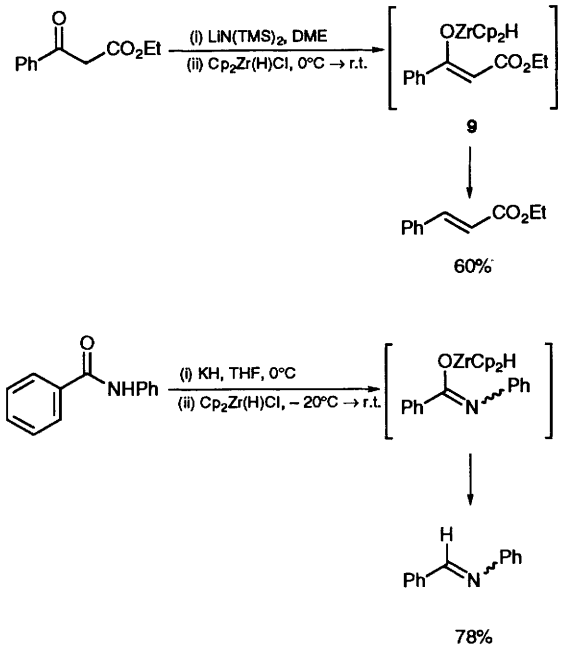
Hydrozirconation of alkynyl stannanes gives a highly efficient synthesis of *Z*-alkenyl stannanes *via* the 1,1-dimetallic species **8**. The dimetallic intermediates **8** offer the potential for regioselective

functionalization using the differences in reactivity between alkenyl stannanes and alkenylzirconates (**Scheme 5**).[12]



Scheme 5

A novel synthesis of α,β-unsaturated esters has been developed *via* reductive deoxygenation of β-ketoesters. Generation of the zirconium enolate **9** followed by hydrozirconation and β-elimination gives the corresponding α,β-unsaturated ester (**Scheme 6**).[13] The extension of this work to amide and lactam deoxygenation is of particular synthetic utility (**Scheme 6**).[14]



Scheme 6

An alternative method for the generation of alkenyl zirconates involves zirconium-mediated carboalumination of alkynes.[15] A recent paper reports a significant increase in the rate of carboalumination in the presence of water, such that reaction can be achieved at $-23°C$.[16]

2.2 Allyl zirconium species

The generation of allyl zirconium species *via* β-elimination of the alkoxy group from the zirconocene complexes of α,β-unsaturated acetals **10** has recently been developed (**Scheme 7**).[17] The allyl zirconium intermediates react in a diastereoselective manner with a variety of aldehydes and ketones to give predominantly *syn* or *anti* 1,2-dioxygenated species in the presence or absence of a Lewis acid respectively. Although allyl zirconium species do not react with alkynes, the allylation of alkynes can be achieved *via* reaction of zirconocene-alkyne complexes **11** (prepared from the corresponding alkyne and $Cp_2ZrBu^n_2$) with an appropriate allylic ether. The reaction is highly regioselective with C–C bond formation occurring only at the γ-position of the allylic ether. β-Elimination of the alkoxy substituent in the zirconacycle intermediate **12** is postulated to account for the formation of the 1,4-diene products (**Scheme 7**).[18]

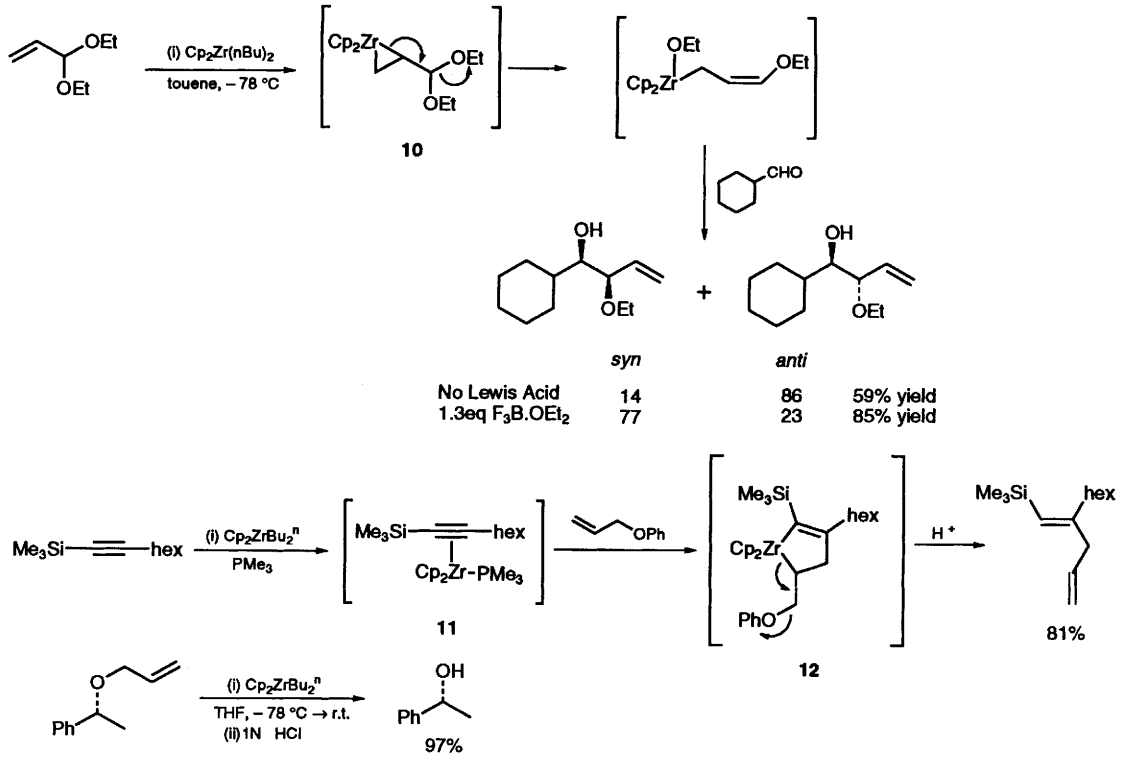
β-Elimination of an alkoxy group in the zirconocene complex of an allylic ether also results in a mild, efficient deprotection method for allyl ethers (**Scheme 7**).[19]

2.3 Zirconacycles in synthesis

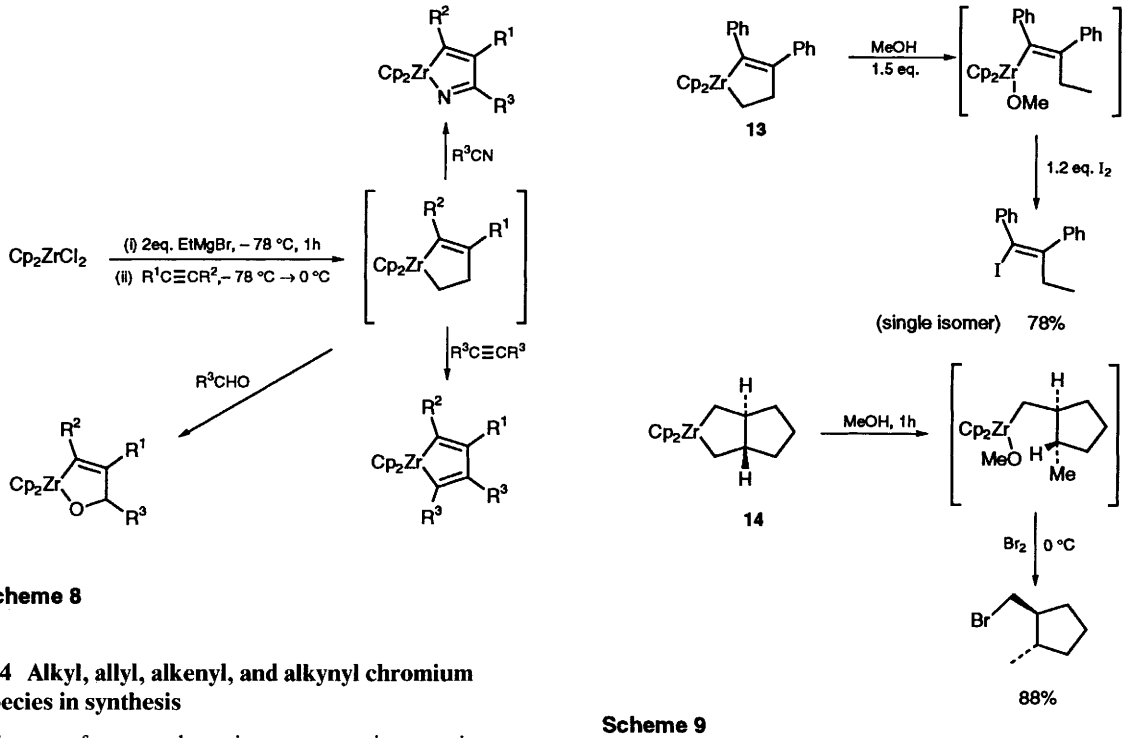
The use of zirconacyclopentenes in synthesis continues to increase; the last year has seen important developments in the methodology of zirconacycle formation and subsequent trapping. A more facile route to these complexes which avoids the use of PMe_3 or hydrozirconation has been reported *via* reaction of diethylzirconocene and an alkyne. Subsequent Cβ–Cβ' bond cleavage, with extrusion of ethylene, provides a convenient source of Cp_2Zr-alkyne complexes which can be trapped by a variety of unsaturated functional groups (**Scheme 8**).[20]

Although the former protocol is limited to the use of diethylzirconocene it has recently been shown that more general pair-selective couplings of alkynes and alkenes can be achieved if excess alkene is present.[21]

Important methods for the regioselective functionalization of the C–Zr bonds of zirconacyclopentenes and zirconacyclopentanes have also been introduced in the last year and these greatly increase the synthetic potential of zirconium-mediated coupling reactions. For example, protonation of zirconacyclopentenes **13** occurs regioselectively at the alkylcarbon–zirconium bond[22] whilst the corresponding symmetrical zirconacyclopentane **14** undergoes selective monoprotonation, allowing halogenation of the remaining alkyl–zirconium bond (**Scheme 9**).[23]



Scheme 7

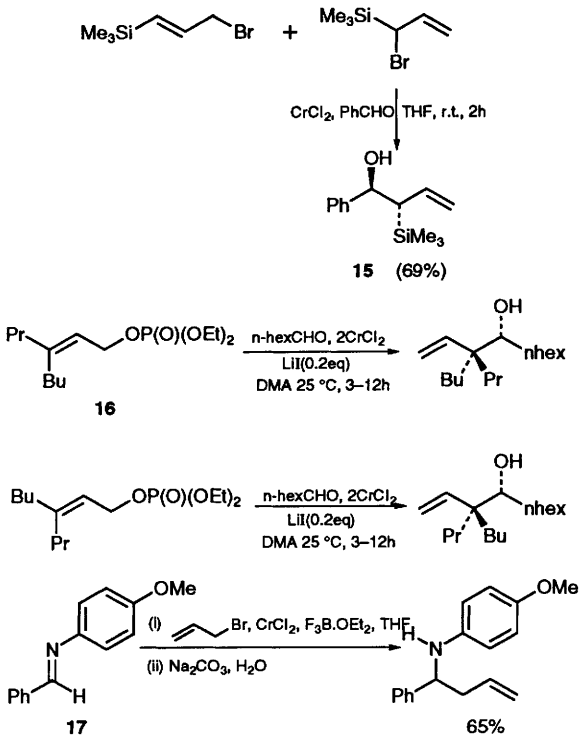


Scheme 8

Scheme 9

2.4 Alkyl, allyl, alkenyl, and alkynyl chromium species in synthesis

The use of organochromium reagents in organic synthesis has been rapidly increasing over the past decade; of particular note is the increased use of allyl, alkenyl, and alkynyl chromium reagents in C–C bond forming reactions.[24] The period under review witnessed some useful extensions of the methodology, particularly in the field of γ-substituted allyl chromium reagents. The first silyl substituted allyl chromium reagents have been shown to react with aldehydes in a highly regio- and diastereoselective manner to give *anti* β-hydroxysilanes **15** (**Scheme 10**).[25] Although this class of reaction is normally highly diastereoselective regardless of the stereochemistry of the starting allylic halide, it has now been demonstrated that γ,γ-disubstituted allylic phosphonates **16** react with $CrCl_2$ and aldehydes without equilibration of the allyl chromium intermediate (**Scheme 10**).[26]

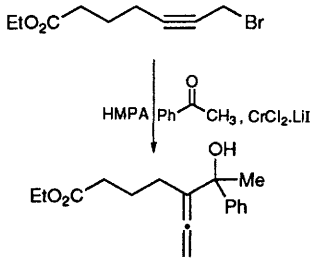


Scheme 10

The highly stereoselective reaction of γ-substituted allyl chromium reagents with aldehydes in an intramolecular sense has recently been utilized as a key step in the total synthesis of Acerosolide.[27] A new development is the reaction of allyl chromium species with activated aldimines **17** to give homoallylic amines (**Scheme 10**).[28]

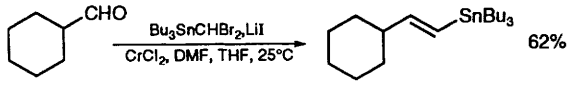
The reaction of propargylic chromium species with aldehydes[29] has been extended to functionalized propargylic reagents. This work exemplifies the selectivity of formation of the chromium(III) intermediate since ester, cyano, or chloro groups do not interfere (**Scheme 11**).[30]

The intramolecular cyclization of alkynyl iodides onto aldehydes mediated by $CrCl_2/NiCl_2$ has continued to be applied to organic synthesis; two elegant examples of this approach are the total synthesis of the macrocycle taxamycin[31] and the oxabicyclo [7.2.1] enediyne moiety from a sensitive furanoside precursor.[32]



Scheme 11

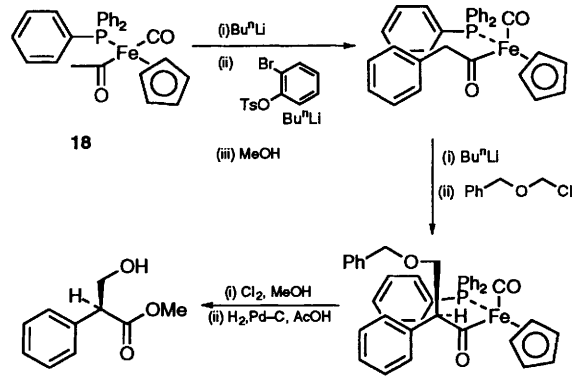
The use of a *gem*-dichromium reagent derived from $Bu_3SnCHBr_2$ with aldehydes has been demonstrated to give *E*-vinyl stannanes (**Scheme 12**).[33] This procedure is complementary to the *Z*-vinyl stannane synthesis reported by Lipshutz (**Scheme 5**).[12]



Scheme 12

2.5 Acyl transition metal complexes in synthesis

Applications of stoichiometric transition metal-acyl complexes have largely involved exploitation of the stereochemical control exerted by the chiral auxiliary $CpFe(CO)PPh_3$. Highlights include the asymmetric synthesis of (−)-Actinonin and (−)-epi-Actinonin,[34] (3*R*,4*S*)-Statine,[35] as well as the synthesis of *S*-(−)-methyl tropinate **19** *via* a novel benzyne-mediated arylation of the homochiral complex **18** (**Scheme 13**).[36]



19 (44% overall)

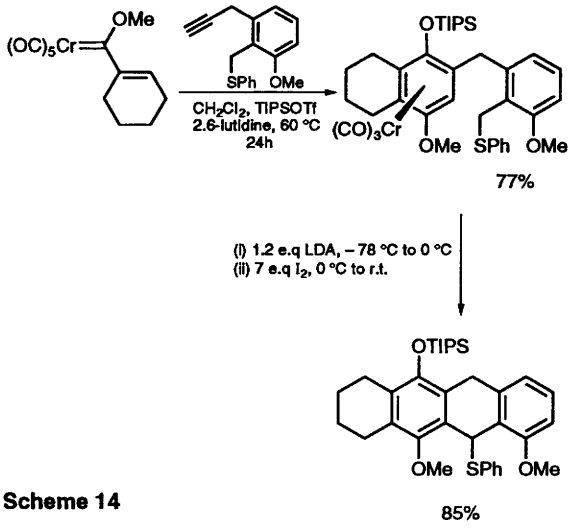
Scheme 13

A series of homochiral organometallic NADH mimics which exert their stereocontrol *via* attachment of the chiral auxiliary $CpFe(CO)PPh_3$ to the C-3 carbonyl of the 1,4-dihydronicotinoyl moiety have been investigated. These complexes stereoselectively reduce ethyl benzoylformate with high enantiomeric excess.[37]

3 Transition metal carbene complexes in synthesis

The period under review witnessed interesting extensions of the use of chromium, molybdenum, and tungsten carbene complexes in organic synthesis. Particular highlights include a novel dipeptide synthesis and the intramolecular trapping of carbenes in a variety of ring-forming reactions of potential synthetic interest.

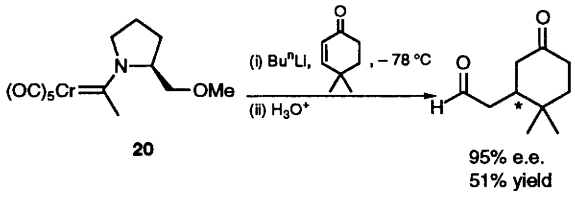
The classical reactivity of Fischer carbenes has now been coupled with subsequent intramolecular nucleophilic substitution of the intermediate (η^6-arene)$Cr(CO)_3$ complexes. This tandem reaction sequence involves a crucial *in situ* protection of the phenol generated in the first step and can provide a novel entry into tetracyclic systems (**Scheme 14**).[38]



Scheme 14

The classical reaction of vinyl chromium carbene complexes with alkynes depicted in **Scheme 14** has been shown to proceed with improved rate under milder conditions using dry state absorption conditions first applied to the Pauson–Khand cyclization. Promotion of ligand exchange in the intermediate carbene complexes *via* donor centres on the solid support is believed to accelerate the reaction.[39]

Anions of aminocarbenes **20** have been shown to undergo exclusive 1,4-addition to enones; indeed, chiral carbene complexes give good diastereoselectivities in their Michael additions. These reactions display the highest facial selectivity observed in enolate-type additions to enones; they proceed *via* a kinetically controlled process and readily yield the free organic product *via* oxidation (**Scheme 15**).[40]

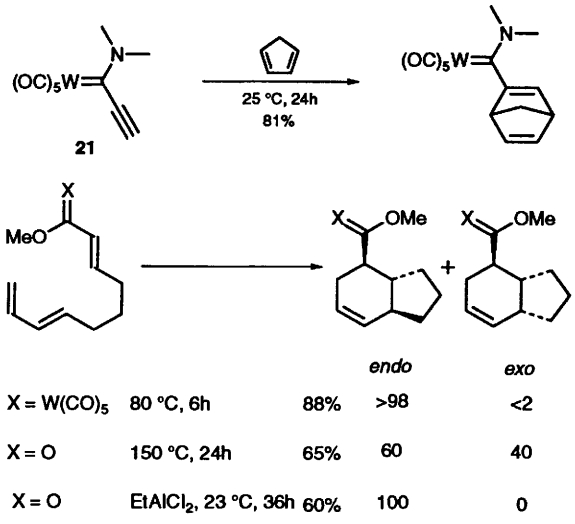


Scheme 15

In contrast to classical metalloenolates the delocalized aminocarbene anion is a soft nucleophile.

The carbene functionality also significantly modifies the reactivity of the dienophile in Diels–Alder reactions; for example, the alkyne complex **21** undergoes a facile cycloaddition with cyclopentadiene in contrast to the free propriolic amides which do not react (**Scheme 16**).[41] Similar effects are seen in the intramolecular Diels–Alder reaction; the carbene moiety acts as an internal Lewis acid, giving rise to higher *endo*/*exo* selectivities and shorter reaction times (**Scheme 16**).[42]

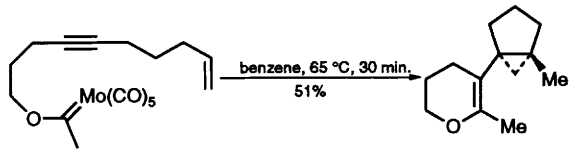
The use of a silicon tether to promote the intramolecular alkyne trapping of Fischer carbenes has also been reported, leading to a novel synthesis of functionalized quinones under photochemical conditions.[43] Intramolecular trapping of a carbene with



			endo	*exo*
X = $W(CO)_5$	80 °C, 6h	88%	>98	<2
X = O	150 °C, 24h	65%	60	40
X = O	$EtAlCl_2$, 23 °C, 36h	60%	100	0

Scheme 16

a pendant alkyne generates a second carbene species which, in the presence of an internal alkene trap, gives rise to a novel, tandem ring-forming process (**Scheme 17**).[44]



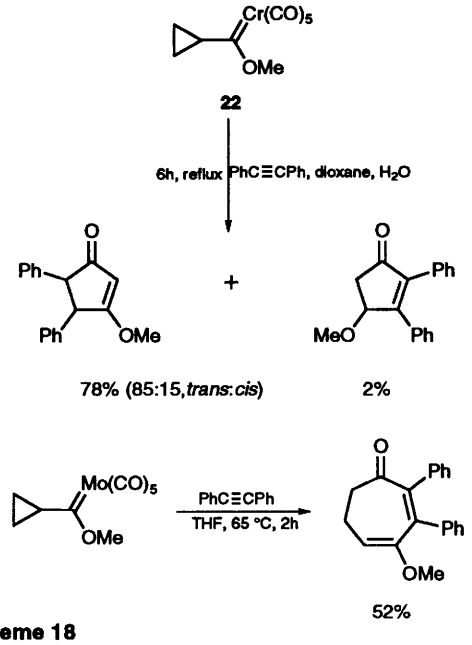
Scheme 17

A number of publications have appeared on intermolecular ring-forming reactions from carbene complexes, in particular leading to five- or seven-membered rings. Herndon has demonstrated an interesting divergence of reactivity between cyclopropylcarbene-chromium complexes **22** and their molybdenum and tungsten analogues. The former, on trapping with alkynes, give predominantly five-membered ring products whilst the molybdenum and tungsten analogues give seven-membered rings (**Scheme 18**).[45] A similar difference in reaction pathway is found in the reaction of simple alkyl carbene complexes with alkynes; the chromium derivatives yield cyclopentenones whilst the molybdenum and tungsten analogues yield 1,3-dienes.[46]

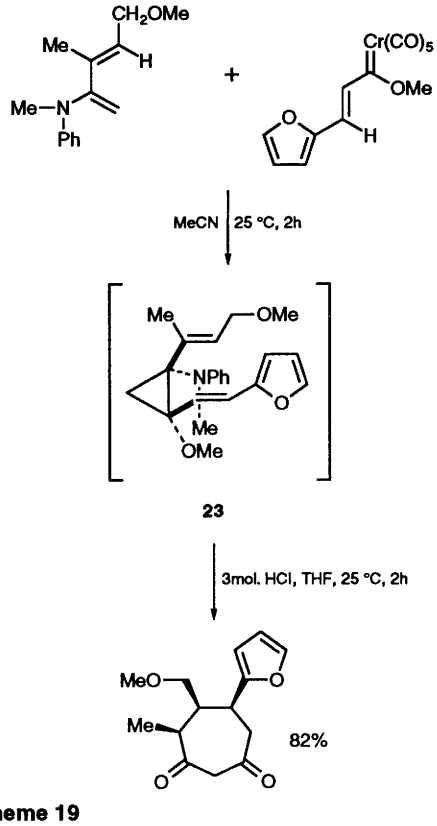
Seven-membered rings can be formed from vinyl chromium carbenes, however, *via* an interesting Cope rearrangement on the initially formed cyclopropane **23** (**Scheme 19**).[47] The potential for stereocontrol of this process has been exploited by Barluenga *via* use of a chiral 2-amino-buta-1,3-diene.[48]

A novel entry into γ-lactones has been reported *via* C–H insertion of an *in situ* generated non-heteroatom stabilized carbene complex **24** (**Scheme 20**). Using this methodology, Eldanolide was prepared in 50% overall yield with high *trans*-stereoselectivity (**Scheme 20**).[49]

One of the highlights of chromium carbene chemistry has been the photolytic coupling of chromium aminocarbene complexes to give a



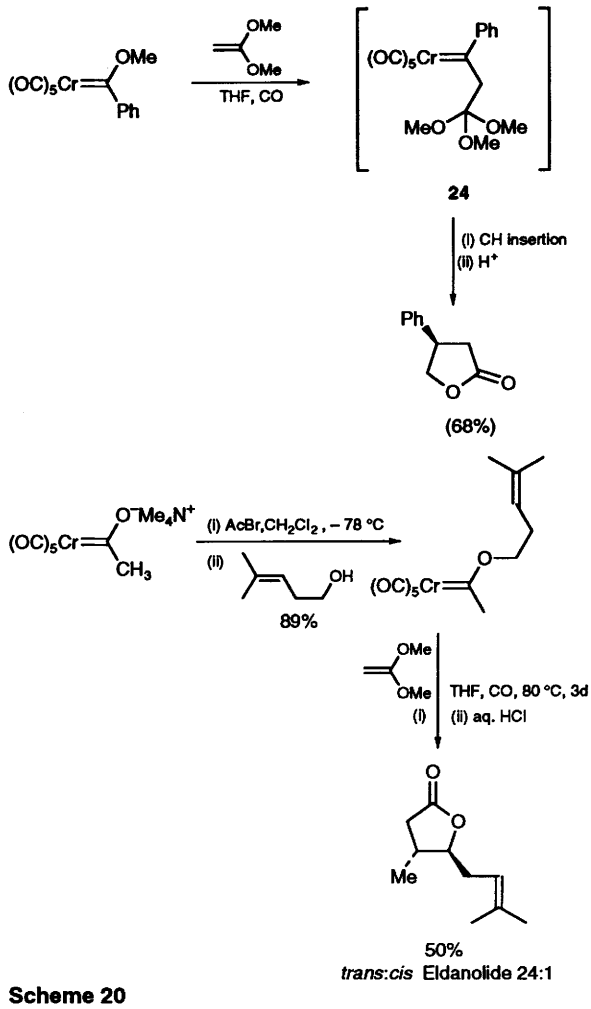
Scheme 18



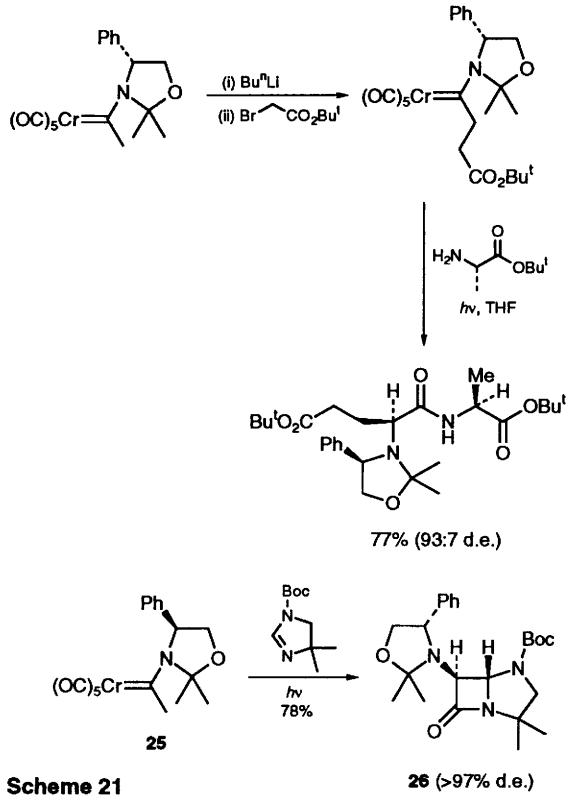
Scheme 19

stereoselective peptide synthesis *via* chiral ketene complexes (**Scheme 21**).[50] The intramolecular trapping of similar chiral aminoketene complexes facilitated a new synthesis of arylglycines.[51] The photolysis of optically active aminocarbene chromium complexes **25** with *N*-protected imidazolines has also been shown to give α-amino protected azapenems **26** with high diastereoselectivity (**Scheme 21**).[52]

Recently, Petasis has reported a new convenient method for the methylenation and benzylidenation of

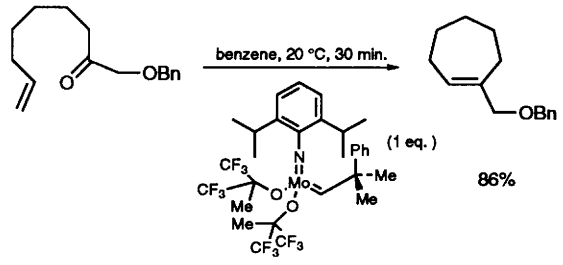


Scheme 20



Scheme 21

aldehydes, ketones, esters, lactones, and amides *via* dimethyl- and dibenzyl-titanocene derivatives respectively. He has extended this methodology to the synthesis of vinylsilanes and vinylcyclopropanes.[53] However, these reactions require rather high temperatures and give a low *Z*/*E* selectivity. Grubbs has recently reported the new carbene species **27** which selectively reacts with the alkene of an olefinic ketone to form a new alkylidene complex *via* olefin metathesis; subsequent intramolecular carbonyl olefination leads to cycloalkenes (**Scheme 22**).[54] This strategy is effective for the synthesis of five-, six-, and seven-membered rings; the more reactive tungsten analogue of **27** allows the formation of cyclic enol ethers from acyclic olefinic esters.



Scheme 22

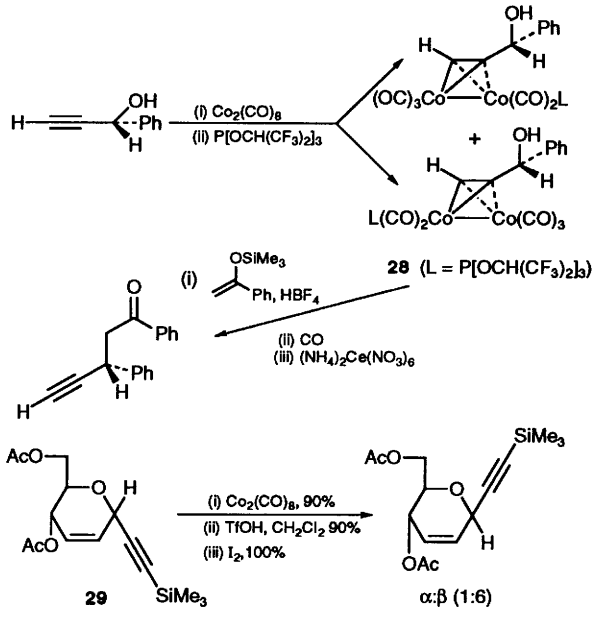
4 η^2-η^6-Complexes in organic synthesis

4.1 η^2-Complexes in organic synthesis

4.1.1 η^2-Alkyne dicobalt hexacarbonyl complexes

The Nicholas reaction of dicobalt hexacarbonyl stabilized propargyl cations with nucleophiles has been widely used in organic synthesis, in particular to avoid the allenic by-products associated with classical propargylation reagents. Few examples of reactions with nitrogen nucleophiles have been published; however, Roth has now demonstrated the facile reaction of a range of cobalt-stabilized propargylic cations with primary and secondary amines, although a mixture of mono and bis propargylated products may be obtained from reactive primary amines.[55] An efficient C-3-propargylation of indoles has also been reported *via* reaction with cobalt-stabilized propargylic cations; no products from attack at the indole nitrogen or other aromatic positions were detected.[56]

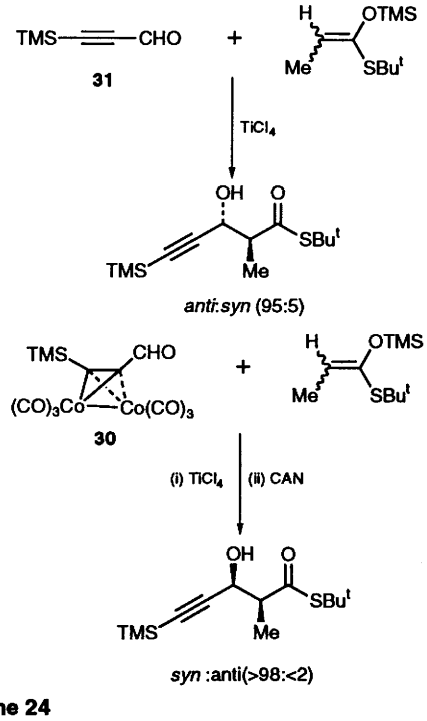
A novel diastereoselective propargylation reagent has been reported by Nicholas in which replacement of one of the CO ligands on cobalt with the π-acceptor ligand tris(1,1,1,3,3,3-hexafluoroisopropyl)phosphite gives a more electrophilic chiral complex **28**, capable of stereocontrolled reaction with carbon nucleophiles. The complexes **28** are formed as easily separable diastereoisomers from chiral alcohol precursors; reaction of a single diastereoisomer with silyl enol ethers proceeds with complete retention of configuration at the propargylic carbon atom (**Scheme 23**).[57] Propargylic cations are presumably implicated in the α to β epimerization of C-1-alkynyl substituted pyranose derivatives **29** *via* their dicobalt hexacarbonyl derivatives (**Scheme 23**).



Scheme 23

This acid-mediated transformation was also examined using 2-substituted $\Delta_{3,4}$ substrates. The even higher α:β ratios observed with these substrates was attributed to the unfavourable interaction of the bulky coordinated alkyne with the pyranose 2-substituent in the α-anomer.[58]

A high degree of stereocontrol has also been observed in the additions of nucleophiles to complexes of propynal with hexacarbonyldicobalt **30**; addition of *O*-silylketene-*O*,*S*-acetals gives rise to a highly *syn* selective aldol reaction which complements the corresponding *anti* selective aldol reactions of uncomplexed propynal **31** (**Scheme 24**). This methodology has been applied to the synthesis of β-lactams[59] and the antibiotic Blastmycin.[60]



Scheme 24

4.1.2 η^2-Complexes of zirconocene

η^2-Complexes of imines have been widely used as a means of functionalizing the α-position of amines; this process has been carried out in a highly enantioselectve manner through the use of a chiral zirconium reagent to give homochiral allylic amines.[61] Taguchi has adopted an alternative approach *via* attachment of a chiral group onto the nitrogen of the precursor aldimine **32** (**Scheme 25**). Although a degree of stereocontrol could be observed in the formation and trapping of the η^2-imine complexes, the reactions were highly temperature dependent.[62]

The activation of positions α to nitrogen in an aromatic system has been extended from pyridines to pyrazines by Jordan. The η^2-pyrazine complexes are formed from the cationic complex $Cp_2Zr(CH_3)(THF)^+$ **33** *via* a C–H activation/CH_4 elimination sequence (**Scheme 25**).[63]

4.2 η^3-Complexes in organic synthesis

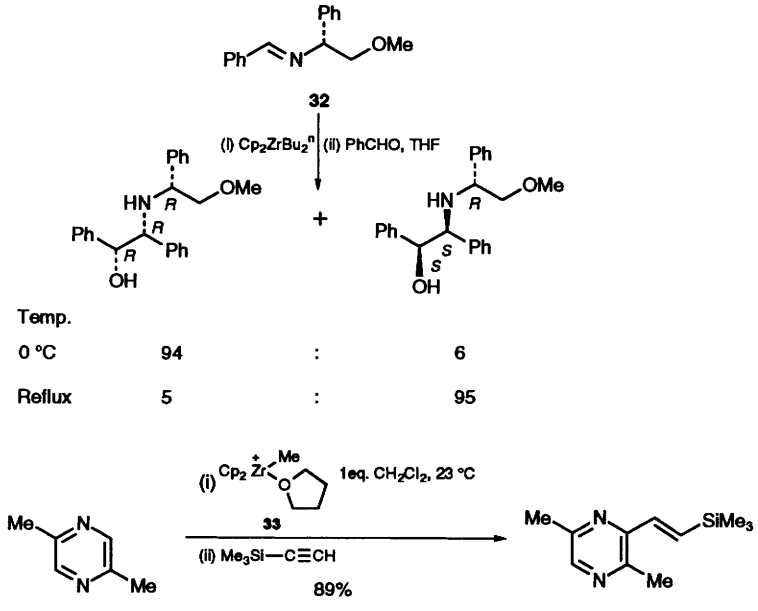
4.2.1 η^3-Complexes of iron tetracarbonyl

The regio- and stereo-selective substitution of an allylic leaving group is commonly achieved *via* π-allyl palladium intermediates in a catalytic manner; however, the more electrophilic π-allyl complexes of iron tetracarbonyl react with a wider range of nucleophiles in a similar but stoichiometric manner. The high degree of stereocontrol associated with reactions *via* cyclic η^3-iron intermediates is exemplified by the synthesis of C-5 substituted pyrrolidinones **34** (**Scheme 26**).[63] Complexation of the homochiral pyrrolidinone **35** gave a mixture of *cis* and *trans* η^2-complexes **36** which could be separated. Lewis acid catalysed reaction with allylsilanes occurred *via* the corresponding η^3-complexes with predominant inversion or retention respectively. Acyclic stereocontrol has also been achieved in the reaction of nitrogen nucleophiles with (*E*)-(4*S*)-(−)-benzyloxypent-2-enoic ethyl ester **37** *via* formation of the intermediate π-allyl complex **38** and regioselective γ-attack on the face of the complex away from the bulky metal moiety (**Scheme 26**).[64]
The Lewis acid catalysed reactions of nucleophiles with iron tetracarbonyl complexes of γ-benzyloxy-α,β-unsaturated ketones **39** also proceeds, to give exclusively the γ-substitution products, with retention of double-bond configuration (**Scheme 26**).[65]

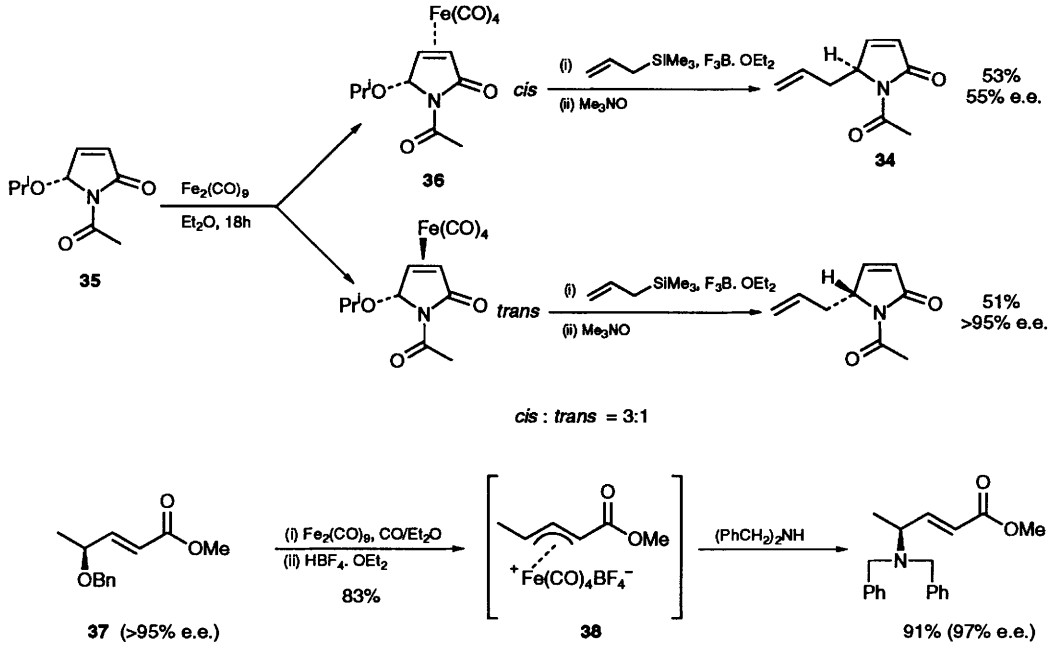
π-Allyl palladium complexes can undergo facile *syn*/*anti* isomerization to the favoured *anti* isomer; however, the corresponding iron tetracarbonyl systems appear stable to isomerization; for example, *E* or *Z* vinyl silanes may be prepared *via* regioselective γ-attack on the stereochemically defined silyl substituted *syn* and *anti* π-allyl complexes **40** and **41** respectively (**Scheme 27**).[66]

4.2.2 η^3-Allyl molybdenum complexes in organic synthesis

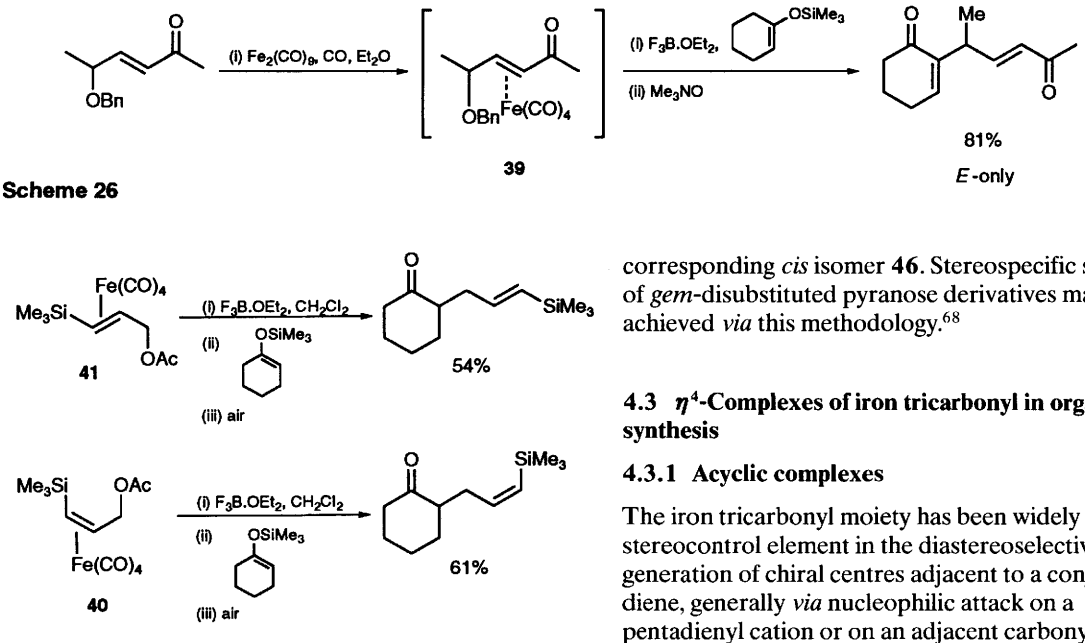
The reactions of aldehydes with allyl molybdenum complexes occurs with high stereoselectivity; however, to date, the ready availablility of homochiral allyl boron and allyl titanium reagents has led to their preferential use in synthesis. Faller has now reported the resolution of η^3-2-methallyl molybdenum complexes *via* the covalent attachment of a camphorsulfonate ligand to the metal. Although this procedure does not yield the homochiral parent η^3-allyl complex, the 2-methallyl complex **42** is



Scheme 25



Scheme 26



Scheme 27

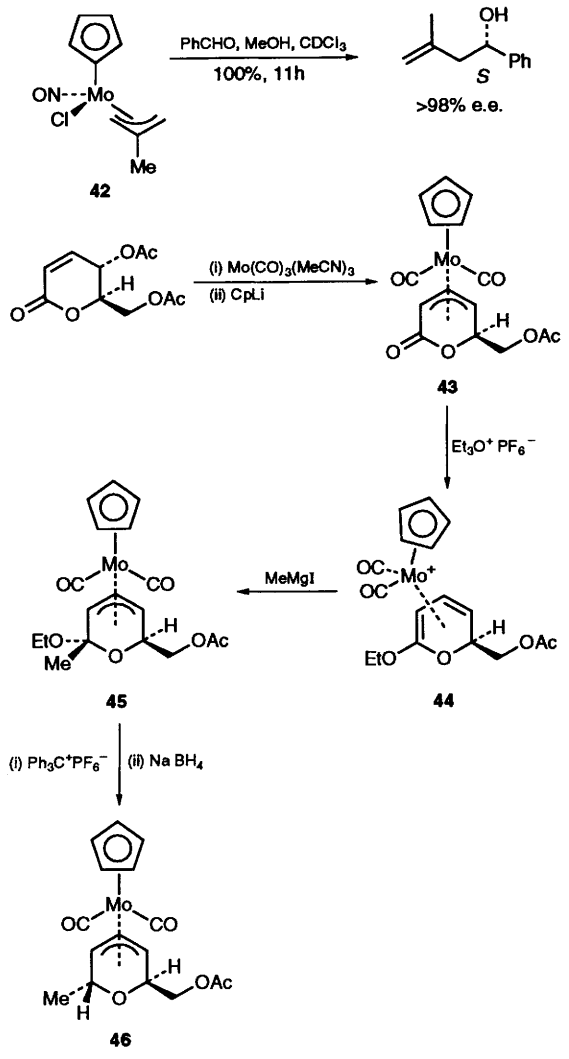
accessible and reacts with aldehydes to give enantiopure allylic alcohols (**Scheme 28**).[67] Cyclic η^3-allylmolybdenum complexes have been used in the enantiospecific synthesis of pyranose derivatives; reaction of the readily available lactone complex **43** (**Scheme 28**) with $Et_3O^+PF_6^-$ generates the air-stable cationic complex **44** which can be reacted with nucleophiles in a highly regio- and stereo-specific manner. The incoming nucleophile approaches the allyl moiety away from the metal, to generate the *trans* isomer **45**. Reformation of the cationic complex and hydride addition gave the corresponding *cis* isomer **46**. Stereospecific synthesis of *gem*-disubstituted pyranose derivatives may also be achieved *via* this methodology.[68]

4.3 η^4-Complexes of iron tricarbonyl in organic synthesis

4.3.1 Acyclic complexes

The iron tricarbonyl moiety has been widely used as a stereocontrol element in the diastereoselective generation of chiral centres adjacent to a conjugated diene, generally *via* nucleophilic attack on a pentadienyl cation or on an adjacent carbonyl group. Methodology exists for preparing homochiral diene iron tetracarbonyl complexes either *via* classical resolution[69] or enzymatic kinetic resolution[70] and these techniques have been expanded upon in the last year.[71]

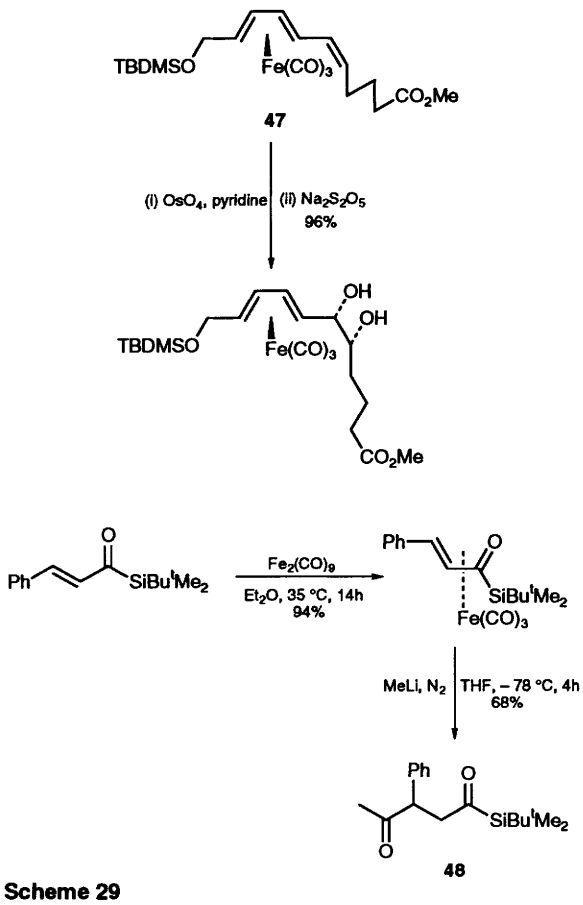
The utility of homochiral η^4-diene iron tricarbonyl complexes in synthesis is exemplified by the recent synthesis of hydroxylated eicosatetraenoic acids by Lellouche and Grée. The key step involves diastereoselective dihydroxylation of the alkene adjacent to the complexed diene moiety of **47** (**Scheme 29**).[72] The diastereoselective alkylation of carbanions generated α- to the complexed dienyl moiety of racemic tricarbonyl(methyl-hexa-3,5-dienoate)iron



Scheme 28

has also been reported.[73] Application of the resolution procedures discussed above should permit the use of this methodology in homochiral synthesis.

The η^4 complexes of α,β-unsaturated ketones with iron tricarbonyl have been extended to the corresponding α,β-unsaturated acyl silanes (**Scheme 29**).[74] Reaction with alkyllithiums generates 1,4-dicarbonyl products **48**, in accord with the chemistry of other η^4-α,β-unsaturated ketone complexes of iron tricarbonyl.



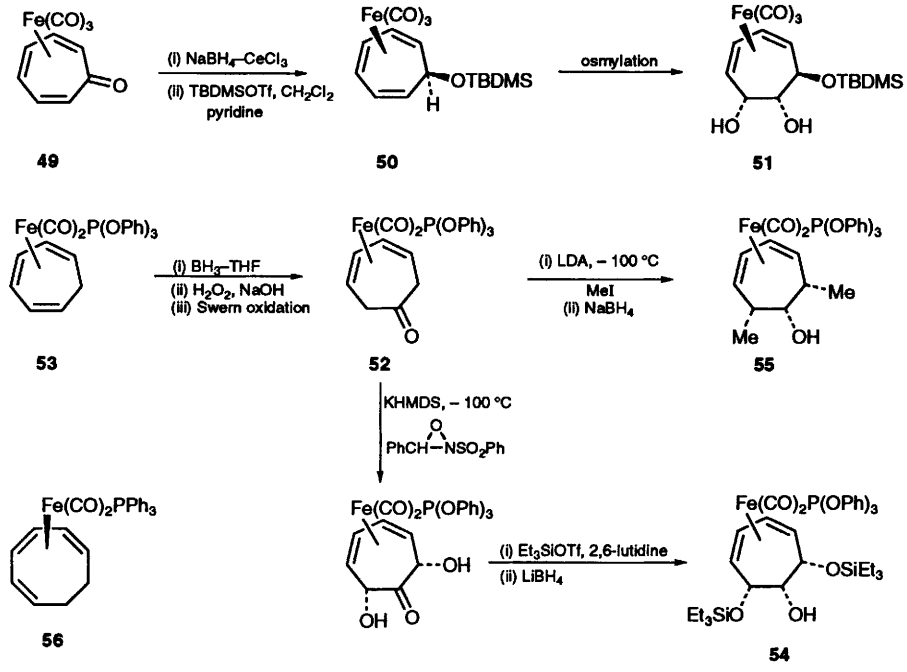
Scheme 29

4.3.2 Cyclic systems

The regio- and stereo-selective functionalization of cycloheptadienones, cycloheptatrienones, and cyclooctadiene *via* their η^4-iron tricarbonyl-type complexes has resulted in some particularly useful applications to organic synthesis in the past year. For example, (η^4-tropone)Fe(CO)$_3$ **49** can be stereoselectively reduced to the protected alcohol **50**; subsequent osmylation gives the single triol derivative **51**, a key precursor for the synthesis of heptitol derivatives (**Scheme 30**).[75] The corresponding cycloheptadienone complex **52** has been prepared *via* highly regio- and stereo-selective iron tricarbonyl directed hydroboration of the η^4-triene complex **53** followed by oxidation (**Scheme 30**). Double hydroxylation of **52** is accomplished *via* sequential treatment with KHMDS and the Davis oxaziridine reagent; alcohol protection and reduction of the central carbonyl moiety then affords the protected triol **54** with three contiguous chiral centres. Dimethylation of **52** followed by reduction of the central carbonyl gives the alcohol **55**. This material is a key precursor for the synthesis of the C-10 to C-13 portion of Calyculin A and the C-19 to C-25 subunit of Swinholide A (**Scheme 30**).[76] It should be noted that in the cycloheptadiene work, one of the ligands on the iron has been replaced with triphenylphosphite, a poorer π-acceptor which reduces competing reactions on the CO ligands. This strategy has been crucial in controlling the chemistry of the corresponding cyclooctadiene derived complexes where replacement of one CO by PPh_3 gives the versatile key intermediate **56** (**Scheme 30**), which can be functionalized either by hydroboration of the uncomplexed alkene, nucleophilic attack on the η^5-dienyl complex, or Friedel–Crafts type alkylation.[77]

4.4 η^5-Cyclohexadienyl iron tricarbonyl cations in synthesis

Nucleophilic attack onto η^5-cyclohexadienyl tricarbonyl iron cations is well researched and occurs exclusively at the termini of the π-system on the face



Scheme 30

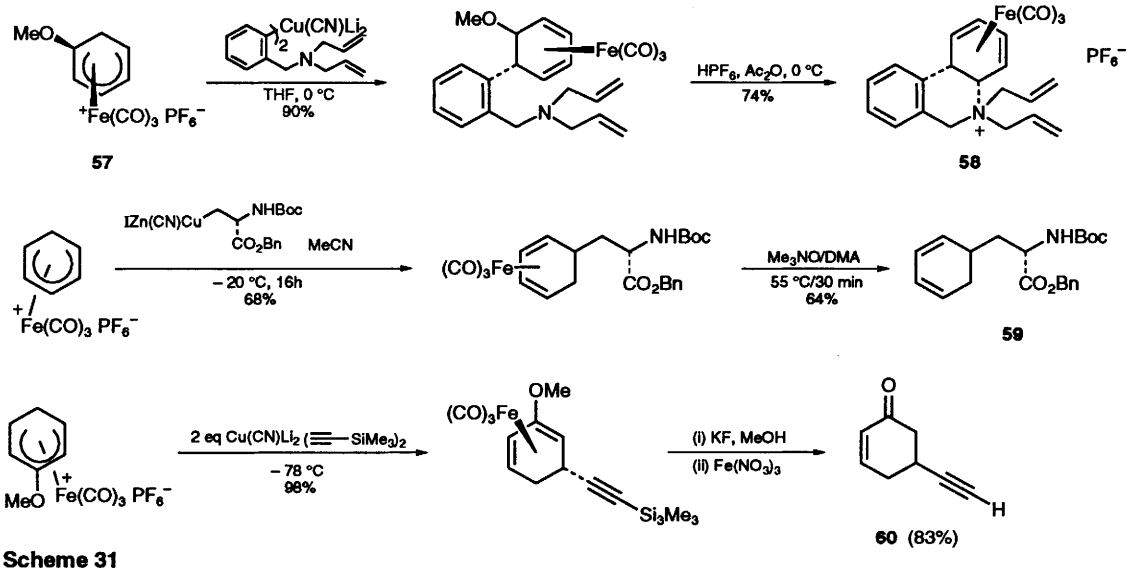
away from the metal moiety. The application of this type of methodology to the synthesis of alkaloid skeletons has recently been reviewed,[78] although McKillop and Stephenson subsequently published a synthesis of tetrahydrophenanthrene derivatives **58** *via* cuprate attack onto the η^5-cyclohexadienyl cation **57** followed by regeneration of the cationic system and spontaneous intramolecular ring closure (**Scheme 31**).[79] Other applications of nucleophilic attack onto η^5-cyclohexadienyl cations have been numerous in the past year; highlights include nucleophilic attack by serine derived zinc/copper reagents in the synthesis of α-substituted amino acids **59** (**Scheme 31**)[80] and nucleophilic attack by alkynyl cuprates to give the substituted cyclohexenone **60** (**Scheme 31**).[81]

The corresponding acyclic η^5-dienyl tricarbonyl iron cationic complexes have been generated in enantiomerically pure form by Donaldson, and applied to the enantioselective synthesis of 5-hydroxyeicosatetraenoic acid methyl ester. A key step involved the reaction of the homochiral cation complex **61** with a cuprate to give the dienediynoate **62** (**Scheme 32**).[82] The ester was subsequently reduced to the aldehyde which was subjected to a second stereocontrolled nucleophilic attack to introduce the chiral centre α-to the diene as required in the natural product.

4.5 η^6-Complexes in organic synthesis

4.5.1 η^6-Arene chromium tricarbonyl complexes in organic synthesis

The preparation of simple enantiomerically pure η^6-arene chromium tricarbonyl complexes as synthons

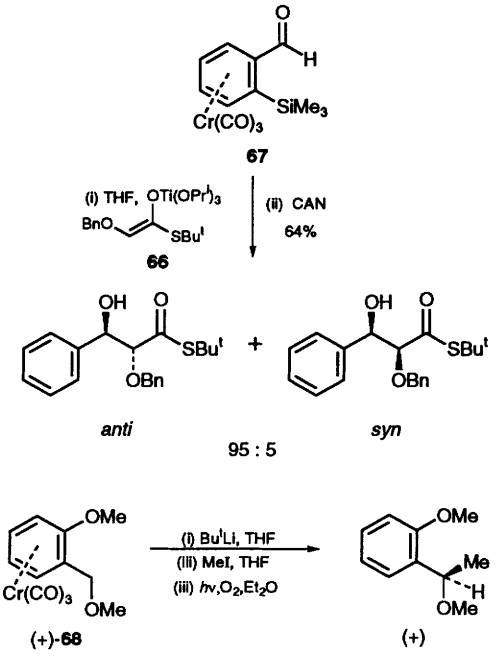


Scheme 31

has been well studied in recent years; the best methods involve resolution of *o*-substituted benzaldehyde chromium tricarbonyl complexes *via* the formation of diastereomeric derivatives.[83] A potentially exciting new approach involves the catalytic asymmetric induction of planar chirality in η^6-(1,2-dichlorobenzene)$Cr(CO)_3$ **63**, *via* palladium-catalysed cross coupling with a vinyl metal species in the presence of a chiral ligand on palladium, although the enantioselectivities to date have been low (**Scheme 33**).[84] Applications of such enantiomerically pure complexes to organic synthesis include the diastereoselective 1,4-additions of cuprates to *o*-substituted *E*-enone complexes **64** (**Scheme 33**)[85] and diastereoselective aldol reactions on the complexed acetophenone **65** (**Scheme 33**).[86]

The nucleophilic addition of the titanium enolate of *S*-t-butylbenzyloxyethanethiolate **66** to the enantiomerically pure aldehyde **67** has been used to give the *anti* aldol product in a highly stereoselective reaction (**Scheme 34**).[87] Stereoselective benzylic alkylation of enantiomerically pure complexes **68** has also been demonstrated (**Scheme 34**).[88]

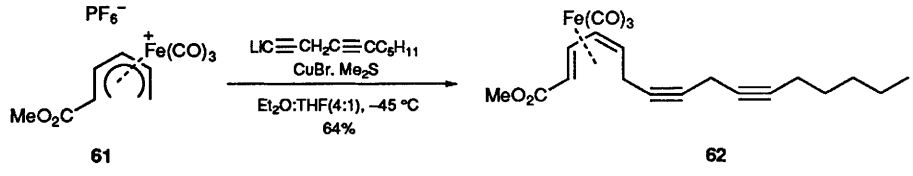
The susceptibility of arene chromium tricarbonyl complexes to nucleophilic attack on the η^6-arene ligand has continued to be exploited. Kundig has extended the previously published tandem nucleophilic addition acyl transfer methodology to homochiral oxazolidinone substituted arene ligands



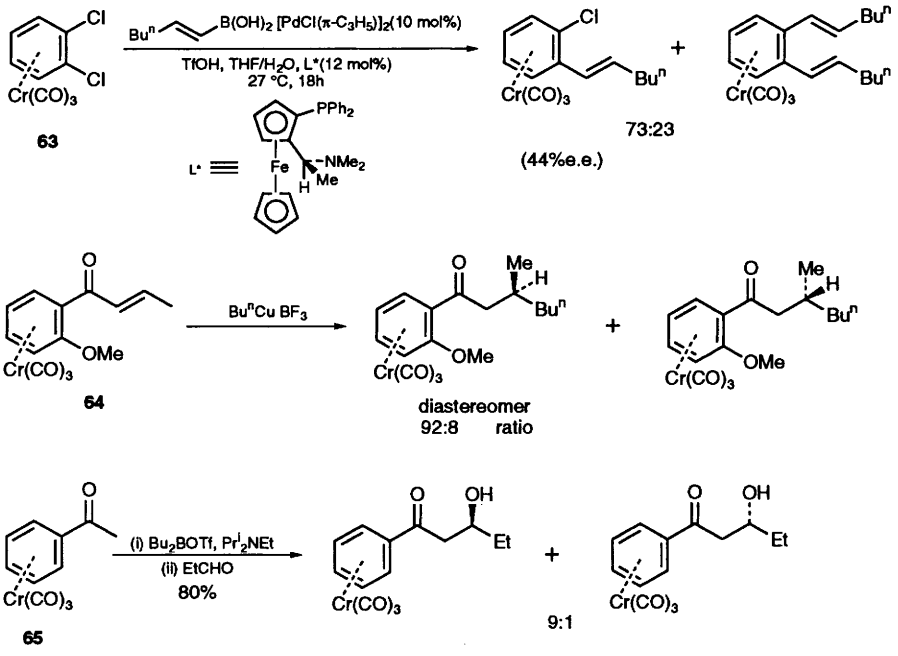
Scheme 34

69; two new chiral centres are generated on a highly functionalized six-membered ring (**Scheme 35**).[89]

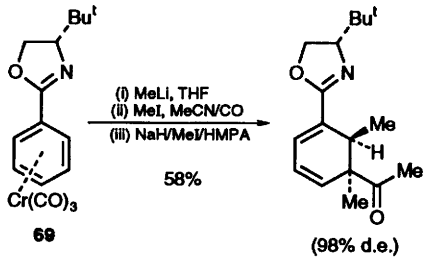
Two total syntheses have recently been described by Semmelhack, both of which involve the nucleophilic



Scheme 32

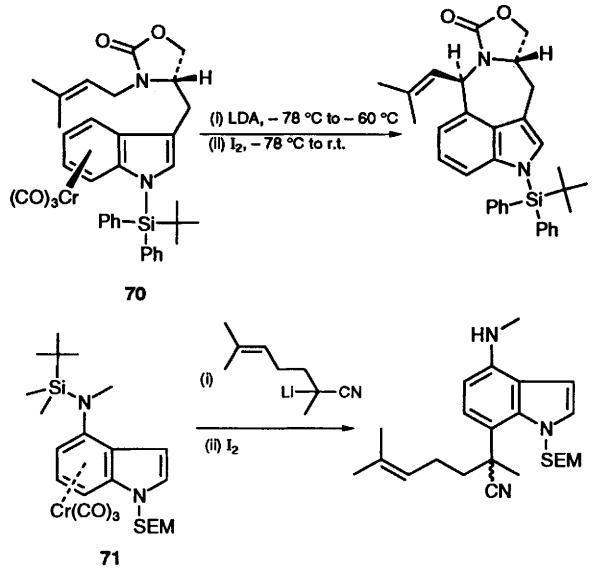


Scheme 33



Scheme 35

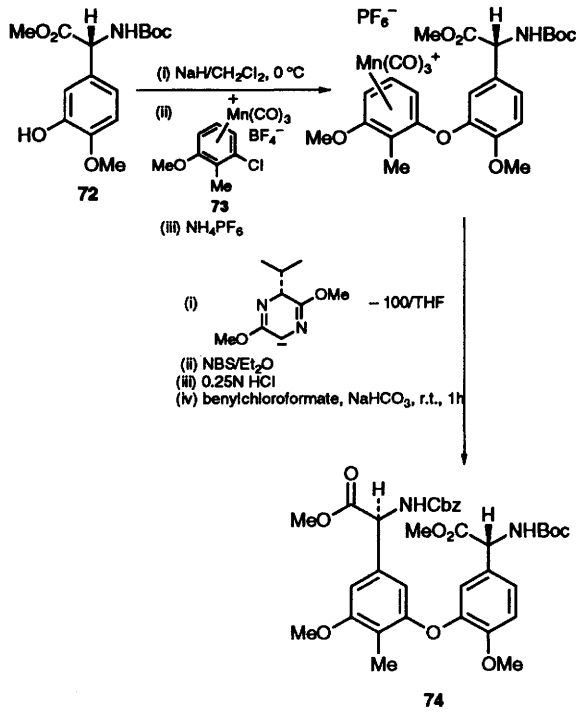
attack of a stabilized carbanion on an (η^6-indole)Cr(CO)$_3$ moiety as the key step. In the total synthesis of Clavucipitic acid an α-amido carbanion is used in the key step of a stereoselective, intramolecular attack on the indole C-4 position of **70**;[90] whilst in a formal total synthesis of Telocidin A the nucleophile is an α-cyano stabilized carbanion which attacks the indole C-7 position of **71**, the alternative C-4 position being blocked (**Scheme 36**).[91]



Scheme 36

4.5.2 η^6-Arene manganese tricarbonyl cations in organic synthesis

η^6-Arene manganese tricarbonyl cations have been less thoroughly investigated than their neutral chromium tricarbonyl counterparts; however, their cationic nature renders them more reactive to nucleophilic attack on the coordinated arene. Grignard reagents,[92] enolate anions, and malonate anions have all been shown to add in an efficient manner; moreover, improved preparative procedures for cationic arene manganese tricarbonyl complexes make their use in organic synthesis more appealing.[93] Pearson has used this methodology in an extension of his previous work[94] to prepare the diaryl ether subunit of Ristocetin A. The key step involves the nucleophilic attack of the protected aryl glycine phenoxide anion **72** onto the arene manganese tricarbonyl cation **73** to generate a highly functionalized diaryl ether which is then subjected to a second nucleophilic attack by the Schöllkopf glycine enolate equivalent to give, after deprotection, the target compound **74** (**Scheme 37**).[95]



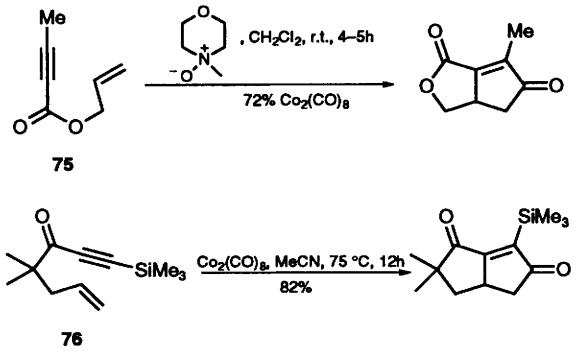
Scheme 37

5 Transition metal mediated cycloadditions in organic synthesis

5.1 The Pauson–Khand and related cycloadditions

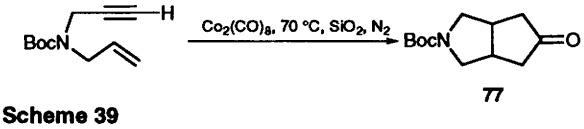
There have been significant improvements in the Pauson–Khand reaction in the last few years; in particular, the use of amine *N*-oxides or phosphine oxides to generate a free coordination site on the cobalt moiety[96] and the use of dry state absorption conditions[97] or sonication[98] to lower the reaction times and temperatures. The use of DMSO in dichloromethane (or benzene) has also been shown to promote the Pauson–Khand reaction.[99] The use of pendant coordinating ligands to accelerate the intramolecular reaction has been explored; for example, pendant sulfides capable of liberating a free coordination site on the cobalt allow high conversions after 15 minutes at 71°C.[100] Recently, the scope of the reaction has also been extended with the finding that electron-deficient alkenes and alkynes can participate. For example, cyclization of the conjugated alkynoates **75** can be achieved using the mild amine *N*-oxide mediated conditions, although the alkyne must bear a terminal substituent for good yields (methyl or phenyl for example) (**Scheme 38**).[101] 1,6-Enynes **76** undergo cycloaddition in acetonitrile at 75°C despite the electron-deficient alkyne moiety; the choice of solvent and the beneficial effect of a *gem*-dialkyl substituent in the ring-closure contributes to the success of this process (**Scheme 38**).[102]

The classical intramolecular Pauson–Khand cycloaddition of *N*-protected propargylamines usually gives unsaturated products *i.e.* 3-azabicyclo[3,3,0]oct-1-ene-7-ones. However, performing the reaction under the dry state absorption



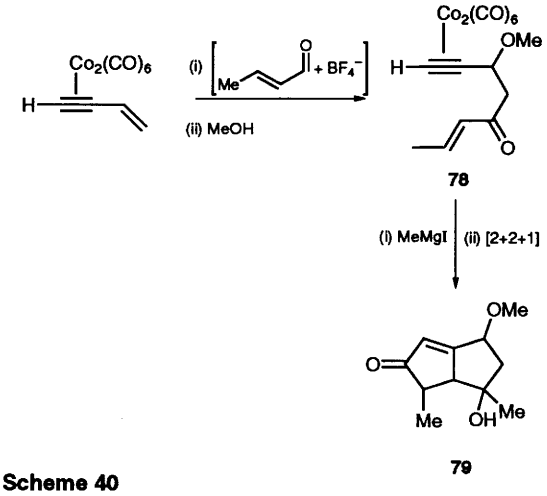
Scheme 38

conditions *vide supra* in an inert atmosphere gives exclusively the saturated bicyclic system **77** (**Scheme 39**).[103]



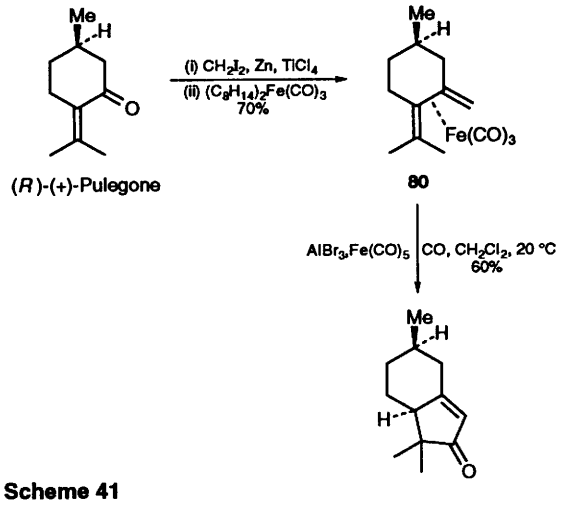
Scheme 39

Several applications of the classical Pauson–Khand reaction to total synthesis have been reported in the last year, including the preparation of pentalenone,[104] whilst the milder amine *N*-oxide promoted cycloadditions have been used in the total synthesis of Loganin[105] and (−)-Kainic acid.[106] A combination of the ability of cobalt complexed alkynes to stabilize a propargylic cation and then to promote a cycloaddition has been used before as a strategy in total synthesis.[107] A new version of this approach involves the electrophilic addition of an α,β-unsaturated carbonyl compound to a cobalt complexed conjugated enyne to give the Pauson–Khand precursor **78**; after reduction of the α,β-unsaturated ketone to an allylic alcohol, this then cyclizes to afford the highly functionalized bicyclic system **79**. A range of tri- and tetra-cyclic skeletons were prepared using this powerful methodology (**Scheme 40**).[108]



Scheme 40

The Pauson–Khand type cyclization reaction has also been achieved with $Mo(CO)_6$ in the presence of DMSO,[109] $W(CO)_5THF$,[110] $Ni(CO)_4$,[111] and $Fe(CO)_5$.[112] A potentially useful iron-mediated carbonylative cycloaddition of 1,1,3 trisubstituted conjugated dienes **80** has also been reported (**Scheme 41**).[113]



Scheme 41

5.2 Titanium- and zirconium-mediated cycloadditions

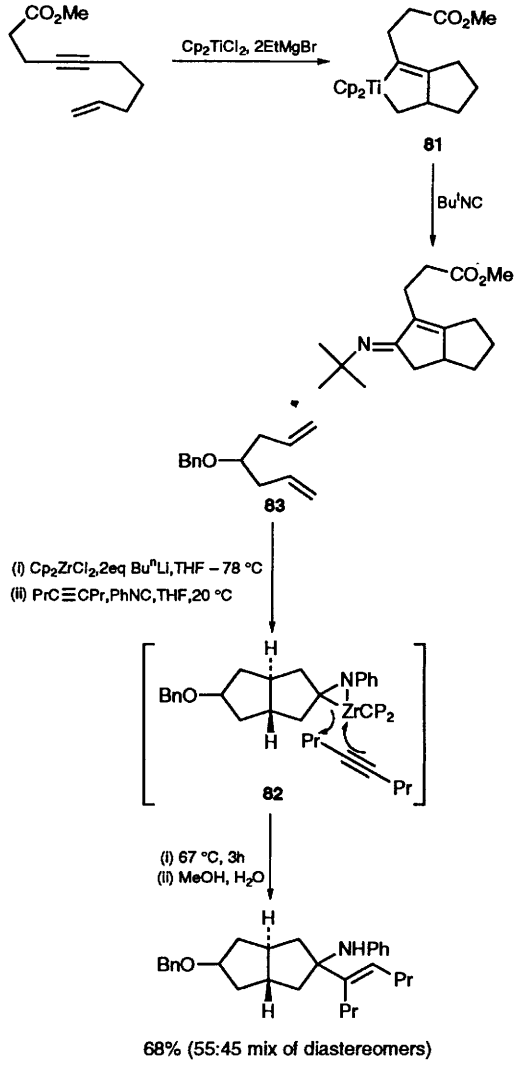
The well known reductive cyclization of enynes mediated by zirconium or titanium metallacycle formation has continued to be applied to organic synthesis. The lower oxophilicity of titanium *versus* zirconium allows a wider functional group tolerance in this type of reaction. Advances have been made in methods for functionalization of the intermediate metallacycles (see also section 1.3); for example, trapping of metallacycle **81** with an isocyanide allows the introduction of an exocyclic nitrogen (**Scheme 42**),[114] and whilst one further C–C bond forming step has been incorporated by interception of the η^2-imine complex **82** from isocyanide trapping of the intermediate zirconacycle formed from cycloaddition of the diallyl species **83** (**Scheme 42**).[115]

A particularly elegant application of the zirconium-mediated carbonylative cyclization strategy is the recently published synthesis of Dendrobine by Mori in which the key step involves a regio- and stereo-controlled construction of the tricyclic Dendrobine skeleton **85** in a single step from an enantiomerically pure carvone derivative **84** (**Scheme 43**).[116]

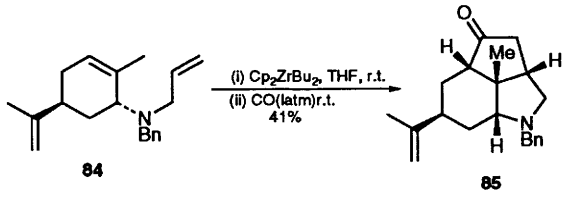
Stille has recently published a carbocycle-forming reaction which occurs *via* intramolecular insertion of alkynes into Ti–C bonds (**Scheme 44**).[117] This type of reaction has previously been accomplished with alkyl magnesiums and alkyl lithiums. The advantage of the titanium species is their relative stability towards hydrolysis and air oxidation. The reactions proceed in high yield under Lewis acid catalysis.

5.3 Cobalt-mediated cyclotrimerizations

The formation of aromatic rings *via* cobalt-mediated [2 + 2 + 2] cycloadditions has continued to be applied



Scheme 42

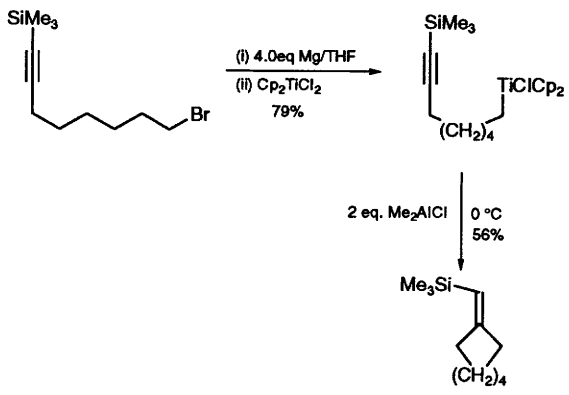


Scheme 43

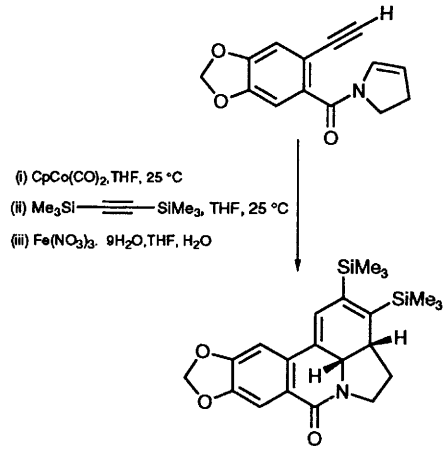
in synthesis;[118] a particularly interesting report concerned the use of supercritical water (374°C) to promote the cyclotrimerization of alkenes.[119] A recent approach to the synthesis of the alkaloid Lycorane (**Scheme 45**) illustrates the rapid construction of polycyclic systems *via* the cobalt-mediated [2 + 2 + 2] cyclization strategy.[120]

5.4 Higher order [6π + 4π] and [6π + 2π] cycloadditions

A relatively new development in metal promoted cycloaddition chemistry is the use of chromium tricarbonyl coordinated trienes in higher order [6π + 4π] and [6π + 2π] cycloaddition reactions.

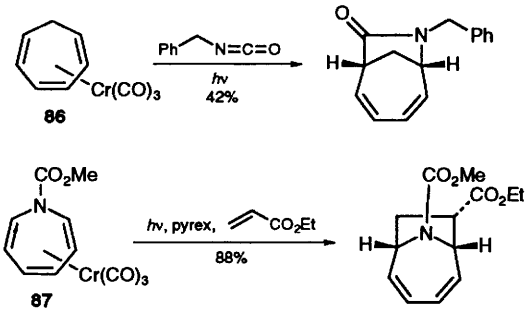


Scheme 44



Scheme 45

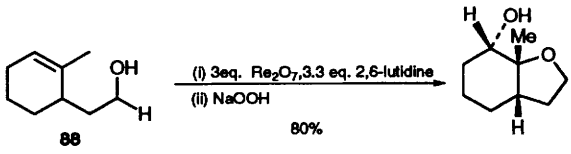
Several synthetically useful variants of this strategy have been reported over the past year, including reactions of coordinated cycloheptatrienes **86** with isocyanates (**Scheme 46**)[121] and the reaction of coordinated *N*-carboxyazepines **87** with 4π and 2π systems (**Scheme 46**).[122] The intramolecular versions of these reactions have also been reported[123] and, more significantly, a catalytic version.[124]



Scheme 46

5.5 Rhenium-promoted cycloadditions

One stoichiometric rhenium-promoted cycloaddition reaction is of particular note, namely the oxidative cycloaddition of γ-alkoxyalkenes (*e.g.* **88**), mediated by Re_2O_7 (**Scheme 47**).[125] This reaction presumably



Scheme 47

proceeds *via* the perrhenate ester which undergoes a Sharpless-type [2 + 2] addition to the double bond, affording a metalaoxetane.

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