Stoichiometric organotransition metal complexes in organic synthesis

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Reviewing the literature published between 1 September 1993 and 31 August 1994

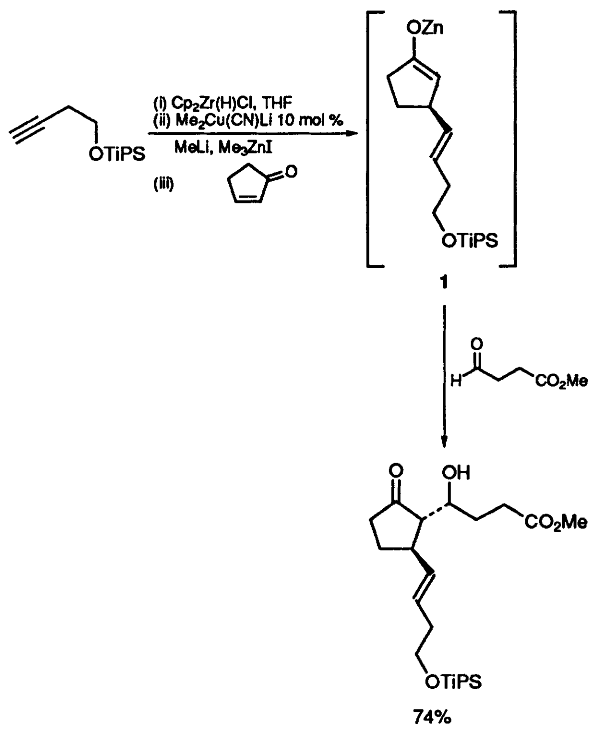
1 Introduction

This review covers the literature from 1 September 1993 to 31 August 1994 and is a selective account of recent developments in the application of stoichiometric organotransition metal chemistry to organic synthesis. The format is similar to last year's review[1] although the section on carbene complexes has been further subdivided. New areas which have come to the fore in the last year include the use of manganese enolates for regioselective ketone alkylation (Section 2.7), the use of η^2-osmium complexes to control the reactivity of aromatic systems (Section 4.3) and the synthesis of peptides containing unnatural amino acids using chromium carbene complexes (Section 3.4). Notable synthetic applications of η^4-diene tricarbonyl iron complexes (Section 6.1) and the intramolecular Pauson–Khand reaction (Section 9.1) have been published. Several general reviews have appeared covering organozirconium chemistry,[2] higher order transition metal promoted cycloadditions[3] and organonickel chemistry;[4] an interesting account of the relative electrophilicity and nucleophilicity of organometallic complexes has also appeared.[5] Other reviews relevant to a particular area are cited in the text.

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

2.1 Hydrozirconation methodology

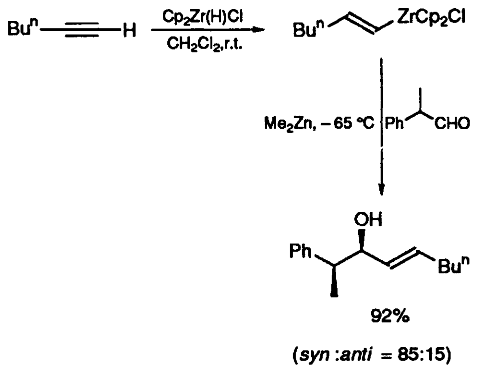
New and useful extensions to the classical hydrozirconation methodology originally developed by Schwartz[6] have continued to be published this year. A simple but noteworthy example is the preparation of tritiated Schwartz reagent which should prove useful for the regioselective radiolabelling of molecules undergoing metabolic studies.[7] Of particular interest to the synthetic organic chemist are methods to elaborate the C–Zr bond formed in hydrozirconation reactions. Lipshutz has developed a catalytic version of his earlier work on the copper-mediated transfer of vinyl groups from zirconium to the β-position of enones.[8] Key to this advance was the addition of Me_3ZnLi which regenerates the copper species $Me_2Cu(CN)Li$ *in situ* without reacting with the enone. The zinc enolate **1** formed in this procedure may be trapped by an aldehyde in a remarkable six step one-pot synthesis of the prostanoid skeleton (**Scheme 1**). This work should



Scheme 1

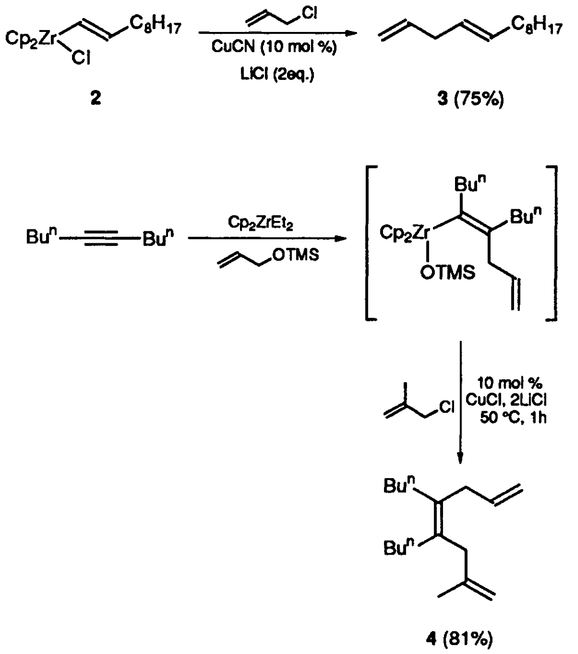
be compared with that of Wipf who has published a similar process whereby alkylzirconium species add to the β-position of enones in the presence of 3–10 mol% CuBr.SMe$_2$ or CuCN. Here the resulting zirconium enolate may be trapped with an aldehyde; the addition of alkylzincs to regenerate the catalytic copper(I) species is not necessary.[9]

Wipf has also published an efficient synthesis of allylic alcohols via dialkylzinc-mediated transmetallation of alkyne hydrozirconation products and aldehyde trapping.[10] An important aspect of this work is the stereoselective addition to α-substituted aldehydes to give predominantly the *syn*-isomer (**Scheme 2**). This is an improvement over the non-selective AgClO$_4$-mediated coupling of alkenylzirconates with aldehydes developed by Suzuki.



Scheme 2

In another synthetically useful procedure involving copper catalysis, Takahashi has prepared a variety of dienes or 1,4,7-trienes.[11] Trapping of an alkyne hydrozirconation product **2** with allyl chloride in the presence of catalytic CuCN gives the skipped diene **3** accompanied by a small amount of dimerization product. Use of the previously reported allylation of zirconacycles[12] followed by a copper-catalysed allylation gives the 1,4,7-trienes **4** (**Scheme 3**).



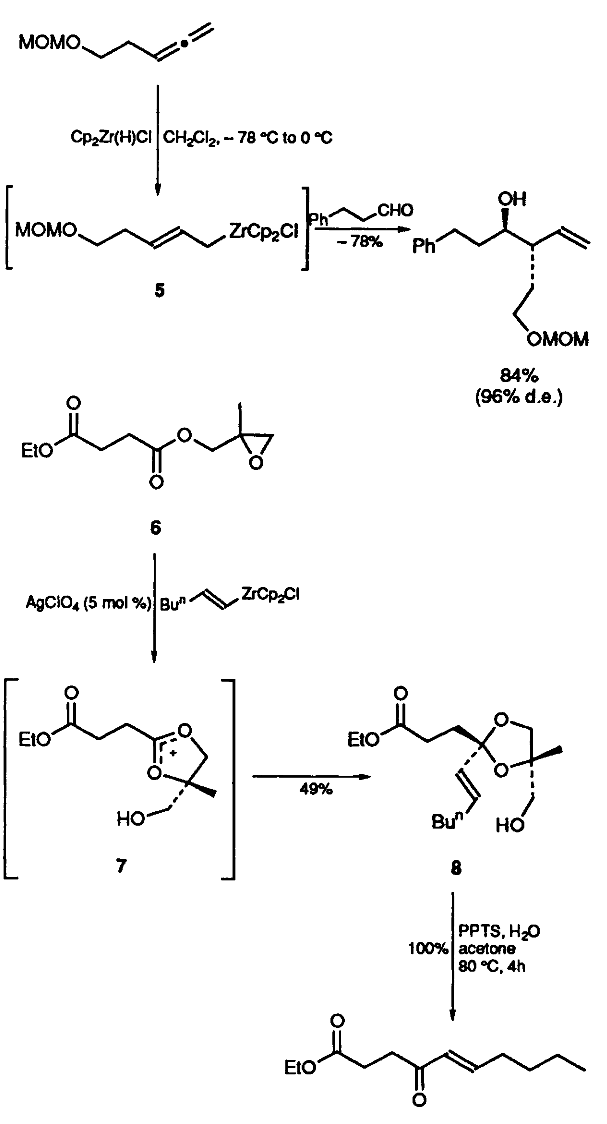
Scheme 3

Chemoselective hydrozirconation of alkenes or alkynes in molecules containing reactive carbonyl groups has been achieved by the simple expedient of protecting the carbonyl as the acyl silane.[13] This prevents both hydride addition to the carbonyl and intramolecular chelation of the carbonyl oxygen to the coordinatively unsaturated zirconium, thereby rendering it unreactive under transmetallation conditions.

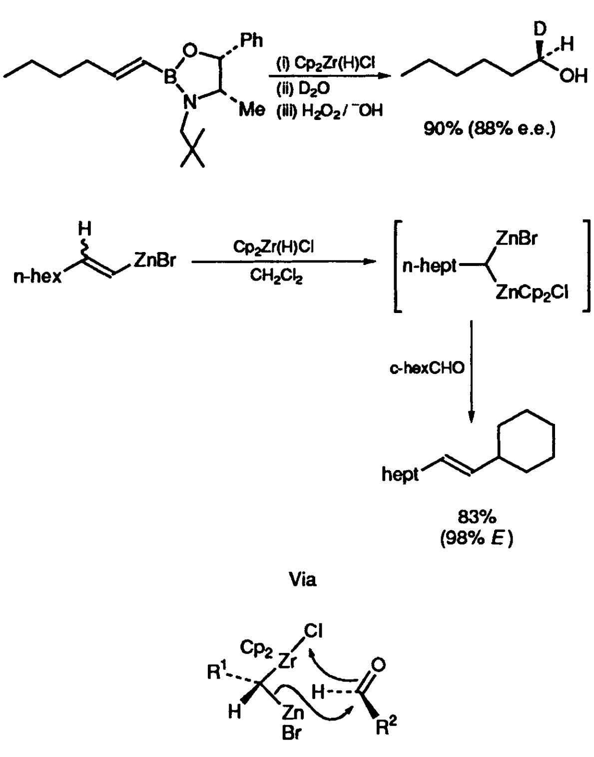
Following his work on the hydrozirconation of allenylstannanes to give terminal dienes,[14] Suzuki has reported the hydrozirconation of an isolated terminal allene and subsequent trapping of the allylzirconium species **5** with aldehydes and ketones to give homoallylic alcohols in a highly regio- and stereo-selective manner (**Scheme 4**).[15] Low temperatures and the use of dichloromethane as solvent are crucial to the success of these reactions.

Wipf has published an interesting series of reactions which further exploit the AgClO$_4$-mediated epoxide rearrangements published last year.[16] Treatment of the succinate **6** with hexenylzirconocene in the presence of 5 mol% AgClO$_4$ initially generates the cationic intermediate **7** which undergoes a chelation-controlled attack of the alkenyl zirconium reagent to give the acetal **8** (**Scheme 4**).[17] A version of this reaction catalytic in zirconium (10 mol%) and AgClO$_4$ (10 mol%) was also reported in the same paper.

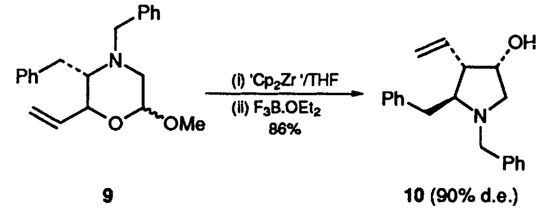
Srebnik has continued his elegant work on the hydrozirconation of vinylboranes[18] to give α-haloboranes which are valuable intermediates for aminoboronic acid synthesis.[19] This provides a useful



Scheme 4



Scheme 5



Scheme 6

alternative to the methodology of Matteson.[20] Of particular note is the use of optically pure vinylboranes bearing a chiral ligand on boron which undergo diastereoselective hydrozirconation (**Scheme 5**).[21] The hydrozirconation of alkenylzincs to give the 1,1-bimetallic of Zn and Zr has been published by Knochel; trapping with aldehydes give (*E*)-alkenes in a highly selective manner (**Scheme 5**).[22]

2.2 Allyl zirconium species

Taguchi, Takahashi, and co-workers have pioneered the generation of allylzirconium species by β-elimination of an alkoxy group in the zirconocene complex of an allylic ether.[23] This methodology has now been applied to a highly diastereoselective ring-contraction process.[24] For example, treatment of the homochiral vinylmorpholine **9** with 'Cp_2Zr' gave the pyrrolidine **10** via an intermediate allyl zirconium species (**Scheme 6**).[25] The stereochemistry of the product depends only on the configuration of the amino acid used to prepare the vinylmorpholine. This method was used to prepare the pyrrolidizine alkaloid (–)-macronecine in five steps (10% overall yield) from *N*-Boc-L-proline methyl ester. Taguchi has also used this type of ring-contraction to prepare cyclobutanes from 4-vinylfuranosides.[26]

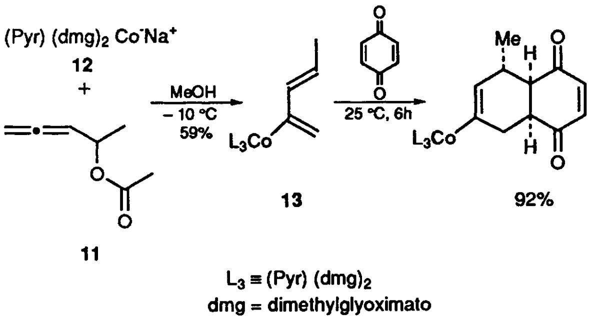
2.3 Alkyl, allyl, alkenyl, and alkynyl chromium species in synthesis

This topic has recently been the subject of an excellent review by Hodgson;[27] however, several subsequent publications have extended the synthetic applicability of alkyl, allyl, alkenyl, and alkynyl chromium reagents. Wipf has developed a low-temperature version of the Nozaki–Hiyama coupling reaction which allows the addition of organochromium reagents to sensitive molecules.[28] Hodgson has recently reported an efficient homologation of aldehydes to the corresponding methyl ketones via Cr^{II}-mediated addition of Me_3SiCBr_3.[29] Also of note, Taddei has used a classical Nozaki coupling to prepare hydroxyethylene isosteres of peptidic linkages[30] and Kibayashi has used the coupling as the key step in a synthesis of allopumiliotoxins 267A and 339A.[31]

2.4 Alkyl and alkenyl cobalt species in synthesis

Most of the chemistry associated with these species has involved the use of alkylbis(dimethylglyoximato)cobalt complexes as radical-trapping and radical-generating reagents. In particular, the mild homolytic functionalization of the organic ligand has been applied to organic synthesis.[32] However, a recent publication from Orsini dealt with the application of Co^0 species to C–C bond formation in a cobalt version of the Reformatski-reaction.[33] The active species $Co[PMe_3]_4$ was generated *in situ* from $CoCl_2$ and PMe_3. This method has the advantage of mild reaction conditions and higher yields when compared with the zinc-mediated Reformatski-reaction; moreover, only 1,2 addition is observed with enones. The disadvantage is the use of PMe_3; however, in the same paper Orsini also demonstrated that the reaction proceeds with catalytic amounts of $CoCl_2/PMe_3$ as long as magnesium turnings are added to the reaction (magnesium alone does not mediate the coupling).

An interesting paper from Welker has highlighted the use of η^1-cobalt substituted butadiene complexes in Diels–Alder cycloadditions.[34] The diene complexes are prepared in high yield from the corresponding allene **11** and a stabilized cobalt anion **12** (**Scheme 7**). A bulky cobalt ligand at the 2-position of the diene serves to enforce a predominantly *s-cis* diene conformation such that Diels–Alder reactions occur under mild conditions; moreover, the reaction of dienophiles with complex **13** proceeds in an *exo*-selective manner in contrast to standard Lewis acid or thermal Diels–Alder reactions. The cobalt-containing products may be functionalized in a variety of ways with maintainance of stereochemical integrity.

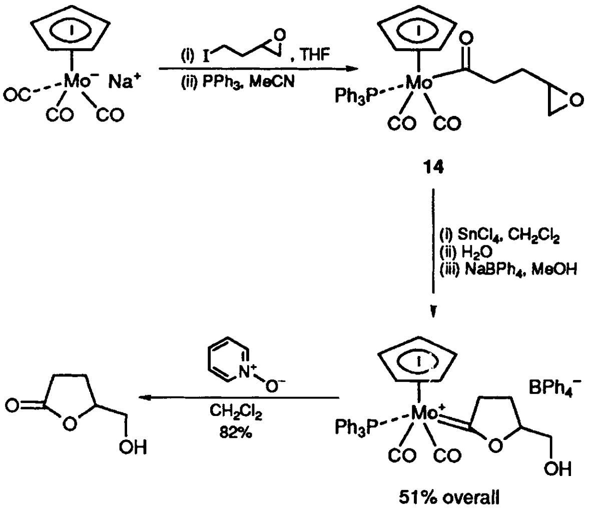


Scheme 7

2.5 Acyl transition metal complexes in synthesis

Davies has published an efficient method for the kinetic resolution of the widely used chiral auxiliary $CpFe(CO)PPh_3COMe$ via aldol reaction of the lithium enolate with (1*R*)-(+)-camphor,[35] whilst Brunner has used the auxiliary in an asymmetric synthesis of a precursor to verapamil.[36]

Marson has published an interesting application of molybdenum acyl complexes to the synthesis of hydroxymethyl lactones and spiroketals (**Scheme 8**).[37] The key to this process is the $SnCl_4$-mediated intramolecular cyclization of the acyl oxygen of **14** onto a pendent epoxide.



Scheme 8

2.6 Chiral rhenium complexes in synthesis

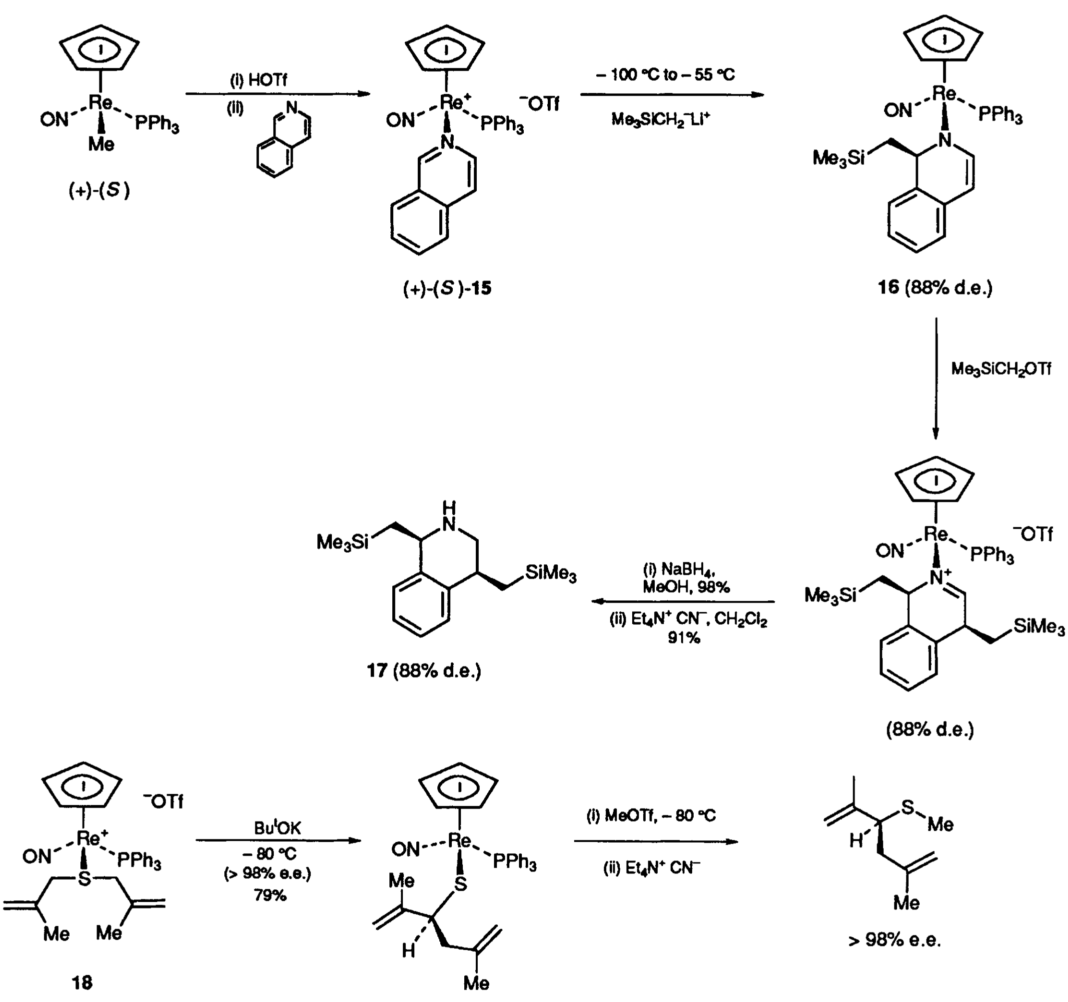
Gladysz has published an interesting procedure for the synthesis of optically pure 1-substituted or 1,4-disubstituted tetrahydroisoquinolines via coordination of isoquinoline to the chiral auxiliary $CpReNO(PPh_3)$ to give the homochiral (+)-(S)-cation **15** (**Scheme 9**).[38] This cation, on treatment with Me_3SiCH_2Li at −55°C, generates the enamine **16** (88% d.e.) which can subsequently be alkylated at the 4-position (also 88% d.e.). Reduction of the iminium salt and removal of the auxiliary gives the optically pure tetrahydroisoquinoline **17** in good yield. The same chiral auxiliary has been used by Gladysz for the enantioselective synthesis of sulfides via a [2,3] sigmatropic rearrangement of the ylid derived from the coordinated diallyl sulfonium salt **18** (**Scheme 9**).[39]

2.7 Manganese enolates

Several papers have appeared over the last year which highlight the use of manganese enolates for the regioselective monoalkylation of ketones. This chemistry represents a significant advantage over the corresponding lithium enolates which often give non-regioselective or polyalkylated by-products. Manganese enolates are efficiently obtained by reaction of ketones with Mn-amides [*e.g.* PH(Me)NMnCl] at −10°C to 20°C in THF; subsequent alkylations are greatly facilitated by the addition of a polar solvent such as DMSO.[40] Trapping of the enolates with Me_3SiCl gives silyl enol ethers in a highly regioselective manner.[41] Alternatively, manganese enolates may be obtained by transmetallation of the corresponding lithium enolates.[42]

3 Group 6 transition metal carbene complexes in synthesis

A large volume of work has been published in this area over the last year, particularly in the field of chromium



Scheme 9

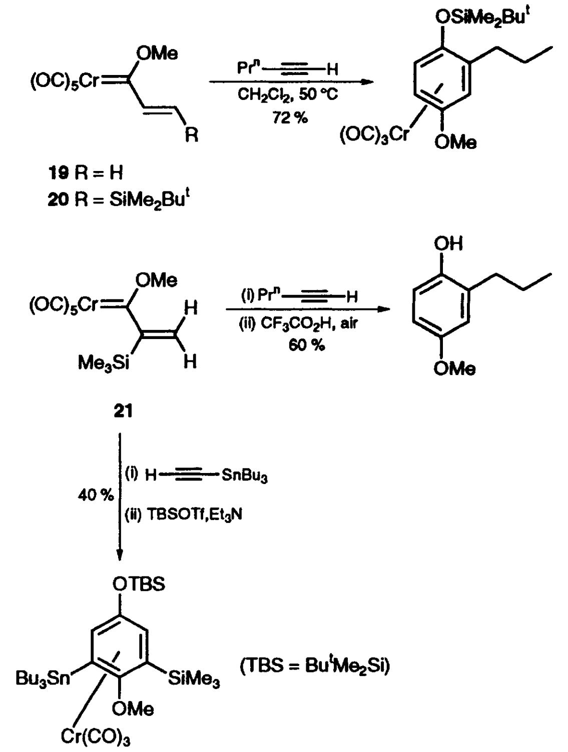
carbene chemistry and readers are referred to a good short review by Schmalz[43] which highlights the major developments in chromium carbene complexes as applied to organic synthesis.

3.1 Annulation reactions

Group 6 transition metal carbene mediated reactions have been the subject of intense mechanistic study; Wulff[44] and Harvey[45] have published papers which allow rational predictions of reactivity and reaction pathways to be made in this complicated area and their results, coupled with further understanding of the processes involved, will allow optimization of synthetically useful carbene-mediated reactions.

Key synthetic advances have also been made in the last year; for example, a simple and efficient new preparation of alkoxycarbene complexes containing functional groups in the alkoxy moiety has been reported which involves the alkylation of tetramethylammonium alkoxide salts with alkyldiphenylsulfonium salts.[46] Treatment of the vinylcarbene complex **19** (**Scheme 10**) with alkynes to produce phenols has not proven synthetically useful; however, Wulff has demonstrated that the α- or β-silylvinylcarbene complexes **20** or **21** are useful synthons, stable enough to undergo annulation reactions.[47] In **20** the silicon moiety migrates to the phenolic oxygen, rendering the products stable and isolable while for **21** the silicon is incorporated in the product aromatic ring and may be replaced (*e.g.* by proteodesilylation as illustrated). The regiochemistry of the alkyne insertion is of note; the larger alkyne substituent is incorporated adjacent to the phenolic oxygen. For stannyl substituted alkynes this regiochemistry is reversed thereby placing tin *meta* to the phenolic oxygen. For stannyl substituted alkynes this regiochemistry is reversed thereby placing tin *meta* to the phenolic oxygen (**Scheme 10**);[48] the tin residue can subsequently be exchanged with lithium or substituted using palladium-mediated couplings. Chan has used silyl substituted alkynes in an approach to regioselective quinone synthesis; as observed for the stannyl group above, the silyl is incorporated *meta* to the phenolic oxygen and can be converted into iodide to allow subsequent palladium-catalysed reactions.[49]

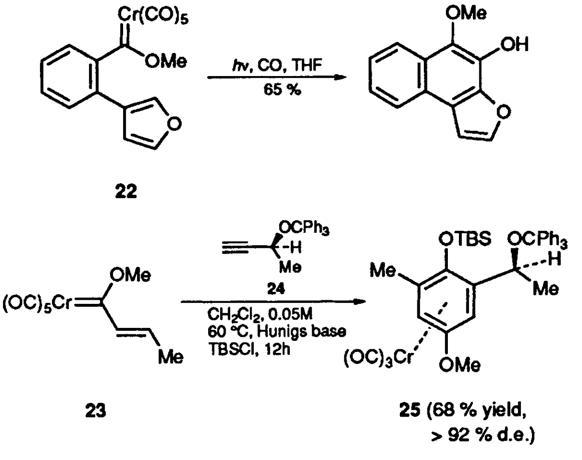
Following on from his earlier work,[50] Merlic has published an efficient photochemical benzannulation of biarylcarbene complexes which proceeds with particularly good chemoselectivity with furyl and



Scheme 10

naphthalene substituted substrates (**Scheme 11**).[51] Synthesis of the biaryl carbene precursor **22** is accomplished in high overall yield using a palladium-catalysed cross-coupling.

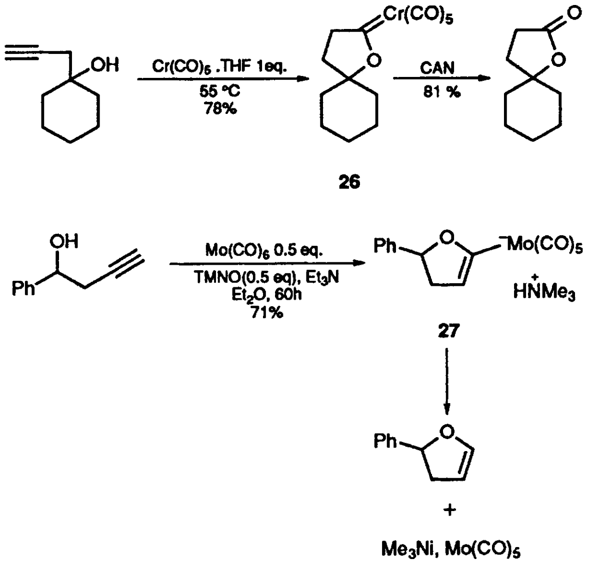
Wulff has recently published a stereoselective synthesis of an arene $Cr(CO)_3$ complex in which benzannulation of the propenyl complex **23** with the homochiral alkyne **24** leads to **25** with remarkably high diastereoselectivity (> 92%). The propargylic oxygen appears to play a key stereoelectronic directing role (**Scheme 11**).[52]



Scheme 11

3.2 Spirocycle synthesis

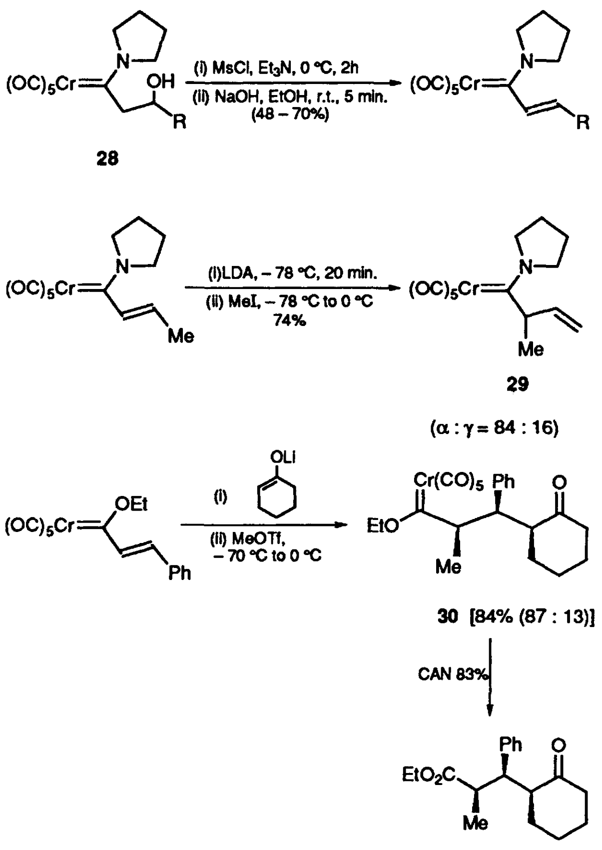
Two papers have been published which explore the chromium-mediated cyclization of 1-alkyn-4-ols. Quayle has prepared a variety of spirocyclic carbene complexes **26** via exposure of the alkynols to THF.$Cr(CO)_5$ generated from photolysis of $Cr(CO)_6$ in THF (**Scheme 12**).[53] Oxidative removal of the chromium reveals the target γ-lactones. Similarly, McDonald has found that chromium, tungsten, or preferably molybdenum hexacarbonyl can be used to cyclize 1-alkyn-4-ols to the corresponding 2,3-dihydrofurans in the presence of trimethylamine-*N*-oxide (TMNO), which induces the loss of one CO ligand;[54] note that less than one equivalent of metal is required since molybdenum is lost from the intermediate **27** under the reaction conditions to generate a catalytically active species. This should be compared with the requirement for oxidative removal of the metal in the work of Quayle.[53]



Scheme 12

3.3 Vinyl carbene complexes

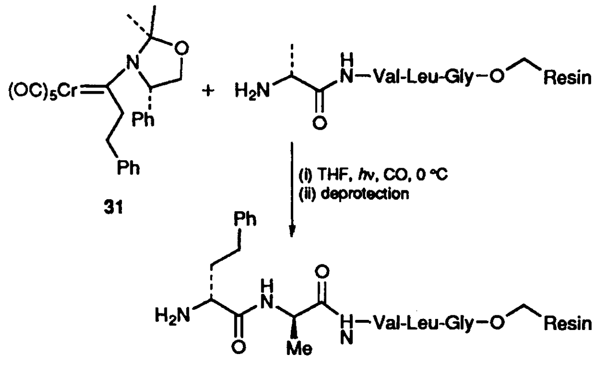
A simple and efficient procedure for the preparation of alkylidenepyrrolidinocarbenes of chromium has been published by Maiorana and Papagni using the base-catalysed elimination of the previously precedented aldol products **28** (**Scheme 13**).[55] The reaction of these alkylidene complexes with LDA at low temperature and trapping with electrophiles gives predominantly the α-substituted products **29** (**Scheme 13**).[56] Of particular interest is the stereoselective tandem Michael addition–alkylation of ketone enolates to vinylalkoxycarbene complexes published by Nakamura (**Scheme 13**).[57] The high yields in most of these reactions offer advantages over the corresponding Michael addition of ketone enolates to α,β-unsaturated esters which are less efficient. Particularly noteworthy are the high *syn* stereoselectivity and the options for subsequent functionalization of the carbenoid products **30**. A useful example of the Michael addition of imines to alkynylcarbene complexes of chromium leading to an efficient three-step synthesis of 2*H*-pyrroles has also been published.[58]



Scheme 13

3.4 Amino acid and peptide synthesis

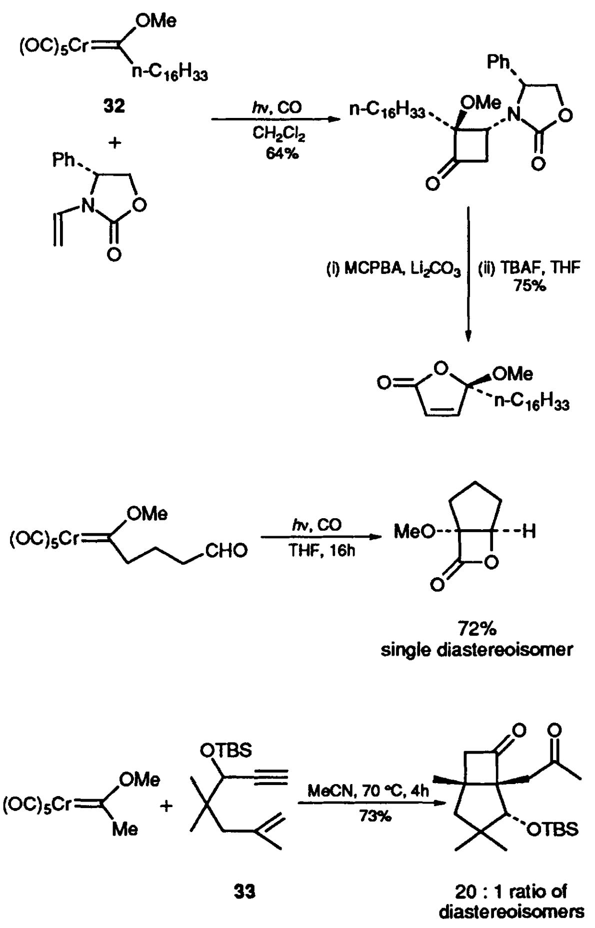
Hegedus has continued his elegant work on stereoselective peptide synthesis via photolytic coupling of chromium aminocarbene complexes.[59] Photolysis of optically pure chromium aminocarbene complexes **31** in the presence of peptide methyl esters gives the protected tetrapeptide esters in good yield; moreover, this reaction can be achieved with the peptide supported on Merrifield resin (**Scheme 14**).[60] The main advantages here are that the coupling is induced by visible light and that unnatural amino acid fragments may be directly incorporated into the growing peptide chain without the need to presynthesize the amino acid directly. The synthesis of homochiral unnatural amino acids has also been achieved.[61]



Scheme 14

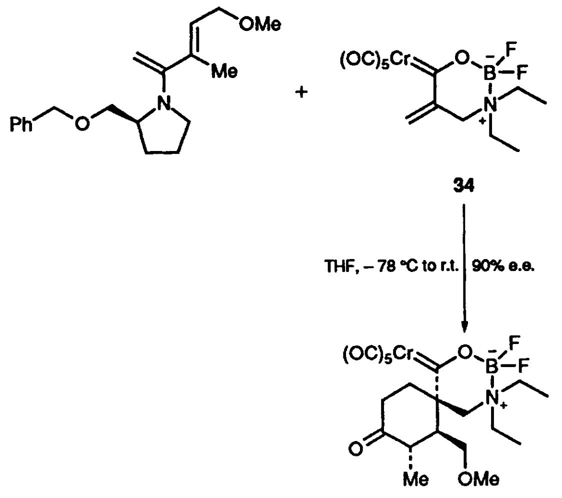
3.5 Carbene-mediated cycloadditions

Hegedus has published a detailed study of electronic effects on the stereochemical outcome of the [2 + 2] cycloaddition of chromium carbene complexes with imines to form β-lactams.[62] Optically active butenolides have been prepared using the photolytic [2 + 2] cycloaddition of chromium alkoxycarbene complexes **32** to homochiral ene-carbamates (**Scheme 15**).[63] Although cyclobutanone formation in the above case is relatively rapid, the corresponding [2 + 2] cycloaddition of chromium alkoxycarbene complexes with aldehydes to give β-lactones is slow and only synthetically useful in an intramolecular sense (**Scheme 15**).[64] Intramolecular [2 + 2] cycloaddition with an alkene to give a metallocyclobutane intermediate has been published by Soderberg as a route to indoles and quinolines.[65] The reaction of Fischer carbene complexes with enynes (*e.g.* **33**) gives cyclobutanones via a similar intramolecular [2 + 2] cycloaddition; high diastereoselectivity is observed in these reactions (**Scheme 15**).[66] Formal [2 + 2 + 1] cycloadditions of aminocarbene complexes have been shown to give trisubstituted cyclopentanes.[67] The corresponding alkoxycarbene complexes give cyclopropanes via [2 + 2] cycloaddition followed by reductive elimination of the metal. The aminocarbenes, however, undergo a second insertion of alkene to the metallocyclobutane intermediate, prior to reductive elimination of the metal.



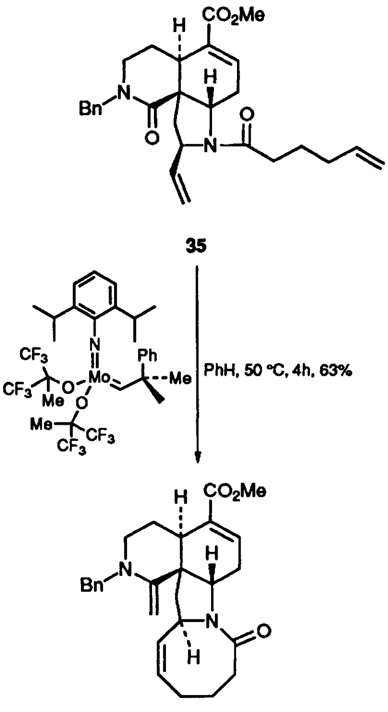
Scheme 15

Diels–Alder-type [4 + 2] cycloadditions of vinylcarbene complexes have been known for some time; the carbene moiety activates the dienophile to the same extent as a Lewis acid catalyst in the standard Diels–Alder reaction. Barluenga has now examined a diastereoselective [4 + 2] cycloaddition using a chiral diene with alkoxyvinyltungsten carbenes.[68] These reactions give predominantly the *endo* products via the *s-trans* vinylalkoxydiene in moderate to excellent diastereoselectivity. The corresponding chromium carbenes can undergo a competing [2 + 1] cyclopropanation/tandem Cope rearrangement leading to seven-membered ring products.[1,68,69] Barluenga has locked the alkoxyvinylcarbenes in an *s-cis* conformation via an internal boron chelate **34** such that subsequent [4 + 2] cycloaddition gives *exo*-selective products in high diastereoexcess (**Scheme 16**).[70] An *exo*-selective [4 + 2] cycloaddition with alkoxyvinylcarbene complexes of tungsten has been reported where the dienophile is locked in the *s-cis* conformation by virtue of a bulky ligand on the alkoxy oxygen atom.[71]



Scheme 16

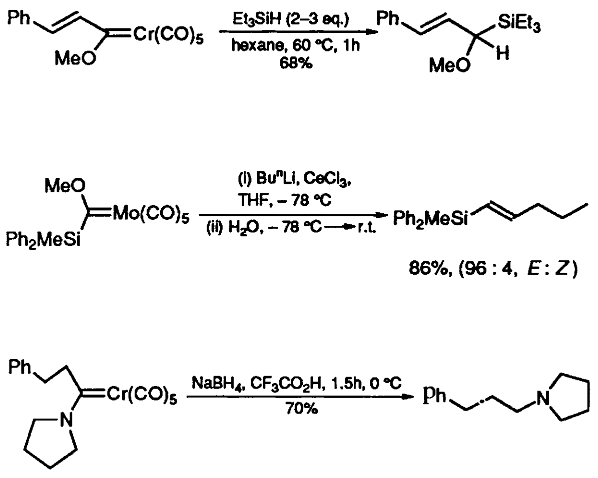
Mention was made in last year's review[1] of the Grubbs metathesis catalyst and several notable applications in synthesis have been published this year. In particular, Martin's approach to the synthesis of manzamine A via the efficient cyclization of the tricyclic precursor **35** deserves mention (**Scheme 17**).[72] Catalytic versions of the Grubbs metathesis reactions are now being developed but will not be discussed further in this review.[73]



Scheme 17

3.6 Cleavage of transition metal carbene complexes

A number of papers have appeared which highlight procedures for removal of the metal atom from transition metal carbene complexes. Chan has studied the insertion of organosilanes into vinylcarbene complexes to give allylsilanes (**Scheme 18**),[74] whilst vinyl silanes may be formed by the addition of alkyllithiums to silyl substituted Fischer carbene complexes (**Scheme 18**).[75] Sodium borohydride in trifluoroacetic acid is effective in removing the metal moiety from amino carbene complexes to give the free amine (**Scheme 18**).[76]



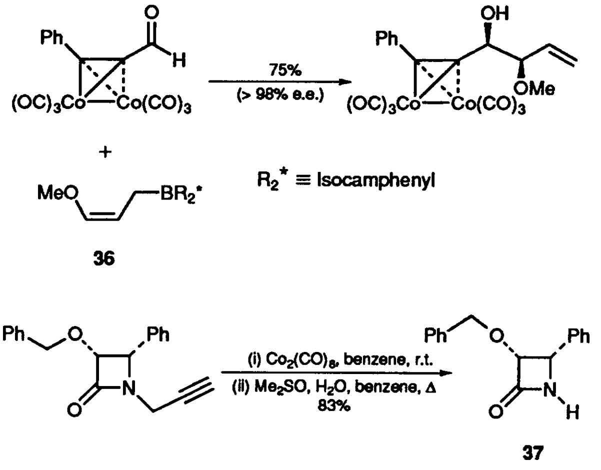
Scheme 18

4 η^2-Complexes in organic synthesis

4.1 η^2-Alkyne dicobalt hexacarbonyl complexes

A good review of η^2-alkyne dicobalt hexacarbonyl complexes applied to the synthesis of enediyne antitumor agents has been published by Magnus;[77] in addition, he has published a more detailed account of the η^2-alkyne dicobalt hexacarbonyl mediated approach to the azabicyclo[7.3.1]enediyne core of dynemicin.[78] A full account of the α to β epimerization of C-1-alkynyl substituted pyranose derivatives via their dicobalt hexacarbonyl derivatives has now been published by Isobe.[79]

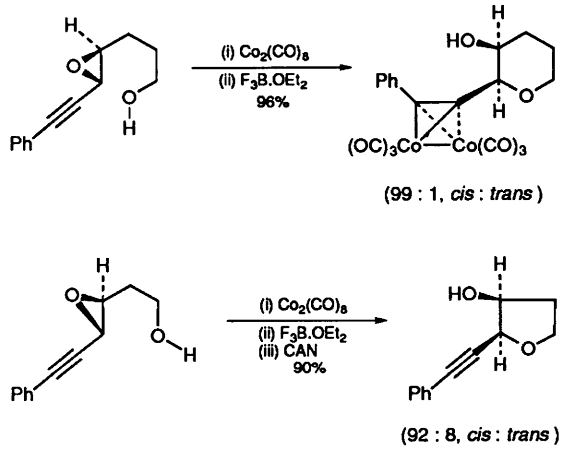
New synthetic applications of η^2-alkyne dicobalt hexacarbonyl complexes include the reaction of cobalt complexed alkynyl aldehydes with homochiral γ-alkoxyallyl boranes **36** to give 3,4-dioxy-1,5-eneyne complexes in enantioselective fashion (**Scheme 19**).[80] The cobalt moiety serves to protect the alkyne and exerts a high degree of stereocontrol in the addition reaction. The Nicholas reaction of dicobalt hexacarbonyl stabilized propargylic cations has been used in an effective, high yielding route to the otherwise elusive *N*-unsubstituted 2-azetidinones **37** (**Scheme 19**).[81]



Scheme 19

A number of applications involving ring-closure reactions have been published in the last year. For example, Hanoaka has applied the Nicholas reaction in an intramolecular sense to give tetrahydropyrans via a 6-*endo* ring-closure onto an epoxide; this reaction occurs with complete retention of stereochemistry at the propargylic position due to the configurational stability imparted to the cationic intermediate by the cobalt moiety (**Scheme 20**).[82] Tetrahydrofuran derivatives may be obtained by a similar intramolecular *endo* ring-closure of cobalt complexed 3,4-epoxyhex-5-yne-1-ols (**Scheme 20**).[83]

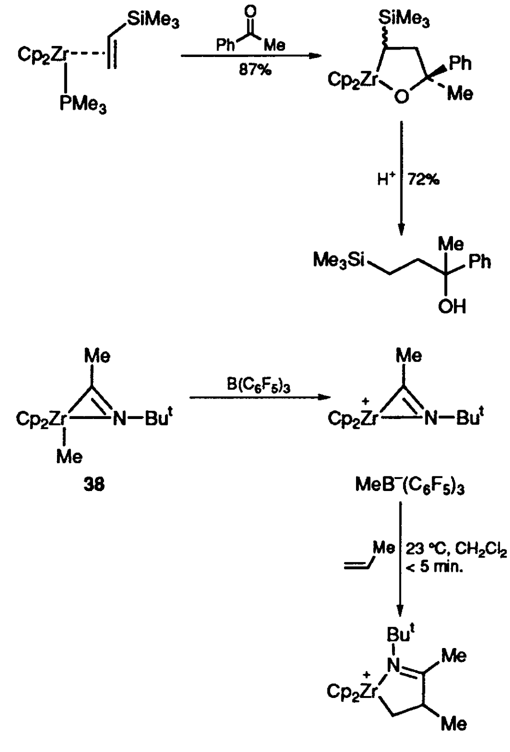
Ring closure onto cobalt stabilized propargylic cations has been exploited by Grove in a synthesis of the morphinan skeleton; the cobalt moiety facilitates kinetically controlled ring-closure to give the desired *cis*-fused products.[84] Intramolecular fluoride and Lewis acid catalysed attack of a silyl enol ether onto a cobalt-stabilized propargylic cation has allowed Tyrrell to prepare five- to six-, and seven-membered rings.[85] Unfortunately, a mixture of kinetic and thermodynamic enolates is obtained for methyl ketones resulting in a mixture of ring closed products. A new strategy has been developed for the $Mn(OAc)_3$ mediated oxidative cycloaddition of enynes with 1,3-dicarbonyl compounds, involving protection of the alkyne with dicobalt hexacarbonyl and thereby directing cycloaddition to the alkene.[86] Lastly, Nicholas has reported that cobalt-stabilized propargylic cations can be reduced by zinc to the corresponding radical species which then undergo efficient intermolecular coupling reactions. This methodology is particularly useful for ring closure reactions.[87]



Scheme 20

4.2 η^2-Complexes of zirconocene

Takahashi has published a detailed account of the reactions of η^2-zirconocene alkene complexes with aldehydes and ketones; excellent regioselectivity in zirconacyclopentane formation can be achieved with vinylsilanes to give γ-silylalcohols after hydrolytic removal of the metal (**Scheme 21**).[88] Carbon–carbon bond formation occurs at the β-position of the vinyl silane. An improved procedure for functionalizing the α-position of amines via η^2-zirconocene complexes of imines has been published by Whitby[89] as well as a detailed study of the kinetics and steric/electronic factors involved in the formation and trapping of η^2-zirconocene complexes of imines.[90]

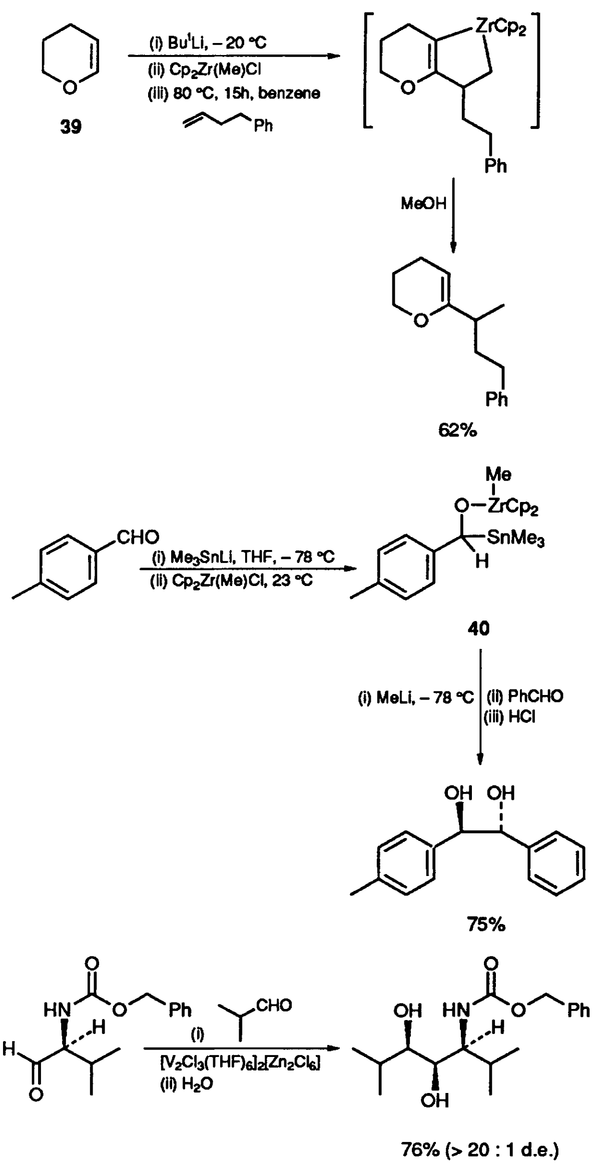


Scheme 21

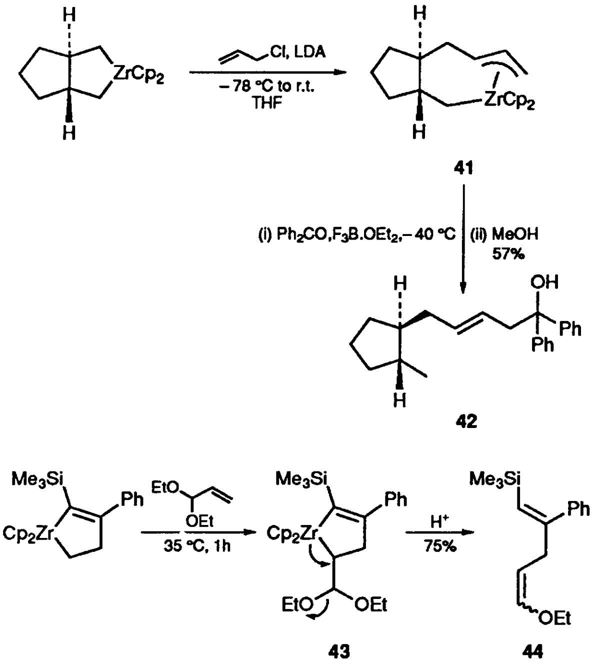
Jordan has extended his work on the functionalization of pyridines α-to nitrogen via the cationic η^2 zirconocene pyridine complex by developing an exciting catalytic, diastereoselective version of the reaction where the zirconium catalyst bears a chiral ethylenebis(tetrahydroindenyl) ligand.[91] The enhanced reactivity towards insertion reactions exhibited by cationic η^2-zirconocene complexes has been exploited by Jordan to activate η^2-(iminoacyl) zirconocene complexes **38** (**Scheme 21**). The increased Lewis acidity of the metal centre on formation of the cationic complex enhances the rate of insertion of alkenes and alkynes such that reactions can be performed at ambient temperature in less than one hour.[92]

η^2-Zirconocene complexes of a variety of species have proven useful for mediating C–C bond formation α to a heteroatom. For example, formation of the η^2-zirconocene complex of 3,4-dihydro-2*H*-pyran **39** has enabled Whitby to prepare a range of 1-substituted dihydropyrans via regioselective insertion of alkenes (**Scheme 22**).[93] The η^2-zirconocene complexes of aldehydes have recently been prepared via treatment of the zirconocene(α-stannylalkoxide) complexes **40** with methyl lithium at low temperature; these species insert aromatic aldehydes and ketones to give 1,2-diols after hydrolytic removal of the metal (**Scheme 22**).[94] This represents a *threo*-selective pinacol-type coupling process with the advantage that unsymmetrical diols may be prepared; unfortunately, aliphatic aldehydes or ketones do not insert. A more versatile vanadium-mediated pinacol-type synthesis of unsymmetric diols has been published by Pedersen which is of more general applicability in synthesis (**Scheme 22**).[95]

Many of the reactions of η^2-zirconocene complexes involve insertion of unsaturated functionality (alkenes, alkynes, carbonyls, *etc.*) to generate a five-membered metallocyclic species. An important aspect of this chemistry is the subsequent functionalization of the metallocycle to give useful organic products. Although this may be achieved by, for example, chemoselective halogenation of the C–Zr bonds,[96] or heterocycle formation,[97] methods of C–C bond formation are limited. Whitby has reported work on the insertion of phenyl isocyanide into zirconacyclopentanes[1] and zirconacyclopentenes;[98] he has also demonstrated that alkyl- and trialkyl-silylisocyanides react similarly.[99] Insertion of lithium chloroallylide into zirconacyclopentanes has also been achieved; the resultant η^3-allyl intermediate **41** may be trapped with aldehydes or ketones to give homoallylic alcohols **42** (**Scheme 23**).[100] Negishi has trapped simple zirconacyclopentanes and zirconacyclopentenes with aldehydes[101] whilst Erker has trapped the simple (butadiene) zirconocene reagent with ketones, nitriles,[102] and $W(CO)_6$.[103] Reaction of zirconacyclopentenes with allylic acetals forms the



Scheme 22



Scheme 23

metallocycle **43** which is irreversibly transformed into the skipped diene products **44** via cleavage of one of the acetal C-O bonds (**Scheme 23**);[104] overall this is very similar to the reaction of allyl ethers with zirconacyclopentenes reported last year by Takahashi.[1,105]
In contrast, reaction of zirconacyclopentenes with homoallylic bromides gives cyclopropanes via a different pathway.[106]

4.3 η^2-Complexes of osmium

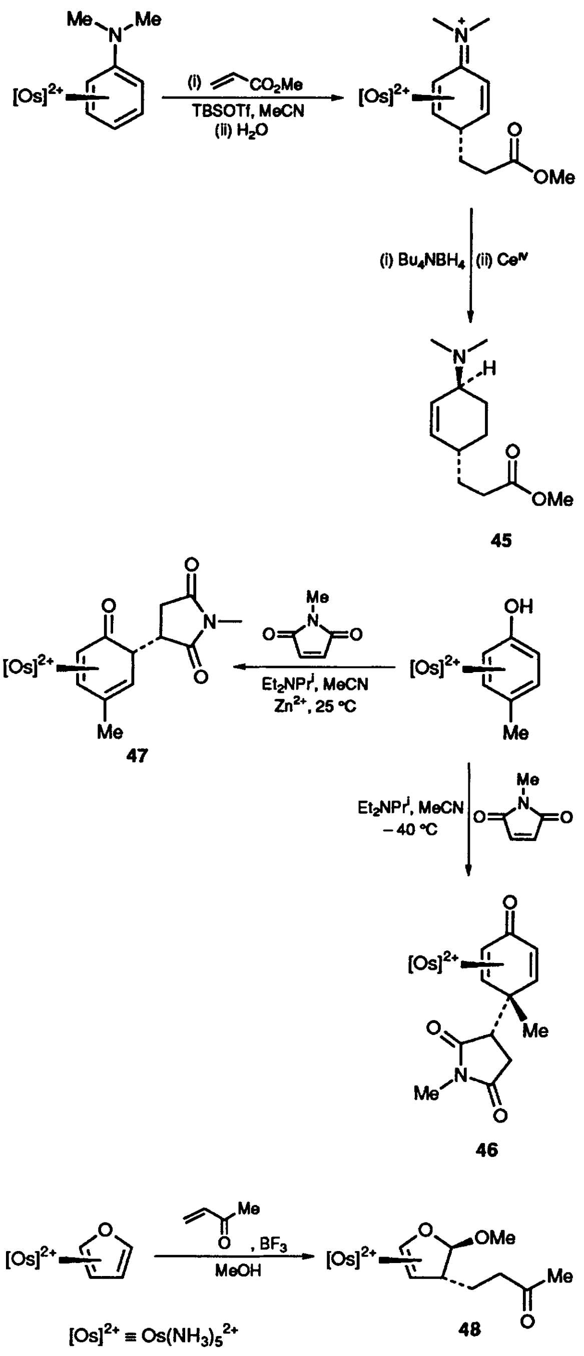
Four papers have been published in the last year from the laboratory of Harman which highlight the use of η^2-complexes of osmium as a tactic for controlling the reactivity of aromatic systems. η^2-Coordination of phenols[107] or anilines[108] to osmium localizes the π-electron density in the non-coordinated diene moiety. Subsequent treatment with Michael acceptors gives a regio- and stereo-controlled electrophilic addition *para* to the heteroatom substituent or *ortho* if the *para* position is blocked; moreover, the osmium moiety stabilizes the resultant diene species, thus facilitating the synthesis of substituted 3-aminocyclohexenes **45** or 4-substituted 2,5-cyclohexadienones **46** and 6-substituted 2,4-cyclohexadienones **47** (**Scheme 24**). η^2-Coordination of furans renders the heterocycle more susceptible to electrophilic attack at the 4-position and less susceptible to polymerization such that complex **48** may be isolated from the reaction with methylvinylketone in methanol (**Scheme 24**).[109] A similar tactic has been used by Harman with pyrrole to facilitate electrophilic attack at the 4-position of the η^2-osmium complex.[110]

4.4 η^2-Complexes of manganese

η^2-Complexes of manganese have been used to protect the alkene moiety of cyclic α,β-unsaturated ketones thereby allowing regioselective α'-deprotonation to form the enolate and subsequent alkylation to give **49**. Good stereocontrol is observed in the case of five-membered rings with the electrophile entering away from the bulky organometallic protecting group (**Scheme 25**).[111]

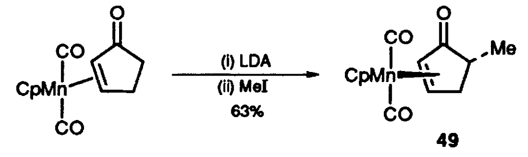
5 η^3-Complexes in organic synthesis

A detailed investigation of the reactions of η^3-allyl iron tricarbonyl anions with electrophiles has been published by Brookhart.[112] Initial electrophilic attack occurs at the metal which, in the presence of PPh_3, undergoes CO insertion and acyl migration to give the α,β-unsaturated enone complex **50** (**Scheme 26**). Brookhart went on to study the effect of substituents in the allylic complex; in particular, the effect of *syn* and *anti* substituents on the regiochemistry of acyl migration. A similar class of acyl migration involving η^3-complexes of iron has been reported by Nakanishi. β,γ-Unsaturated carboxylic ester **51** can be prepared via carbonyl insertion/acyl migration of (η^3-allyl)Fe)CO)$_2$NO complexes which, in turn, are easily prepared from allyl halides (**Scheme 26**).[113] Carbonylation occurs regioselectively at the least-hindered terminus of the allyl ligand and is facilitated by the addition of 1,2-bis(diphenylphosphino)ethane (DPPE). Nakanishi also demonstrated that (η^3-allyl)Fe(CO)$_2$NO complexes undergo conjugate addition to α,β-unsaturated carbonyl compounds to give the corresponding δ,ε-unsaturated carbonyl species in good yield; use of (η^3-1 or -2-trimethylsilyloxyallyl)Fe(CO)$_2$NO complexes gives 1,6-or 1,5-diketones respectively.[114]

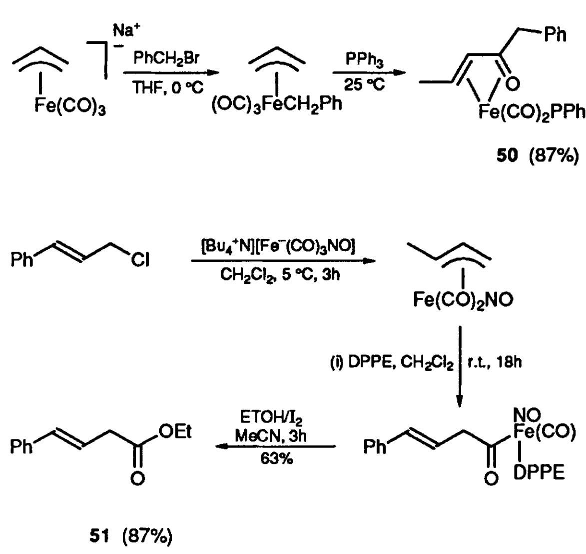


Scheme 24

The use of η^1-iron acyl complexes and arene chromium tricarbonyl complexes to impart stereocontrol in conjugate additions is well documented. New to the repertoire, however, is the use

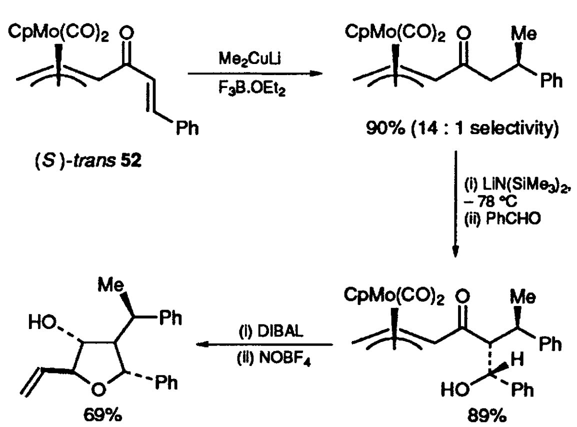


Scheme 25



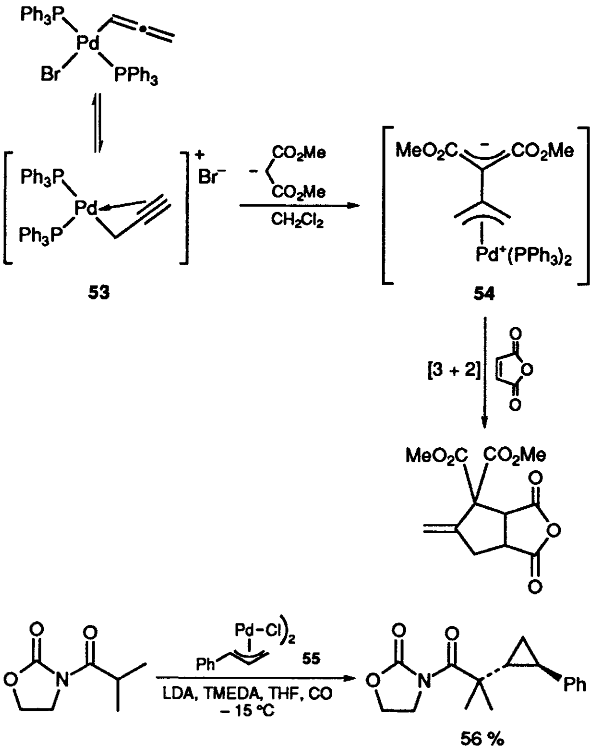
Scheme 26

of η^5-(C_5H_5)Mo(CO)$_2$(π-allyl) fragments as control elements in the conjugate addition; Liu has published two papers which demonstrate their potential in this process for the synthesis of substituted tetrahydrofurans. Of particular interest is the observation that the major isomer from the conjugate addition appears to arise from attack at the least-hindered *Si* face of the disfavoured *s-trans*-enone complex **52** (**Scheme 27**).[115] η^3-(π-Allyl)molybdenum complexes of cyclopentenone have been used by Liebeskind to synthesize 4-substituted-2-cyclopentenones.[116]



Scheme 27

Two interesting papers have been published concerning the nucleophilic addition of carbanions to η^3-allyl palladium complexes. Chen has demonstrated that reaction of the metal allenyl complex **53** with a soft carbanion leads to the zwitterionic complex **54**. This η^3-trimethylene methane species can be trapped by electron-deficient olefins to give cyclopentenoids (**Scheme 28**).[117] Hoffman has shown that η^3-allyl palladium complexes **55** can be trapped with various enolate anions in the presence of TMEDA at the central carbon atom to give a general synthesis of substituted cyclopropanes. At least one aryl substituent is required at the termini of the π-allyl system (**Scheme 28**).[118]



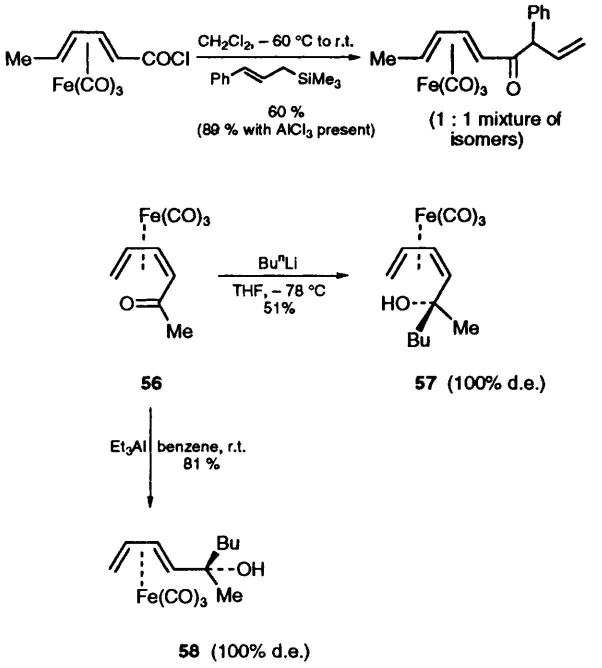
Scheme 28

6 η⁴-Complexes of iron tricarbonyl in organic synthesis

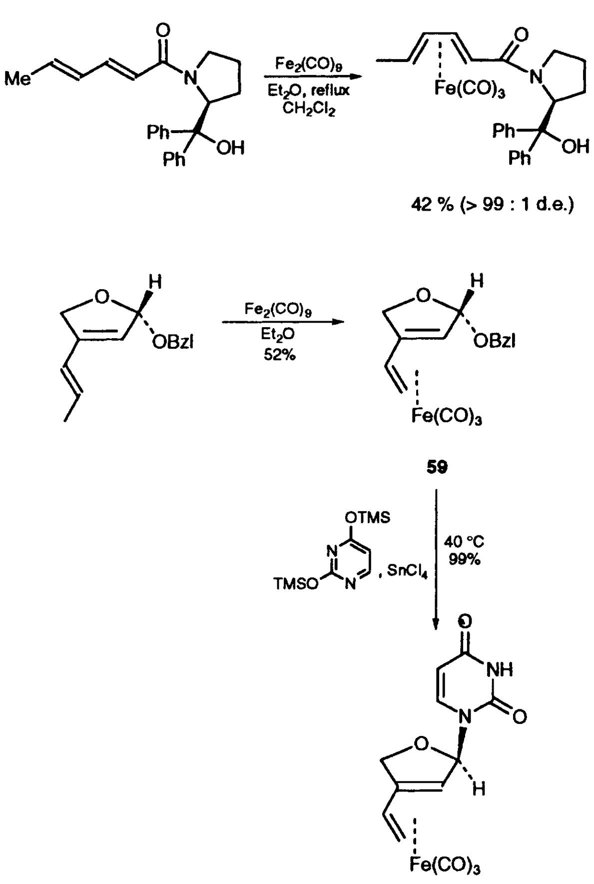
η^4-diene tricarbonyl iron complexes have proven to be useful intermediates in organic synthesis due, in particular, to the stereocontrol exerted by the $Fe(CO)_3$ moiety in addition to protecting the diene from attack. This year the range of reactions involving complexed η^4-dienes has been expanded and new methods for the generation of homochiral complexes have been published.

6.1 Acyclic complexes

The $Fe(CO)_3$ moiety serves as both an activating group (for the acyl chloride) and protecting group (for the diene) in the allylation of α,β-γ,δ-unsaturated acid chlorides (**Scheme 29**);[119] the reaction proceeds under neutral conditions without Lewis acid catalysis except for sterically-hindered allylsilanes. Iwata has studied an interesting series of 1,2-nucleophilic additions to acyclic (*Z*)-dienone complexes **56**; the use of organolithium or organocopper reagents gives the expected tertiary alcohols **57** via nucleophilic attack from the less-hindered *exo* face. However, the use of more Lewis acidic organoaluminium reagents gives stereoisomer **58** via initial (*Z*) to (*E*) isomerization of the dienone (**Scheme 29**).[120] Iwata has also described the efficient stereoselective addition of organocerium reagents to 1-imino-(*E*, *E*)-diene complexes.[121]



Scheme 29



Scheme 30

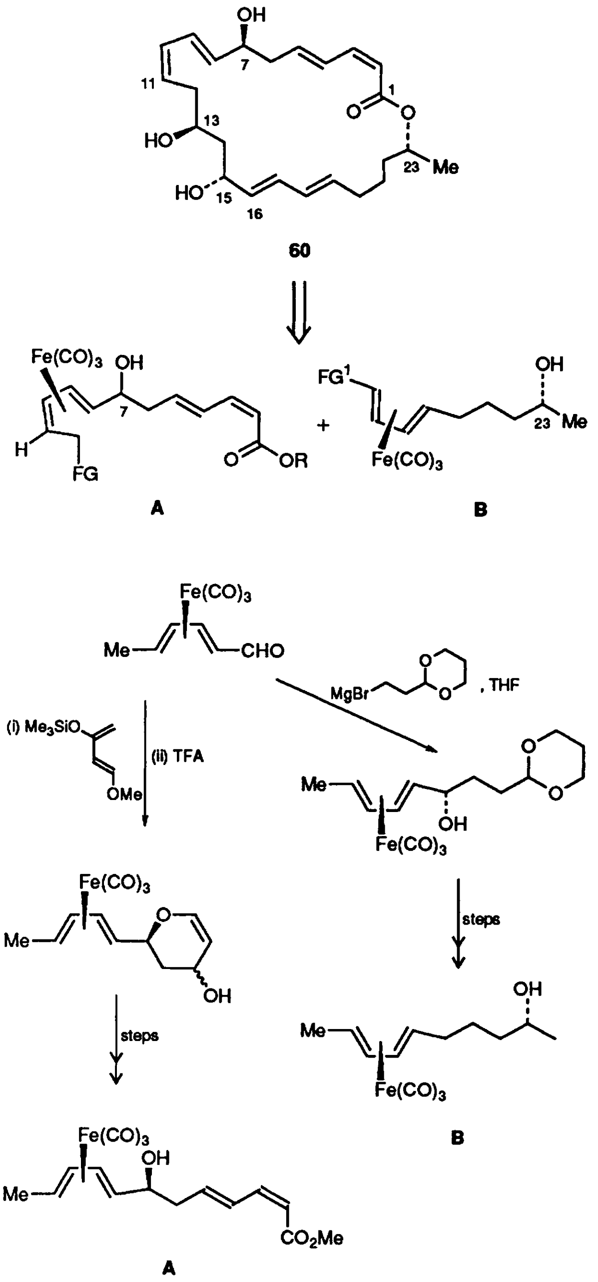
Several papers have been published in the last year on routes to homochiral η^4-diene tricarbonyl iron complexes. In particular, Uemura has extended the previously reported kinetic resolution methods using pig liver esterase or bakers yeast in aqueous sytems to the more favourable use of Lipase in organic solvents.[122] Formation of diastereomeric derivatives has been used by Howell to resolve substituted sorbaldehyde complexes[123] whilst Nakanishi has chromatographically separated diastereomeric η^4-*N*-substituted-2,4-hexadienamide complexes.[124] An interesting and remarkably stereoselective complexation of a diene bearing a proximal chiral auxiliary was recently published by Pearson (**Scheme 30**). Diethyl ether proved the solvent of choice and a bulky chiral auxiliary to block one face of the diene is essential; the best auxiliary contained a coordinating group with the potential to direct the incoming iron. This type of reaction was also applied to the complexation of azadienes via chiral hydrazone derivatives.[125] In a similar vein, Schmalz used the diastereoselective complexation of chiral dienes derived from L-arabinose to give predominantly the *endo* isomer **59** (**Scheme 30**).[126] In a neat extension Schmalz was able to replace the benzyloxy group of **59** with a variety of nucleophiles to give the *exo* derivatives in a stereoselective manner (**Scheme 30**).[127]

Some elegant synthetic applications of η^4-diene tricarbonyl iron complexes have appeared; for example, Donaldson has completed both the C-1 to C-11 and C-15 to C-24 portions of the polyene macrolide macrolactin A **60** in racemic form. Construction of both fragments relies on control of chirality by face selective reactions on η^4-sorbaldehyde tricarbonyl iron (**Scheme 31**).[128] Gree has prepared the C-15 to C-24 fragment using similar methodology but in optically pure form.[129] Saalfrank and Gree have also introduced a pendent allenic residue into a functionalized η^4-sorbaldehyde tricarbonyl iron complex.[130]

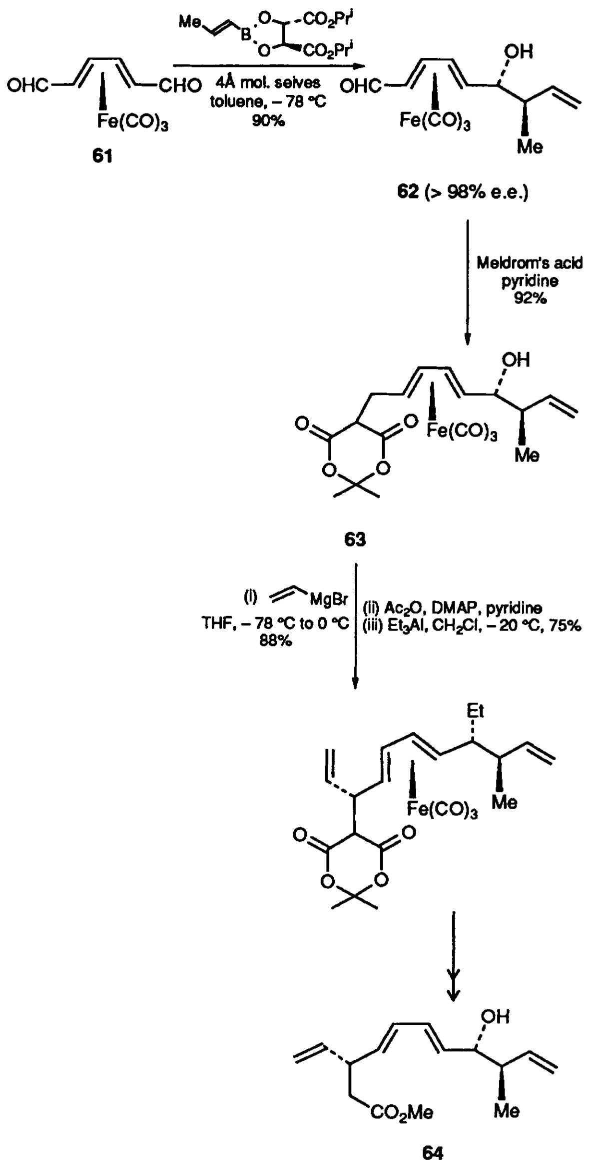
Roush has completed a formal asymmetric total synthesis of ikarugamycin from the simple symmetrically functionalized diene complex **61** (**Scheme 32**).[131] The key steps include highly enantio- and diastereo-selective crotylboration of **61** to give the *exo* diastereoisomer **62** in 90% yield and subsequent condensation with Meldrum's acid to give the conjugated triene **63**. This subsequently undergoes stereoselective *exo* face attack, away from the metal, by vinylmagnesium bromide to introduce the third chiral centre. Lastly, conversion of the α-hydroxy group into a suitable leaving group and treatment with triethylaluminium incorporates the required ethyl group with clean, iron-controlled, retention of stereochemistry to give the key intermediate **64**.

6.2 Cyclic complexes

Yeh has reported an interesting regio- and stereo-controlled synthesis of bridged bicyclic systems via Lewis acid catalysed conjugate addition of



Scheme 31

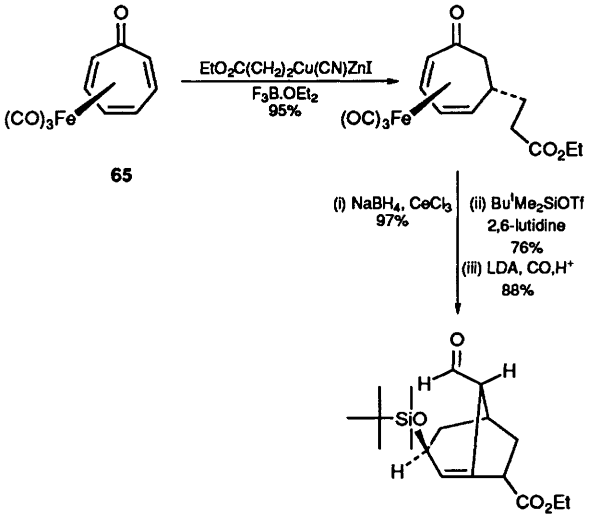


Scheme 32

functionalized zinc-copper reagents RCu(CN)ZnI to (tropone)iron tricarbonyl **65** (**Scheme 33**).[132] The iron tricarbonyl moiety protects the diene functionality in the Michael addition but allows intramolecular closure of the enolate onto the diene in the presence of CO to give the bicyclic product **66**. In a similar paper he has used the same methodology to functionalize tricarbonyltropyliumchromium tricarbonyl.[133]

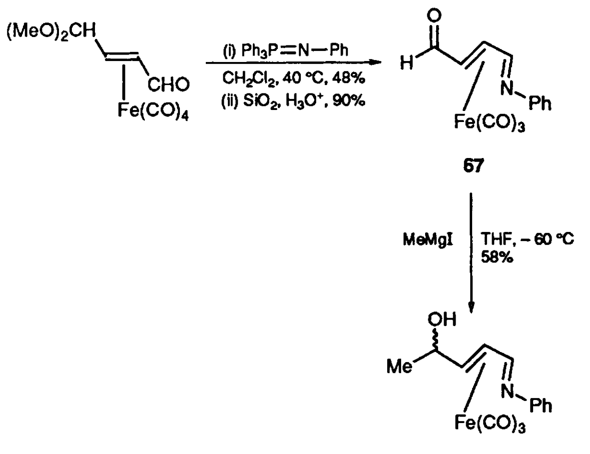
6.3 η^4-Azadiene tricarbonyl iron complexes

Simple η^4-azadiene tricarbonyl iron complexes have been prepared by direct complexation of α,β-unsaturated imines or by the condensation of amines with tetracarbonyliron complexes of α,β-unsaturated carbonyl compounds. The preparation and reactions of functionalized azadiene

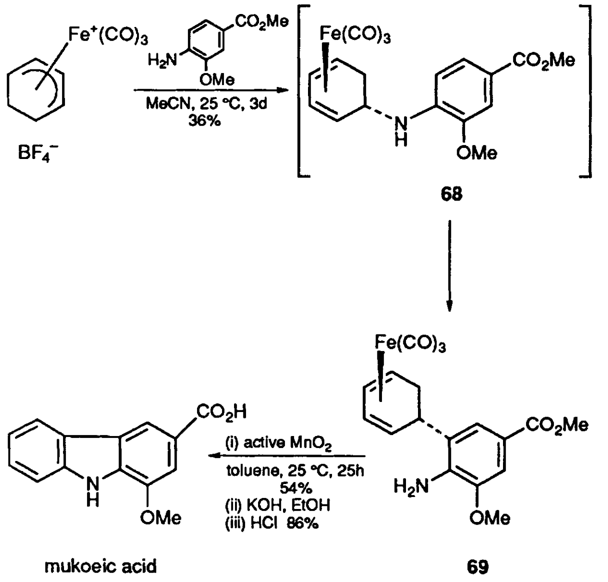


Scheme 33

complexes are only now being explored. Martelli recently reported the synthesis of the formyl complex **67** (**Scheme 34**) via a mild aza-Wittig reaction.[134] Of note is the subsequent reaction with Grignard reagents on the free aldehyde. Reduction of complexed azadienes with $LiAlH_4$ gives the fully saturated amines whilst the free azadienes give allylamines under the same conditions, indicating that coordination of the azadiene activates the ligand to hydride attack.[135] Lastly, Knolker has published an interesting paper which indicates that 1,4-aryl substituted azadiene complexes can act as efficient catalysts for 1,3 diene complexation via transfer of the $Fe(CO)_3$ moiety.[136]



Scheme 34

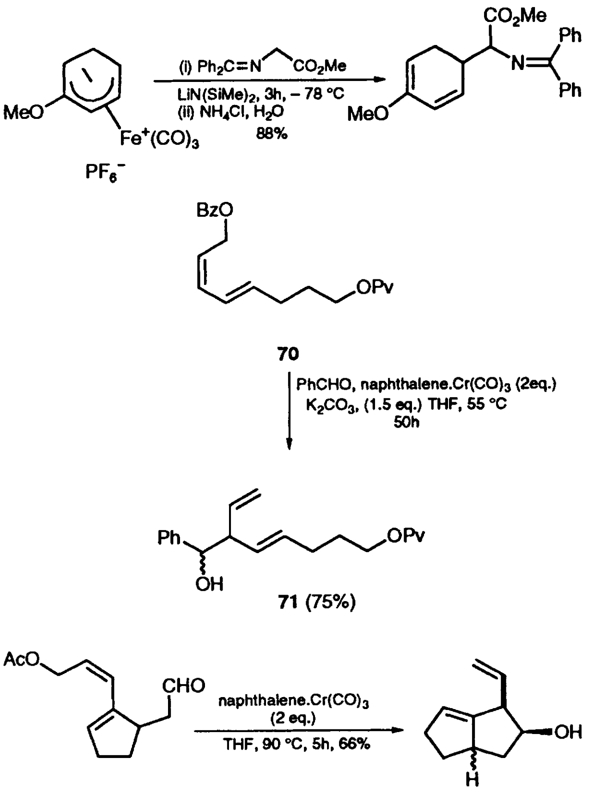


Scheme 35

7 η^5-Complexes in organic synthesis

Knolker has published two full papers on the synthesis of carbazole alkaloids via the electrophilic aromatic substitution of arylamines by tricarbonyl iron complexed cyclohexadienyl cations.[137] The rapidly formed intermediate *N*-alkylated arylamine **68** slowly rearranges to the thermodynamically favoured *C*-alkylated arylamine **69**; subsequent oxidative cyclization gives the carbazole skeleton (*e.g.* for mukoeic acid (**Scheme 35**). A similar oxidative cyclization of complexed cyclohexadienyl cations bearing a pendent alkylamine affords simple indole derivatives.[138] In an extension of previous work, Genet and Stephenson have used Schiff base nucleophiles to attack η^5-cyclohexadienyl tricarbonyl iron cations. This chemistry has the potential to give a general route to substituted phenylglycine derivatives (**Scheme 36**).[139] An interesting study on the regiochemistry of attack at disubstituted acyclic η^5-cyclohexadienyl tricarbonyl iron cations has been published by Donaldson in which the classical nucleophilic attack at the terminus of the coordinated system is affected by the relative steric effects of the substituents.[140]

Shibasaki has published a novel process involving γ-substitution of η^5-pentadienyl chromium complexes. For example, treatment of the pentadienyl benzoate **70** with two equivalents of (naphthalene). $Cr(CO)_3$ in the presence of an aldehyde gives the γ-substituted product **71** in good yield accompanied by a small amount of the γ-protonation product (**Scheme 36**).[141]



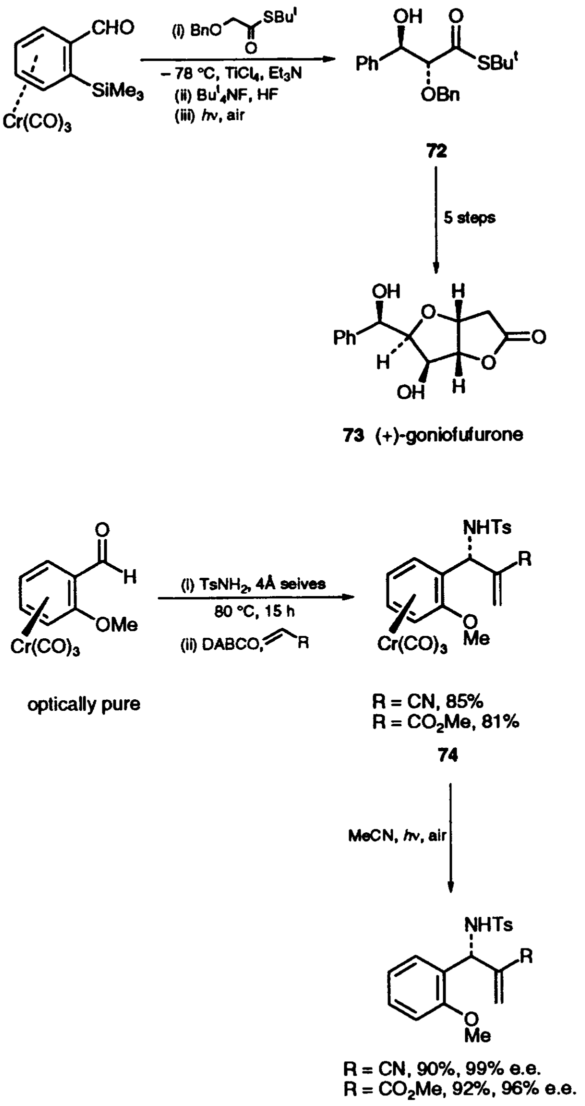
Scheme 36

This selectivity should be contrasted with the generally poor selectivity seen with electrophilic trapping of pentadienyl alkali metal reagents. The intramolecular version of this process looks especially promising (**Scheme 36**).

8 η^6-Complexes in organic synthesis

8.1 η^6-Arene chromium tricarbonyl complexes in synthesis

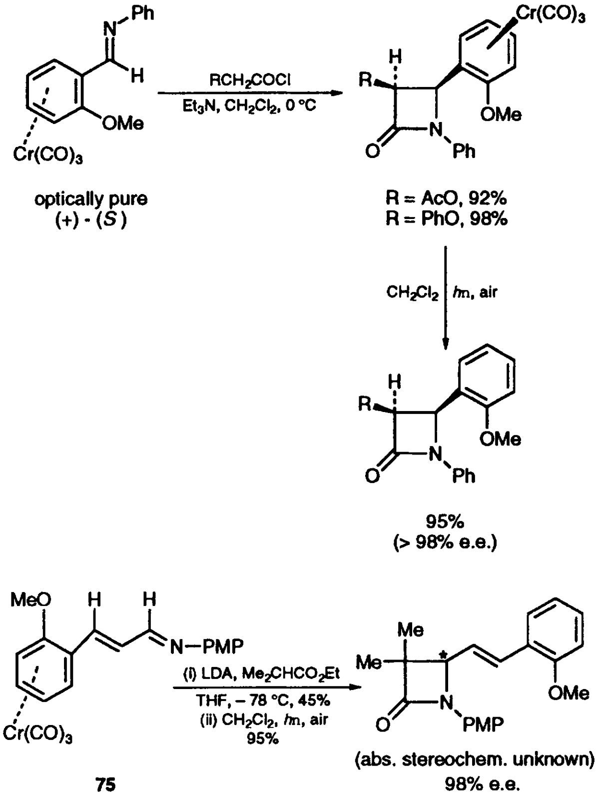
The ready availability of homochiral *ortho*-substituted benzaldehyde chromium tricarbonyl complexes has prompted continued exploration of their synthetic potential. For example, Hanoaka has extended his previously published arene chromium tricarbonyl mediated synthesis of the taxol side-chain intermediate **72** to a synthesis of homochiral (+)-goniofufurone **73** (**Scheme 37**).[142]



Scheme 37

Baldoli and Maiorana have prepared a series of optically pure alkynyl alcohols via attack of alkynyl lithium or magnesium species onto homochiral *ortho*-substituted benzaldehyde chromium tricarbonyl complexes,[143] while Kundig has reported that the coordination of *ortho*-substituted benzaldehydes to chromium tricarbonyl accelerates the Bayliss–Hillman reaction and improves the overall stereoselectivity.[144] Kundig has also demonstrated that the Bayliss–Hillman reaction can be applied to homochiral aldimine complexes to give **74** (**Scheme 37**).[145]

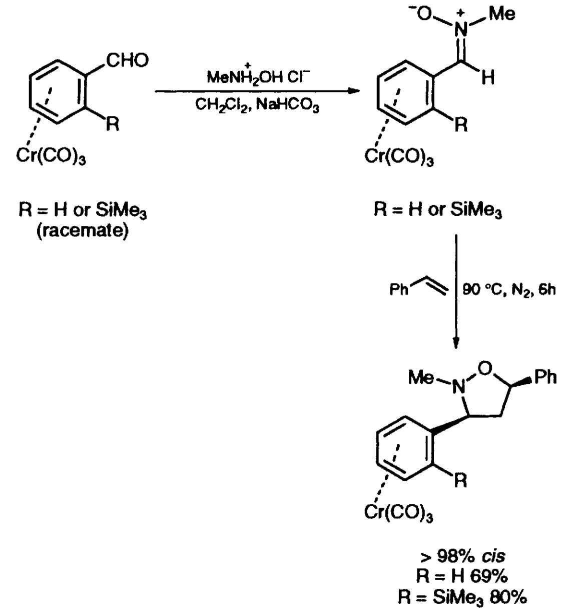
Homochiral aldimine complexes have also been used by Del Buttero and Maiorana in a [2 + 2] mediated ketene cycloaddition to give optically pure *β*-lactams (**Scheme 38**).[146] By analogy with the known mode of nucleophilic attack on complexed benzaldehydes, the predominant stereoisomer is presumed to arise via ketene attack on the *Si* face of the amine away from the bulky Cr(CO)$_3$ unit with the imine *anti* to the *ortho* substituent. In an alternative *β*-lactam synthesis from the same group, remarkable stereocontrol was observed in the addition of lithium ethylisobutyrate to the homochiral 2-methoxycinnamyl-*p*-anisidine complex **75** (**Scheme 38**).[147] Presumably the stereocontrol is again due to nucleophilic attack away from the bulky Cr(CO)$_3$ moiety on the preferred conformation of the imine.



Scheme 38

The concept of facially selective attack on the preferred conformer of an *ortho*-substituted benzaldehyde complex has been used by Hanoaka in 1,3-dipolar cycloadditions of nitrones (**Scheme 39**).[148] In this case the selective formation of the *cis*-3,5-disubstituted isooxazolines arises from the electron-withdrawing effect of the Cr(CO)$_3$ moiety coupled with an electron-rich dipolarophile; the *ortho*-trimethylsilyl group is not essential. The formation of homochiral isooxazolines does, however, require the *ortho*-trimethylsilyl group to impart planar chirality on the nitrone complex.

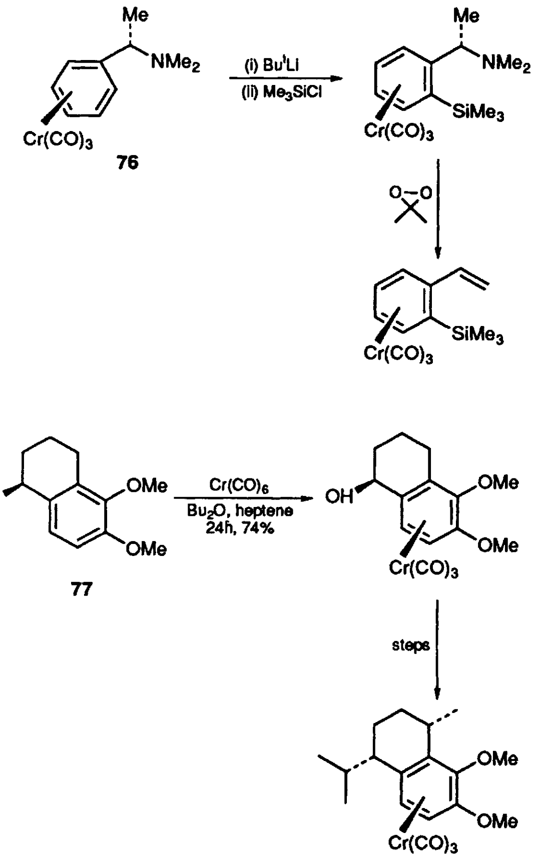
Several groups have published work on the preparation of homochiral *ortho*-disubstituted arene



Scheme 39

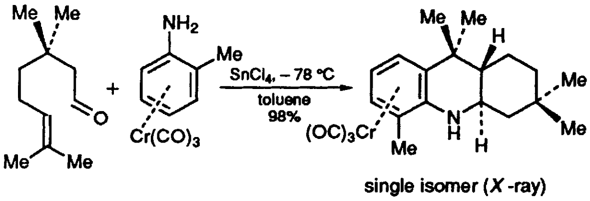
chromium tricarbonyl complexes via an *ortho* lithiation strategy. Green has used a chiral tartrate-derived ligand to direct deprotonation to one of the two prochiral *ortho* positions[149] whilst Simpkins[150] and Kundig[151] have used chiral bases to induce modest to good enantioselectivities (up to 95% e.e.). In a similar approach, Uemura has carried out *ortho* lithiations in the presence of chiral diamine ligands with modest enantioselectivities (up to 82%).[152] Hayashi has published further studies on his interesting palladium-catalysed asymmetric cross-coupling of *meso*-arene chromium tricarbonyl complexes with alkenyl and aryl boronic acids; to date up to 69% e.e. has been achieved.[153] Uemura has used a similar palladium-mediated coupling approach to the racemic synthesis of biphenyls[154] whilst Wulff has carried out palladium-mediated couplings of vinylstannanes with complexed arene chromium tricarbonyl triflates.[155] Thomas has introduced planar chirality into chromium tricarbonyl complexes of *ortho*-substituted styrenes via diasteroselective *ortho*-metallation of the chiral α-methylbenzylamine complex **76** and subsequent dimethyldioxirane-mediated oxidation of the amine and Cope elimination to give the styrene (**Scheme 40**).[156] The dioxirane-mediated oxidation in the presence of the sensitive $Cr(CO)_3$ moiety is of particular interest and has also been used to oxidize alkylthio substituted arene chromium tricarbonyl complexes to the corresponding sulfoxides.[157] Use of Kagan's modified Sharpless reagent affords an asymmetric version of the oxidation reaction[158] which, depending upon the conditions, can give the fully oxidized sulfones.[159]

Use of homochiral arene chromium tricarbonyl complexes in synthesis is exemplified by the work of Jones who has used catalytic amounts of a homochiral ephedrine complex to mediate the addition of dimethylzinc to hydroxyaldehydes in superior enantioselectivities to those obtained with the uncomplexed ephedrine ligands.[160] Schmalz has achieved the asymmetric synthesis of (1S,4S)-dihydroxycalamenene via diastereoselective complexation of the homochiral alcohol **77** and subsequent control of stereochemistry at the benzylic positions by virtue of the steric control imparted by the bulky $Cr(CO)_3$ moiety (**Scheme 40**).[161]



Scheme 40

A potentially useful novel synthetic method involving the diastereoselective intramolecular hetero Diels–Alder reaction of imino arene chromium tricarbonyl complexes has been published by Laschat (**Scheme 41**).[162] This remarkably efficient reaction gives only the *trans* isomer due to the steric control exerted by the $Cr(CO)_3$ moiety. Lastly, Semmelhack and Goti reported a potentially useful, mild method (25°C, 1 h in ethyl acetate) for introducing the $Cr(CO)_3$ moiety via arene displacement from the (η^5-1-methylpyrrole)tricarbonyl chromium complex.[163]



single isomer (*X*-ray)

Scheme 41

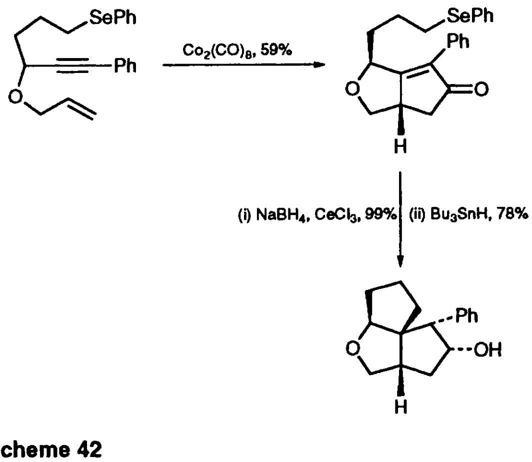
8.2 η^6-Arene manganese tricarbonyl cations and η^6-arene ruthenium cyclopentadienyl cations in organic synthesis

Pearson has continued to exploit the enhanced susceptibility of η^6-arene manganese tricarbonyl cations towards nucleophilic attack by application of this methodology to the synthesis of the CFG ring system of ristocetin A.[1,164] He has also studied chiral auxiliary directed nucleophilic additions to η^6-arene manganese tricarbonyl cations with up to 90% e.e. observed with bulky nucleophiles.[165] η^6-Arene ruthenium cyclopentadienyl cations are similarly activated towards nucleophilic attack and Pearson has used this methodology in a formal total synthesis of the ACE inhibitor K-13.[166]

9 Transition metal mediated cycloadditions in organic synthesis

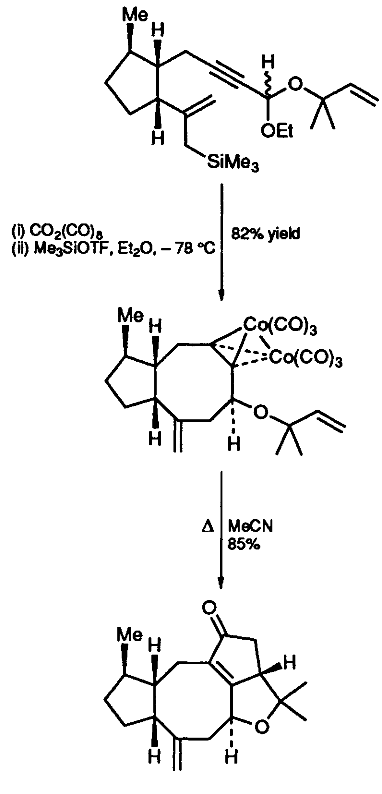
9.1 The Pauson–Khand and related cycloadditions

Significant applications of the intramolecular Pauson–Khand reaction in organic synthesis have appeared this year which demonstrate the generality of this reaction in a range of systems and in the presence of a wide variety of functional groups. For example, Clive has prepared angularly fused triquinanes in good yield and high stereoselectivity by a tandem intramolecular Pauson–Khand cyclization/radical ring-closure process (**Scheme 42**).[167]



Scheme 42

Krafft has prepared the CDE ring system of the pentacyclic steroid xestobergsterol A using an intramolecular Pauson–Khand ring cyclization which allows all the stereocentres to be introduced with correct relative stereochemistry.[168] In a particularly impressive sequence of reactions Schreiber has constructed (+)-epoxydictymene via a tandem Nicholas reaction/Pauson–Khand ring-closure (**Scheme 43**).[169] Marco-Contelles has prepared a number of annulated pyranose systems via intramolecular Pauson–Khand cyclization onto carbohydrate templates.[170] The first example of a reversal of the selectivity in an intramolecular Pauson–Khand cyclization has been reported; cyclization of one stereoisomer of 3,5-dimethyl-4-propargyl-1,6-heptadiene gives predominantly the bicyclic product with both substituents in the more hindered *endo* position.[171]



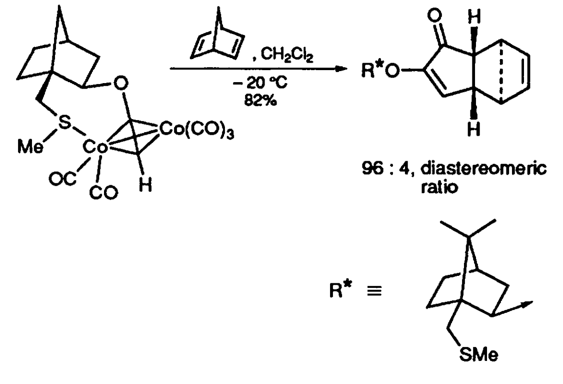
Scheme 43

Advances in the methodology associated with the Pauson–Khand reaction include *in situ* generation of the (alkyne)$Co(CO)_6$ complex from $CoCl_2$ and zinc,[172] and a catalytic version of the intramolecular Pauson–Khand reaction.[173] $Fe(CO)_5$ mediated Pauson–Khand-type reactions have also been explored by Pearson[174] and Knolker.[175]

Asymmetric Pauson–Khand reactions have been studied by Greene using a chiral auxiliary directly attached to the complexed alkyne via an ether linkage in both the inter-[176] and intra-molecular[177] cyclization. De Meijere has placed the chiral auxiliary on the tether between the alkyne and alkene in intramolecular Pauson–Khand cyclizations onto methylene cyclopropanes.[178] All of these methods give moderate induction in most cases with a few examples providing products in > 90% d.e. Higher diastereoselectivities (96:4) could be achieved in intramolecular cyclizations using the 10-methylthio-isoborneol auxiliary which provides a more rigid template for the cyclization reaction by chelation of the sulfide moiety with the metal ligand (**Scheme 44**).[179]

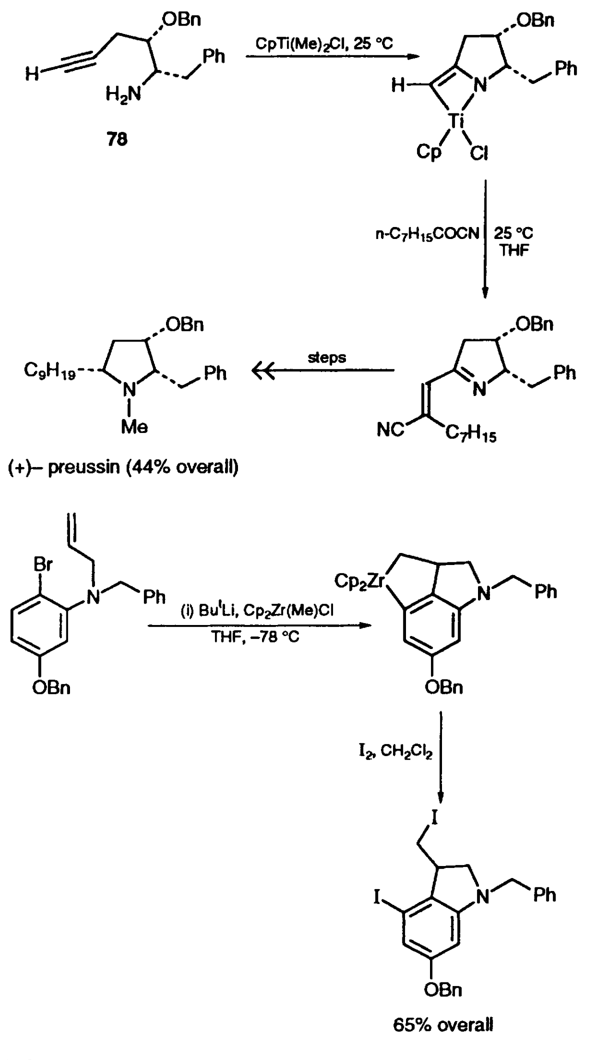
9.2 Titanium- and zirconium-mediated cycloadditions

One of the highlights in this field has been the total synthesis of (+)-preussin by Livinghouse who applied the previously developed imidotitanium-alkyne [2 + 2] cycloaddition to the homochiral precursor **78** in the



Scheme 44

presence of octanoyl cyanide (**Scheme 45**).[180] In an alternative approach to CC-1065, Tietze has applied the methodology of Buchwald to perform an intramolecular zirconium-mediated cyclization of a pendant alkene onto an η^2-benzyne zirconocene complex (**Scheme 45**).[181] Following the elegant total synthesis of dendrobine last year by Mori, a more detailed account of the key zirconocene-mediated ring-closure reaction has appeared, including *X*-ray analysis of the products.[182] Whitby has further exploited the synthetic potential of the zirconocene-mediated cyclization of enynes and diynes bearing nitrogen in the tether to synthesize a variety of piperidine and isoquinoline systems.[183] Several papers have appeared over the last year on catalytic versions of zirconocene-mediated cycloadditions of dienes which are beyond the scope of this review.[184]



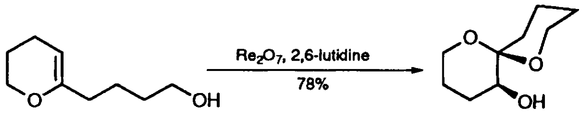
Scheme 45

9.3 Cobalt-mediated cyclotrimerizations

Vollhardt has carried out a regioselective [2 + 2 + 2] cyclotrimerization of α,ω-alkynenitriles with silyl substituted acetylenes to give annulated pyridines.[185] Extension of this methodology to the construction of the C,D ring system of ergot alkaloids was also reported. Malacria has demonstrated the use of allenes as participants in the cobalt-mediated [2 + 2 + 2] cycloaddition reaction.[186]

9.4 Rhenium promoted cycloadditions

In 1992 Kennedy reported the rhenium(III) oxide promoted oxidative cycloaddition of γ-hydroxyalkenes to give, for example, 2-hydroxymethyltetrahydrofurans.[1,187] This methodology has now been applied to spiroketal synthesis (**Scheme 46**) and a [3 + 2] cycloaddition mechanism has been suggested.[188] McDonald has reported a similar PCC-mediated oxidative cyclization of hydroxy polyenes in which he proposes a [2 + 2] cycloaddition mechanism.[189]



Scheme 46

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