Applications of stoichiometric organotransition metal complexes in organic synthesis

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Reviewing the literature published between 1 May 1995, and 30 April 1996
Continuing the coverage in *Contemporary Organic Synthesis*, 1996, **3**, 1

1 Introduction

This article is a review of the literature published between 1 May 1995 and 30 April 1996, and is designed to be a selective account of recent developments in the field of stoichiometric organotransition metals in organic synthesis.

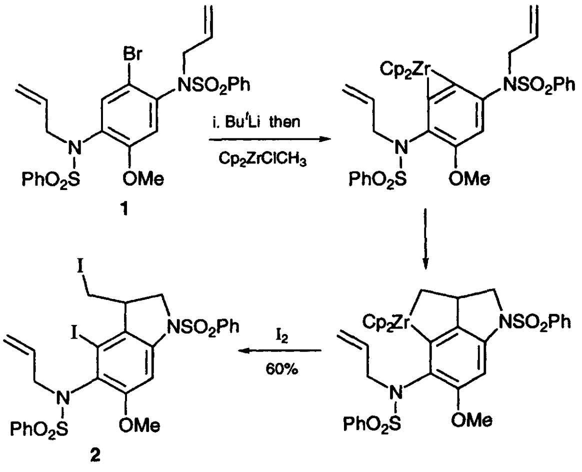
The manner in which the field has been subdivided follows precedent,[1] with preference being given to methods which will be of use to the practising organic chemist.

2 Transition metal alkyl, alkenyl, alkynyl and acyl complexes

This area of chemistry is dominated by the organometallic chemistry of zirconium, which continues to prove itself as a versatile and useful partner for organic substrates.

2.1 Alkyl and alkenyl organozirconium based methodology

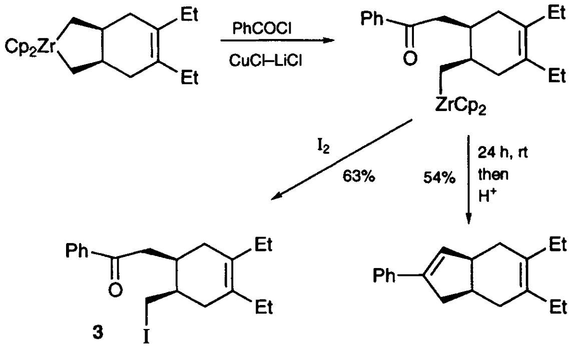
Recent work by Tietze directed towards a synthesis of the anticancer antibiotic CC-1065 utilised an elegant zirconocene mediated cyclisation as the key step (**Scheme 1**).[2] The cyclisation of **1**→**2** is based upon methodology championed by Buchwald, and is presumed to occur *via* transformation of a putative zirconium–didehydrobenzene complex into a



Scheme 1

zirconacyclopentene (the regiochemistry of this process is noteworthy). A transition metal was also essential in forming the final ring of the target: the remaining allyl group within compound **2** was cyclised onto the arene ring by a Heck reaction.

Insertion of novel electrophiles into the carbon–zirconium bond continues to be worthwhile, as each new reaction expands the scope of organozirconium chemistry. Takahashi's group has succeeded in reacting a zirconacyclopentene (which can be prepared from either an alkene or diene) with acyl chlorides, in the presence of copper(I) salts, to yield a zirconium containing ketone complex (**Scheme 2**).[3] In the absence of an external electrophile, intramolecular reaction of the carbon–zirconium bond with the carbonyl group ensued and, after acid treatment (presumably to effect dehydration), this furnished a cyclic olefin in good yield. The identity of the initially formed complex was established by trapping the remaining carbon–metal bond with iodine; this gave compound **3**.

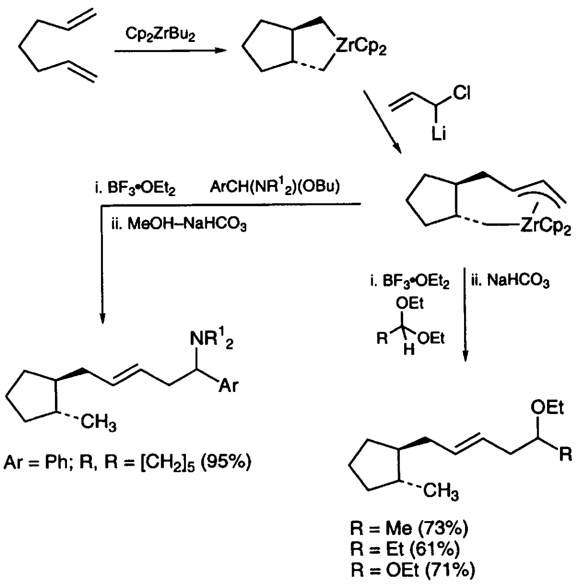


Scheme 2

The general theme of carbon–zirconium bond functionalisation has also been investigated by S. Kim and K. H. Kim who have shown that treatment of either alkenyl or alkyl zirconium species with $Bu_2Sn(OMe)_2$ promotes a transmetallation to the corresponding tin compounds;[4] this approach may prove to be useful in synthesis. Vinyl selenides may also be prepared from alkenyl zirconium compounds by reaction with aryl selenyl bromides.[5]

Srebnik has published an interesting route to boron enolates and α-halo ketones *via* treatment of a vinyl boronate with Schwartz's reagent, followed by (copper catalysed) reaction of the alkyl zirconium bond with an acyl chloride.[6]

Whitby has continued to expand the range of electrophiles that may be used in conjunction with his cyclisation–insertion reaction of dienes (this involves treatment of a diene with 'Cp_2Zr', followed by addition of an allyl halide and strong base, **Scheme 3**). Reactions of the allyl zirconium species formed during the above sequence with acetals, orthoesters, iminium ions and 1,3-dithenium tetrafluoroborate all give impressively functionalised compounds in a succinct manner (**Scheme 3**).[7]

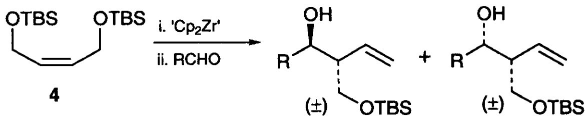


Ar = Ph; R, R = $[CH_2]_5$ (95%)

R = Me (73%)
R = Et (61%)
R = OEt (71%)

Scheme 3

A useful extension of Taguchi's method for preparing allyl zirconium species from allylic alcohols has been reported by Clark.[8] Treatment of the disilyl ether **4** with 'Cp_2Zr' and an aldehyde gave a series of homoallylic alcohols with good to excellent diastereoselectivity (favouring the *anti* isomer) (**Scheme 4**).

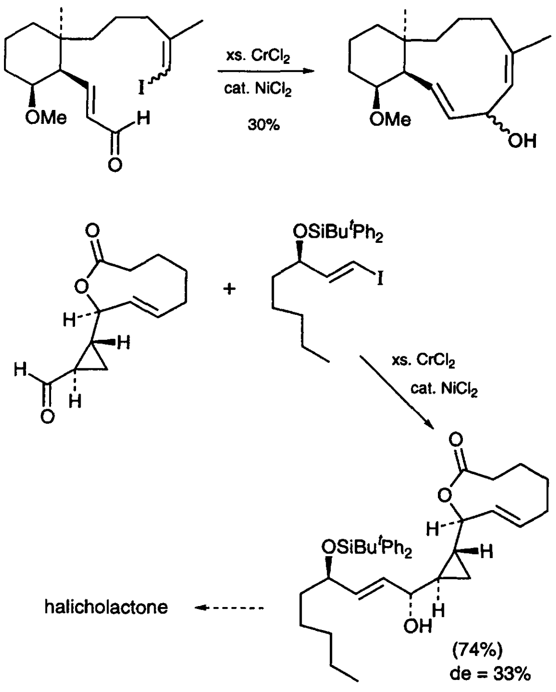


R = Ph (51%) de = 91%
R = Me (51%) de = 86%
R = Pr^i (31%) de = >95%

Scheme 4

2.2 Alkenyl chromium species in organic coupling reactions

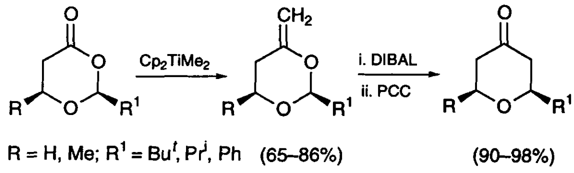
Two groups have utilised the reaction of vinyl iodides with aldehydes as promoted by excess chromium(II) chloride and catalysed by nickel. Procter's group reported an intramolecular version of this reaction during their studies towards a synthesis of solenolide F (**Scheme 5**).[9] Although the reaction proceeded in 30% yield, this may be a consequence of reaction of only one of the vinyl iodide geometrical isomers. Presumably, a stereochemically controlled synthesis of the cyclisation precursor will solve this problem. In addition, a total synthesis of halicholactone was recently reported by Wills *et al.* which used an intermolecular coupling reaction as a crucial step in assembly of the target skeleton (**Scheme 5**).[10]



Scheme 5

2.3 Alkyl titanium and manganese reagents

The reagent Cp_2TiMe_2 has been reported to be a powerful methylenating reagent by Petasis, and applications of this compound are now beginning to appear. Olefination of 1,3-dioxan-4-ones with this reagent led to compounds which are precursors to substituted tetrahydropyrans (**Scheme 6**).[11] Petasis *et al.* have also utilised $Cp_2Ti(CH_2TMS)_2$ and its reaction with alkynes as a method for synthesising vinylsilanes[12] and also for methylenating squaric acids to give α-methylene cyclobutenones.[13]

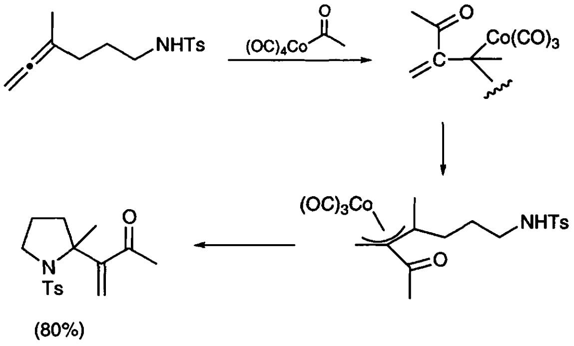


Scheme 6

Rieke has recently published a method for the direct formation of organomanganese bromides from alkyl halides (using lithium, naphthalene and MnX_2).[14] These derivatives will couple with acyl chlorides (*without* transition metal catalysis) to give ketones in good to moderate yields. Another group has also investigated these rather unusual organometallics and shown that they will couple with vinyl iodides to give substituted olefins in the presence of catalytic iron(III) acetylacetonate:[15] this coupling is stereospecific and proceeds in excellent yields.

2.4 Acyl transition metal complexes

The reaction of acyl cobalt complexes with functionalised allenes has been reported by Bates (**Scheme 7**).[16] The requisite acyl cobalt complexes were conveniently prepared from the reaction of alkyl halides with sodium tetracarbonylcobaltate and, upon reaction with an appropriately substituted allene, a cyclisation ensued. This process is presumed to occur *via* addition of the cobalt–acyl bond to the internal π system of the allene, to give an η^3-allyl cobalt system. Intramolecular nucleophilic attack by a variety of functional groups (alcohols, acids *etc.*) all formed five membered heterocycles, substituted with an olefin. This process works particularly well when the nucleophile is a sulfonamide, thus constituting an attractive synthesis of the pyrrolidine nucleus.

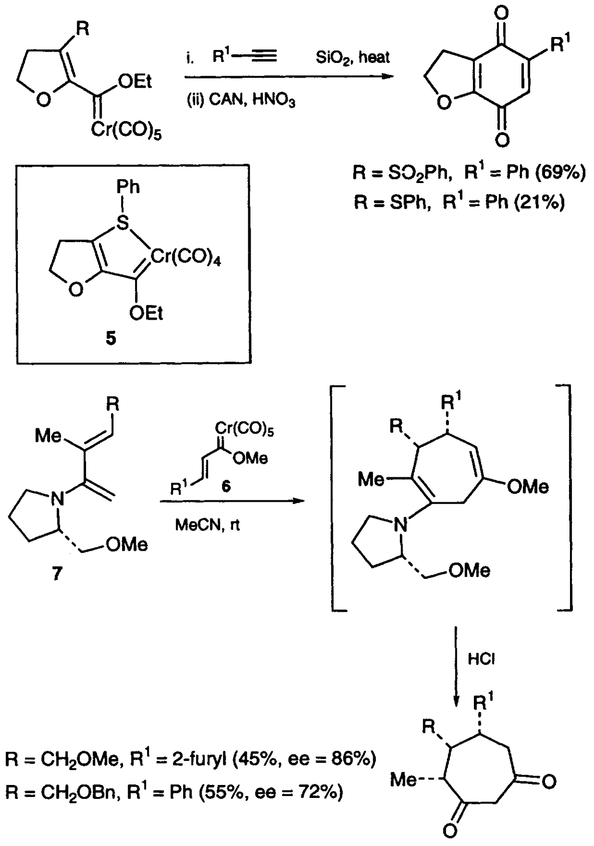


Scheme 7

3 Transition metal carbene and vinylidene complexes

3.1 Annulation reactions

The use of group VI carbenes in the construction of cyclic systems has proved to be a productive area of organometallic chemistry over recent years; the archetypal reaction within this area must be the Dötz reaction of vinyl carbenes with acetylenes.[17] Work published by Quayle has extended this methodology to encompass the construction of a series of annulated quinone derivatives.[18] Reaction of either a sulfone- or sulfide-stabilised vinyl carbene with an acetylene, under Kerr's dry state adsorption conditions, furnished the benzannulated compounds in moderate to good yields (after oxidative work-up). A clue to the mechanism of the annulation process was found in the detection and eventual isolation of an intermediate, namely the chelated tetracarbonyl complex **5** (**Scheme 8**). This complex readily undergoes annulation when resubjected to the reaction conditions, and appears to be a chelated (and 18-electron) form of the 16-electron intermediate formed by dissociation of CO from the vinyl carbene (this is postulated to be the rate determining step in the Dötz reaction).

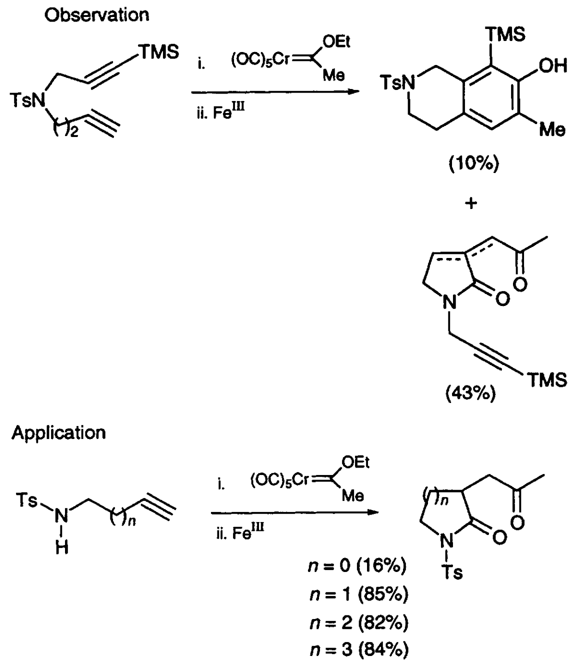


Scheme 8

The reaction of vinyl carbenes with dienes has also been exploited in the synthesis of seven membered carbocyclic compounds.[19] Enantiomerically enriched products were accessible *via* this chemistry, which involved treatment of a series of vinyl carbenes **6** with dienes (substituted with a chiral auxiliary) **7** at room temperature (**Scheme 8**). The ring forming reaction was presumed to occur from a divinylcyclopropane intermediate which arose from carbene ligand transfer to the diene: this compound, which was isolated, then underwent a Cope rearrangement.

Work from Germany has also described the cycloaddition chemistry of alkynyl carbenes with cyclic enamines[20] and that of β-amino vinyl carbenes with alkynes:[21] in both cases, the products were usefully substituted cyclopentadienes.

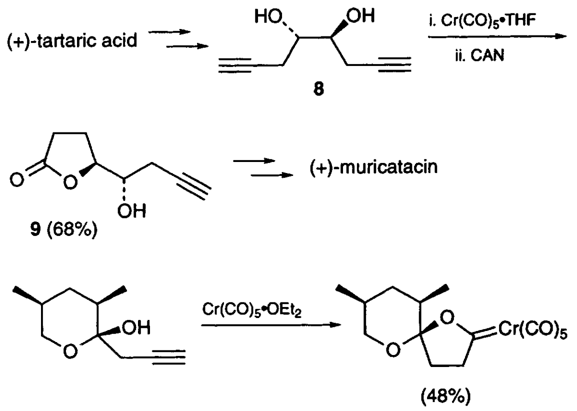
Mori has reported an interesting method for the formation of lactams (with sizes ranging from four to seven membered).[22] This reaction was originally noticed as a by-product in the [2+2+2] cyclisation of diynes and carbenes: the mechanistic hypothesis that emerged and the subsequent development of a general cyclisation method is indeed impressive (**Scheme 9**).



Scheme 9

3.2 Spirocycle formation

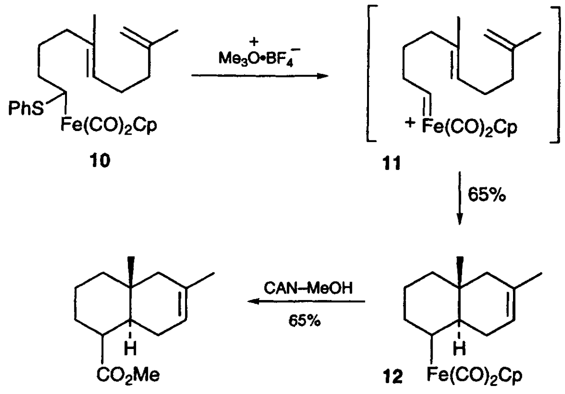
The reaction of but-3-ynyl alcohols with coordinatively unsaturated chromium and molybdenum carbonyls to yield cyclic carbenes has been studied further, with a view to extending the scope of the methodology and allowing the preparation of natural products. Quayle has used this reaction as a key step in his synthesis of (+) muricatacin (**8→9**, **Scheme 10**).[23] Schmidt has also reported work in this area, describing the cyclisation of a series of functionalised but-3-ynyl alcohols, each of which provides useful information about the generality of this method of ring formation (**Scheme 10**).[24]



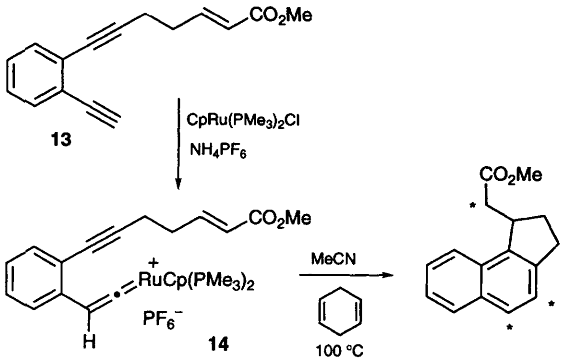
Scheme 10

3.3 Miscellaneous reactions of carbene and vinylidene complexes

Helquist has published some interesting work concerning the potential of cationic iron carbene complexes as initiators for polycyclisations (**Scheme 11**).[25] Compound **10** is a precursor to the transient cationic complex **11**, which was generated by



Scheme 11



Scheme 12

reaction with Meerwein's salt. The cyclisation that ensued furnished the iron-containing bicycle **12** in 65% yield; the iron unit was then decomplexed with ceric ammonium nitrate in methanol. Helquist mentions the intriguing possibility of a variant of this reaction which would utilise a chiral metal fragment (*e.g.* COCpLFe) as an initiator: the enantioselective version of this reaction is awaited with interest.

Several papers have been published which concern the preparation and reactivity of chromium cyclopropyl carbenes: Barluenga and Concellón report that vinylmethoxy carbenes undergo cyclopropanation when treated with chloroiodomethane and methyllithium.[26] The complexes thus formed may be transformed to the corresponding cyclopropyl esters by reaction with pyridine *N*-oxide. The authors point out that the reaction may be used as an indirect route to these esters as the direct transformation of α,β-unsaturated esters to their corresponding cyclopropyl derivatives, using identical conditions, led to a complex mixture of products.

Herndon has published a careful study on the rearrangement of vinyl cyclopropyl carbenes to cyclopentenones.[27] The mechanism of this stereospecific two carbon ring expansion is thought to be related to the Cope rearrangement of divinyl cyclopropanes, alluded to earlier: in this case the conformational requirements of the vinyl group and the carbene unit were probed and it was shown that both must be positioned *endo* to the cyclopropane unit before rearrangement could occur.

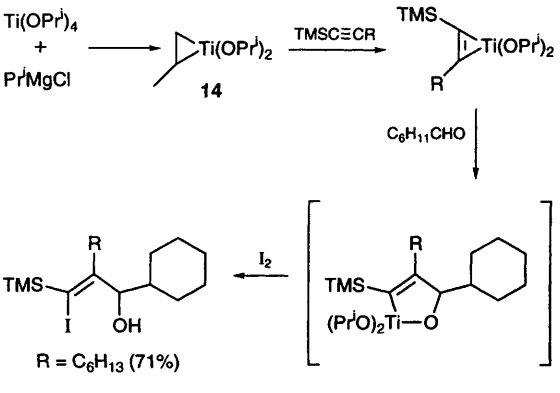
Finn and co-workers have published preliminary results regarding the cycloaromatisation of a ruthenium vinylidene complex formed from an enediyne (**Scheme 12**).[28] Indeed, conversion of the terminal acetylene within **13** into an organometallic complex **14**, served to increase its rate of cycloaromatisation relative to the parent hydrocarbon. The asterisks indicate the position of deuterium in the product when the cycloaromatisation is performed in deuteriocyclohexadiene. This approach to activation of the enediyne system represents a starting point for the construction of derivatives which have controllable cycloaromatisation rates.

4 η^2-Complexes

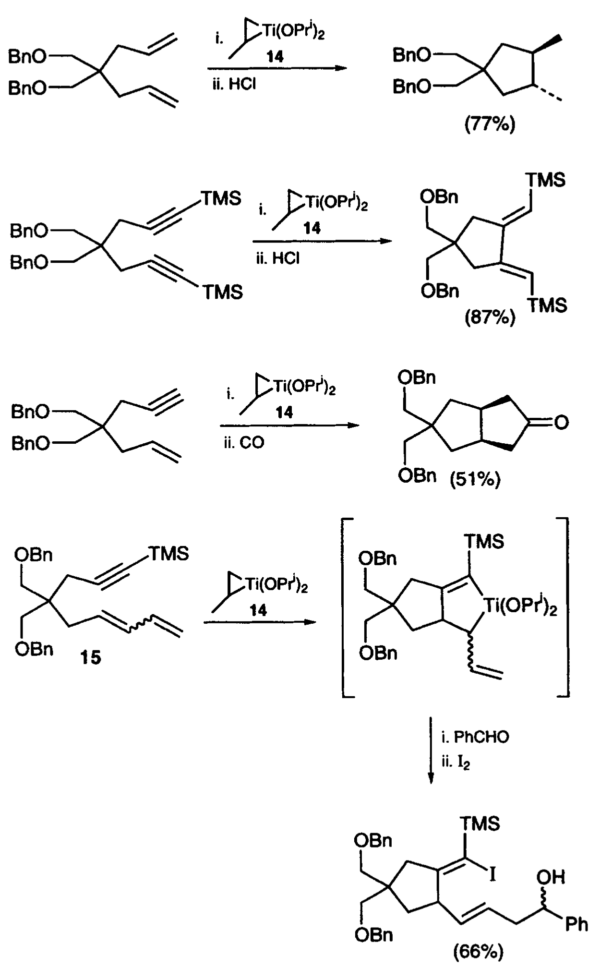
4.1 η^2-Complexes of titanium

Sato and co-workers have been almost solely responsible for the publication of a large body of work regarding the synthesis and reactivity of olefin and alkyne complexes of Ti(OR)$_2$. These complexes are formed by reacting a suitable olefin (or alkyne) with the propene–Ti(OPr^i)$_2$ complex **14**: this reagent (which is easily prepared from titanium tetraisopropoxide and isopropylmagnesium chloride) behaves as a 'Ti(OPr^i)$_2$' equivalent, in a manner reminiscent of the zirconium chemistry described earlier.[29] A simple example involves the reaction of **14** with alkynes (**Scheme 13**) which proceeds to give an addition complex.[30] This complex may be reacted with a series of electrophiles (RCHO, D$_2$O *etc.*) to furnish substituted olefins. The regiochemistry of reaction with an electrophile is difficult to control unless the alkyne is substituted with a TMS group; in this case reaction with two different electrophiles allows sequential replacement of each carbon–metal bond to form stereochemically defined vinylsilanes.

Reactivity of the complex **14** with dienes, diynes and eneynes has also been explored: cyclisation gave a series of titanabicycles which were subsequently



Scheme 13



Scheme 14

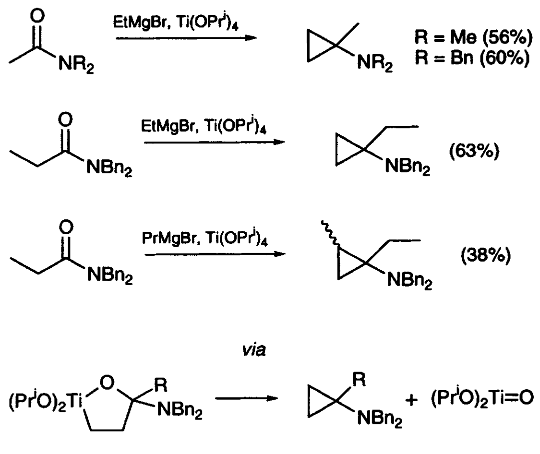
reacted with electrophiles such as HCl, I_2 or CO (**Scheme 14**).[31] Such chemistry puts titanium on an equal footing with both zirconium and cobalt and will have manifold uses in organic synthesis.

Even more elaborate reactivity was discovered when complex **14** was treated with dieneyne **15**, as the complex resulting from cyclisation had both a vinyl- and an allyl-titanium bond, each of which could be substituted separately.[32]

An interesting and useful preparation of cyclopropylamines from amides has been recently published by de Meijere.[33] This reaction involves treatment of a series of *N*,*N*-dialkyl amides with the titanium complex of an alkene (prepared from a Grignard and Ti(OPr^i)$_4$, **Scheme 15**). The inspiration for this work came from the related procedure for the synthesis of cyclopropanols.[34] Presumably, the mechanism of the reaction involves attack at the amide by a metal π complex to give a titanaoxacyclopentane; this is unstable with respect to cleavage to form a titanium oxygen double bond, thus ejecting a cyclopropylamine.

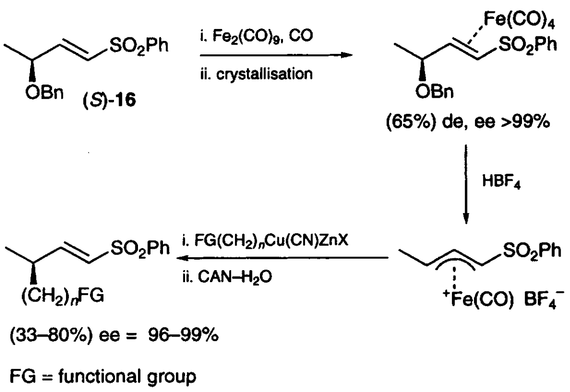
4.2 η^2-Complexes of iron

Enders has continued to explore the synthetic applications of enantiopure iron alkene complexes.[35]



Scheme 15

Complexation of vinyl sulfone **16** with $Fe_2(CO)_9$ under an atmosphere of CO gave the η^2-complex in good overall yield: a crystallisation was necessary to ensure that the complex was stereochemically homogeneous. Ionisation of the allylic ether with acid led to an η^3-cationic iron–allyl system, which was subsequently treated with a series of Knochel-type organozinc-copper reagents (**Scheme 16**). Nucleophilic attack was both stereo- and regio-selective: having performed its task, the iron carbonyl fragment was decomplexed with ceric ammonium nitrate (CAN), thus allowing the formation of enantiopure γ-substituted vinyl sulfones. Of course, participation by the transition metal means that overall the substitution had occurred with retention (*via* double inversion).



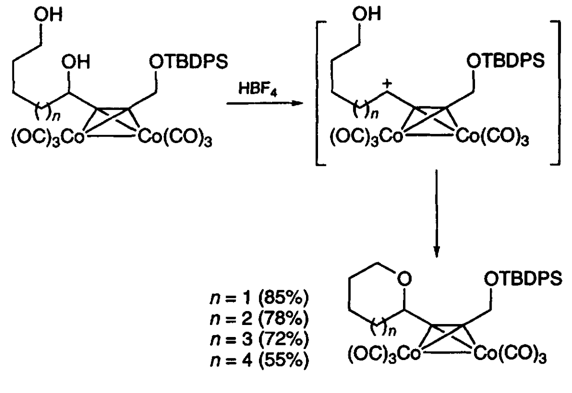
Scheme 16

4.3 η^2-Complexes of cobalt

In forming the dicobalt hexacarbonyl complex of an acetylene, the reactivity and steric environment of the acetylene is altered dramatically.[36] By far the most important reaction of these complexes involves the formation of a carbocation α to a complexed acetylene (which is accelerated many times by the transition metal) and subsequent trapping of this reactive intermediate by a nucleophile: this process is known as the Nicholas reaction.

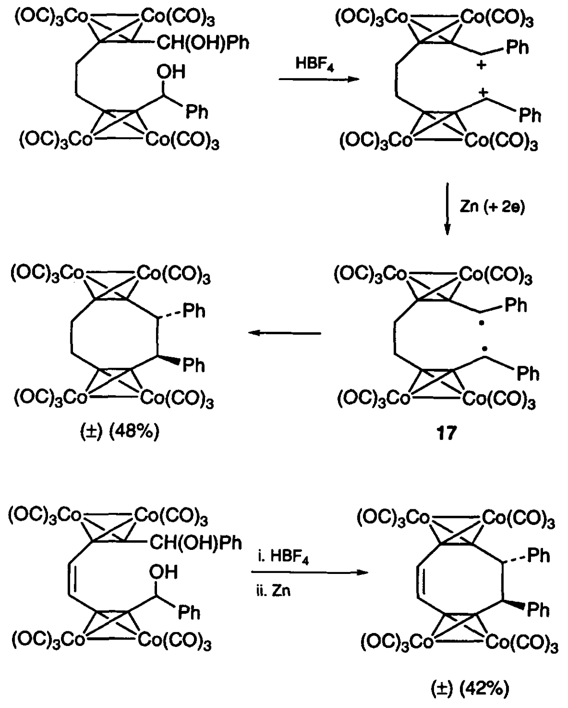
In order that a cation may be generated in the Nicholas reaction, it is clearly essential that a leaving group is attached in the prop-2-ynyl 1-position. Most studies make use of an alcohol or ether group (ionised by treatment with acid, *vide infra*). Green, however, has shown that prop-2-ynyl chlorides may be successfully complexed, ionised and trapped in the Nicholas reaction.[37] Unfortunately, the prop-2-ynyl chloride–dicobalt hexacarbonyl compounds, which are precursors to stabilised cations, could not be isolated due to competing dehalogenation reactions: a solution to this problem was found, however, by performing the complexation, ionisation and trapping experiments without isolation of any intermediates.

As part of a study directed towards the synthesis of marine toxins, Martín has investigated the Nicholas reaction for the formation of cyclic ethers (**Scheme 17**).[38] By using a diol precursor to a cobalt stabilised cation, Martín was able to make the trapping reaction an intramolecular one: this approach proved to be rather powerful for the construction of six to nine membered ethers.



Scheme 17

To complete this section, we would like to draw the reader's attention to a paper by Nicholas on the formation of cyclic eight membered diynes and cobalt complexed enediynes (**Scheme 18**).[39] These motifs are important constituents of a range of highly topical natural products. Construction of such highly strained (and potentially reactive) species was achieved by reduction of a dication with zinc or sodium to yield diradical **17**. Radical coupling ensued to form the cyclic compounds with extremely high diastereoselectivity in favour of the *trans* isomer. Decomplexation of the transition metal to form cyclic diynes was also accomplished: however, liberation of the cyclic enediynes remained elusive!



Scheme 18

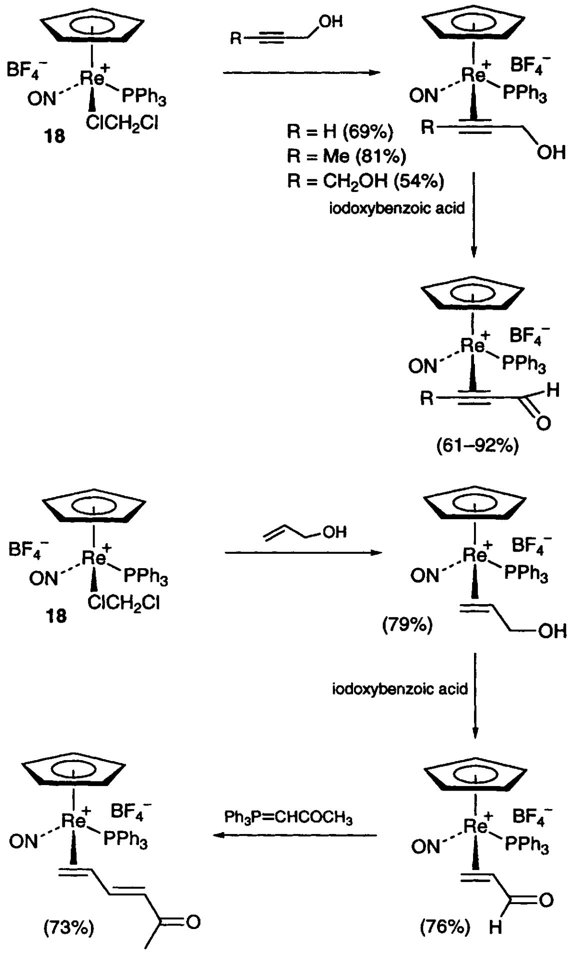
4.4 η^2-Complexes of rhenium

Rhenium complexes of the type Cp(NO)(PPh$_3$)(ClCH$_2$Cl)Re$^+$ BF$_4^-$ (**18**) are known to complex to both alkenes and alkynes. Bearing in mind that the above complexes can also be resolved, they provide an interesting method of achieving asymmetric synthesis. Guillemin has extended the work of Gladysz by investigating the reactivity of unsaturated alcohols with this organometallic fragment (**Scheme 19**).[40] Reaction of **18** with a series of unsaturated alcohols provided the η^2-complexes in good yields. These complexes could then be oxidised (without decomposition of the transition metal moiety) and even olefinated using Wittig chemistry. The products of such manipulation have potential as selectively protected enones or dieneones for more standard synthetic transformations.

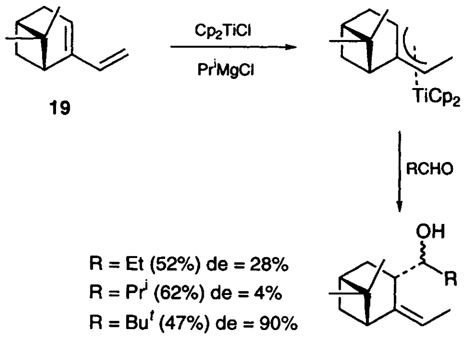
5 η^3-Complexes

5.1 η^3-Complexes of titanium

A method for the selective functionalisation of pinene derivatives using allyl titanium chemistry has been reported recently (**Scheme 20**).[41] Treatment of nopadiene **19** with a titanium(III) complex resulted in the regioselective formation of an η^3-allyl complex which was able to react further with a series of aldehydes. The outcome of these reactions was quite interesting: in each case the aldehyde attacked the endocyclic position of the allyl system from the *endo* face. The remaining (exocyclic) olefin was always formed with a *cis* configuration; indeed, relative configuration at the new hydroxy-substituted centre was the only facet of the reaction which was not completely controlled, and even in this case, use of a bulky aldehyde resulted in the formation of essentially one diastereoisomer.



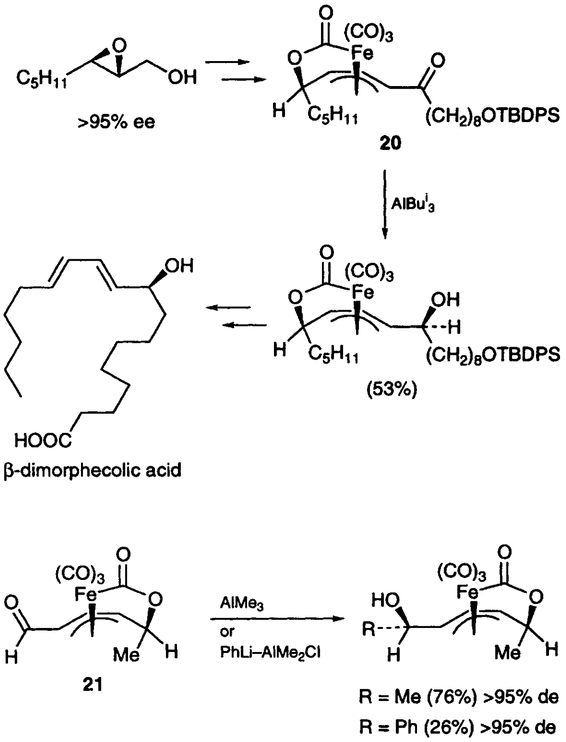
Scheme 19



Scheme 20

5.2 η^3-Complexes of iron

In our review of last year's work, we commented upon the synthesis of iron–diene complexes *via* π-allyltricarbonyliron lactone complexes. This work had an advantage over previous methodology in that the precursors to the organometallic complexes could be prepared in an enantiomerically enriched form by the Sharpless epoxidation. Ley has subsequently used this chemistry to report the first enantioselective synthesis of β-dimorphecolic acid (**Scheme 21**).[42] A key step was the diastereoselective reduction of ketone complex **20** (prepared in 95% ee *via* Sharpless chemistry) with Bu^i_3Al, which duly formed the alcohol centre in the final product.



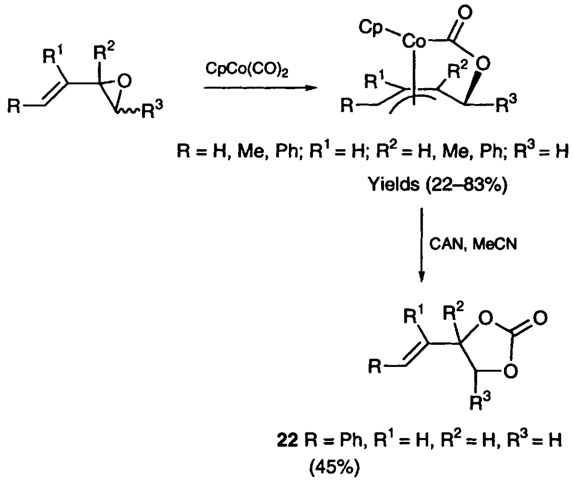
Scheme 21

Ley has also examined the addition of allylstannanes to ketone complexes similar to **20**, and found that the reaction proceeds with extremely high levels of stereocontrol.[43] In each case, conversion of the π-allyltricarbonyliron species to a stereochemically defined iron–diene compound is possible, thus providing a concise route to these versatile organometallic complexes.

Addition of organometallics to 1-formyl-substituted iron–diene complexes is not normally a highly stereoselective process, and mixtures of diastereoisomers are to be expected. Addition of organoaluminium reagents to formyl-substituted π-allyltricarbonyliron complexes (*e.g.* **21**), however, gives good levels of stereoselectivity.[44] If the resulting compounds were to be transformed into iron–diene complexes, then this route obviates the need to use formyl substituted iron-diene complexes at all.

5.3 η^3-Complexes of cobalt

An interesting study on the synthesis and reactivity of π-allylcyclopentadienyl cobaltolactone complexes has been reported by Kerr.[45] These compounds are made by photolysis of the corresponding vinyl epoxides in the presence of dicarbonylcyclopentadienyl cobalt, in a manner reminiscent of the preparation of the analogous iron systems. Once prepared, these compounds are likely to exhibit a wide range of interesting and useful chemistry: they are air stable and appear to be even more resistant to oxidation than the iron complexes mentioned earlier. Initial studies have concentrated on the reaction of these complexes with CAN in the presence of a nucleophile so as to produce functionalised olefins (*e.g.* **22**, **Scheme 22**).

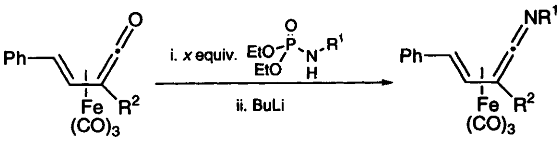


Scheme 22

6 η^4-Complexes

6.1 η^4-Iron–diene complexes

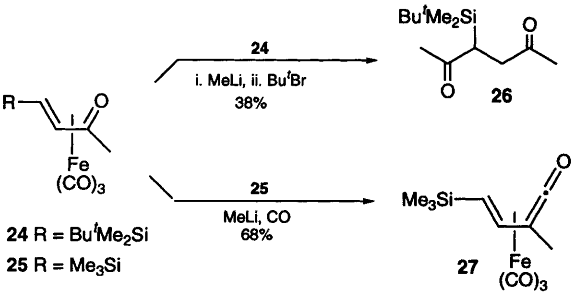
Interest in the use of iron–diene complexes has continued throughout the last twelve month period. The synthesis and reactivity of tricarbonyl(vinylketene)iron(0) complexes has received further attention from Gibson (née Thomas). Recently published results have illustrated that these vinylketene complexes can react with anions of diethyl *N*-alkyl(aryl)phosphoramidates, to provide tricarbonyl(vinylketenimine)iron(0) complexes **23** (**Scheme 23**).[46] The yield of vinylketimine complex was found to be dependent on the steric bulk of the phosporamidate substituent R^1 and the vinylketene complex substituent R^2. The use of phosphoramidate anions derived from chiral amines may provide access to enantiomerically enriched vinylketene complexes.



R^1	R^2	x	23 yield
Et	Bu^t	1.0	50%
Et	Bu^t	1.5	92%
Ph	Pr^i	1.5	87%

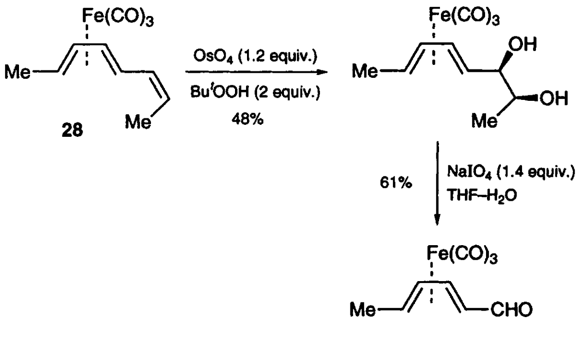
Scheme 23

This group has also investigated the synthesis and reactivity of iron carbonyl complexes of β-silyl substituted α,β-unsaturated ketones (**Scheme 24**).[47] Reaction of vinylketene complex **24** with methyllithium gave the α-substituted diketone **26.** Less bulky silyl substituents were shown to be more labile during this reaction, giving rise to desilylated products . In contrast, when the trimethylsilyl derivative **25** was treated with methyllithium under an atmosphere of carbon monoxide, the silylated vinylketene complex **27** was isolated in 68% yield.



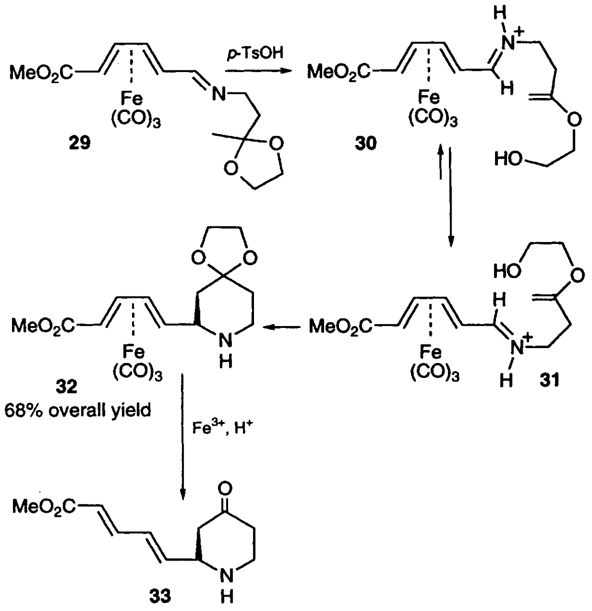
Scheme 24

Previous difficulties encountered during oxidation of the organic ligand within tricarbonyl(triene)iron complexes, caused by competitive oxidative decomplexation of the transition metal, have been overcome recently.[48] Donaldson has shown that (polyene)Fe(CO)$_3$ complexes such as **28** (**Scheme 25**) were stable to a two step osmylation–periodate cleavage sequence, and provided (dienal)Fe(CO)$_3$ complexes in reasonable overall yield.[49] This oxidation procedure provides a convenient route for the creation of unsaturated sites adjacent to the diene ligand, which can then undergo further transformations. The generality of this method was demonstrated through its application to the oxidation of a series of related tricarbonyl(triene)iron complexes.

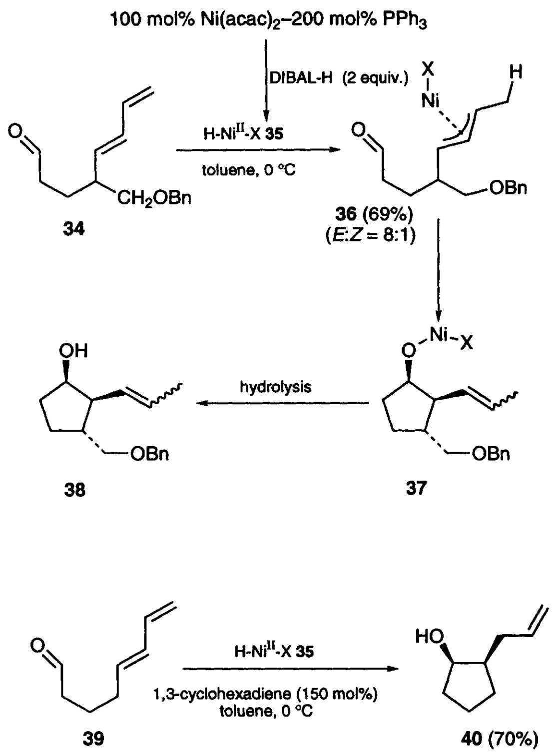


Scheme 25

The use of iron–diene chemistry in stereoselective organic synthesis has continued to provide interesting results. Recent examples include the diastereoselective synthesis of metal-bound 2,3,3a,7a-tetrahydroindoles, using a single electron transfer-mediated oxidative cyclisation.[50] High diastereoselectivities have also been achieved in the formation of heterobicyclic compounds, through the application of an intramolecular cyclisation of iron–diene complexes bearing amino acid derivatives.[51] Chiral 4-piperidones have been prepared by Troin (**Scheme 26**), using the $Fe(CO)_3$ unit as both a protecting and directing group during a diastereoselective intramolecular Mannich reaction.[52] The stereochemistry of the key cyclisation step has been rationalised in terms of the formation of the enol ethers **30** and **31**, with the former being the less stable of the two rotamers due to an increase in steric hindrance . Addition of the enol ether occurs (within **31**) from the face opposite to the bulky tricarbonyliron unit to yield the protected piperidone **32** as the major product (9: 1 mixture of stereoisomers at C-2). Decomplexation followed by acid hydrolysis yielded the optically pure piperidone **33**.



Scheme 26

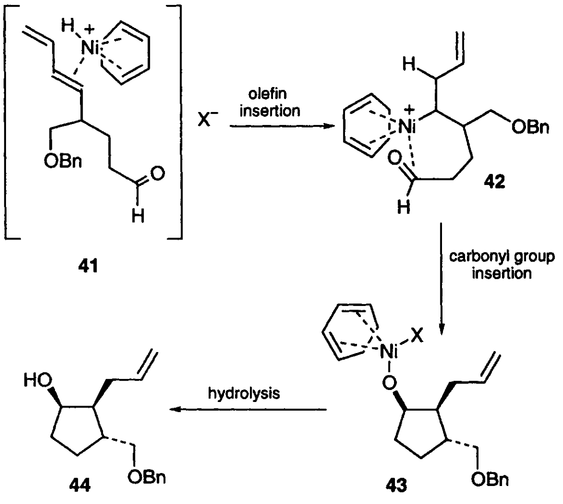


Scheme 27

6.2 η^4-Nickel–diene complexes

Nickel-promoted intramolecular oligomerisation of 1,3-dienes provides a valuable method for the formation of regio- and stereo-chemically defined rings.[53] Earlier reports from Mori *et al.* had outlined the use of a remarkably stereoselective cyclisation of 1,3-dienes (**Scheme 27**).[54] In this process, dienes such as **34** were treated with the nickel hydride complex **35**; the cyclised product **38** was produced stereoselectively through the intermediacy of π-allylnickel complex **36**. In all cases examined, cyclised products having an *internal* olefin on the side chain (as opposed to a terminal one) were formed predominantly. Recently published results have shown that the regiochemistry of this reaction can be altered through the addition of a stoichiometric amount of cyclohexa-1,3-diene to the nickel complex **35**, before addition of the diene substrate.[55] Under these modified reaction conditions, cyclisation of diene **39** provided the *terminal* olefin **40** in a stereoselective fashion.

Preferential formation of the terminal olefin was discovered in all cases examined. These contrasting results were interpreted mechanistically as being a consequence of reaction *via* the cationic Ni^{II} complex **41** (**Scheme 28**), which is formed in the presence of cyclohexa-1,3-diene (or other dienes that can adopt an s-*cis* conformation). Insertion of



Scheme 28

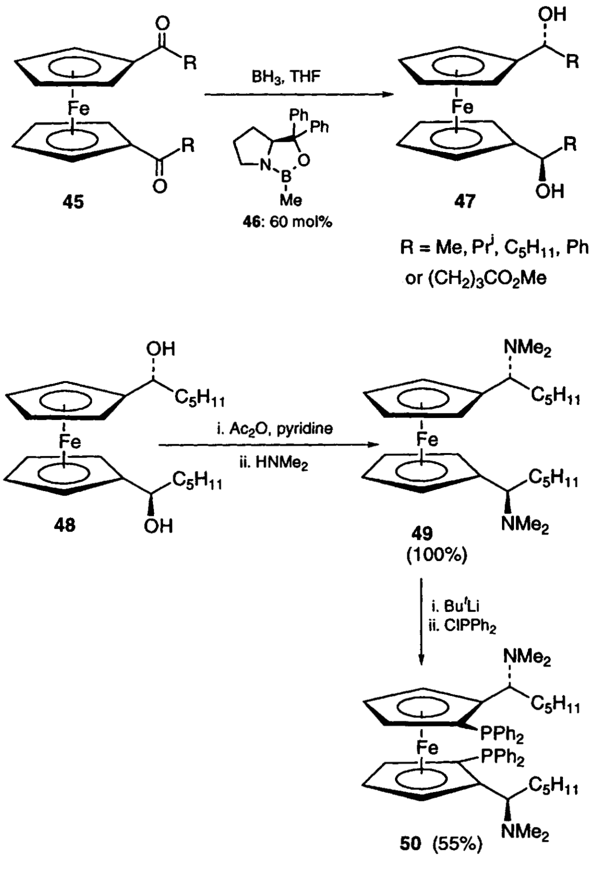
the olefin into the hydride–nickel bond gives complex **42**, which then undergoes carbonyl insertion and hydrolysis to provide the cyclised product **44**.

7 η^5-Complexes

7.1 Stoichiometric ferrocene complexes

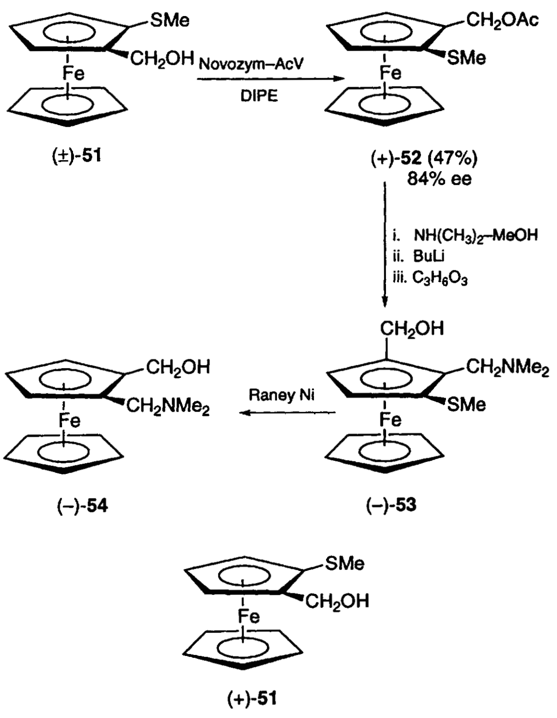
Investigation of the chemistry of ferrocene continues to be an extremely active and varied area of research, confirming the key role that this organometallic plays in many important synthetic transformations. Much of the focus of this work has been concerned with the preparation of chiral ferrocene derivatives, which may then be used as catalysts or ligands in a host of asymmetric transformations.[56]

Knochel has recently communicated a novel approach to C_2-symmetric 1,1′-ferrocenyl diols **47**, using the readily available ferrocenyl diketones **45** (**Scheme 29**).[57] Asymmetric reduction of the ketones was achieved through the use of borane in the presence of the oxazaborolidine catalyst **46**. Use of this catalyst provided the reduced products in excellent yield and >98% ee. The diols so obtained were then elaborated further to provide ligands of interest for potential asymmetric catalysis. Thus, in one example, the bis(dimethylamino) ferrocenyl diphosphine **50**, could be obtained in 55% overall yield from the chiral diol **48** *via* a directed metalation of the dimethylamine derivative **49**. As can be seen, this method provides an extremely efficient entry to C_2-symmetric ferrocenyl diols and aids the further development of asymmetric catalysts.



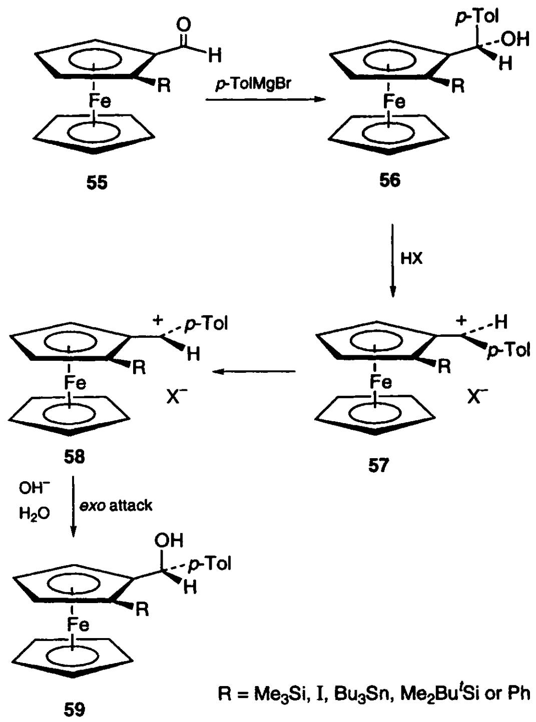
Scheme 29

Enantiomerically enriched ferrocenyl derivatives have also been prepared by Nicolosi *et al.* using a lipase-mediated resolution (**Scheme 30**).[58] In this procedure, a racemic mixture of 2-hydroxymethyl-1-methylthioferrocene (±)-**51** was resolved with Novozym 435 in the presence of vinylacetate, providing the chiral ester (+)-**52**, in 47% yield and 84% ee. If the reaction was allowed to proceed to 60% conversion, then the unreacted enantiomer (+)-**51** could be isolated in 95% ee. The configuration of ester (+)-**52** was established through its conversion to the known amino alcohol (−)-**54** *via* a four step sequence. During this procedure, the amino group was used to control the direction of lithiation, and this protocol provided amino alcohol (−)-**53**. Subsequent reduction gave compound (−)-**54** of known absolute configuration.



Scheme 30

Finally, Kagan has recently published the successful synthesis of a variety of chiral carbocations, which are α to a ferrocene system.[59] The Lewis acidity of these carbocations with regard to initiating a variety of reactions, including the Diels–Alder reaction, was also investigated. The synthesis of these cationic species (**Scheme 31**) commences with the reaction of aldehyde **55** with *p*-tolylmagnesium bromide, to provide the alcohol **56** as a single epimer, in yields ranging from 54 to 90%. The (*S*) configuration at the newly formed stereogenic centre was assumed through *exo* attack at the carbonyl group, with the carbonyl oxygen adopting

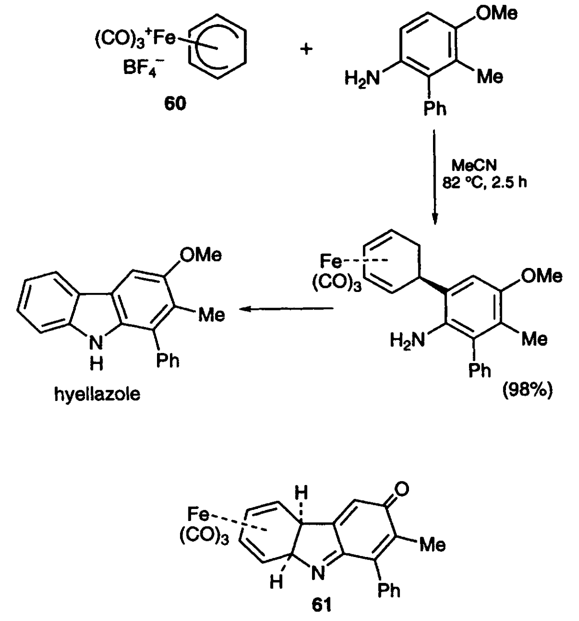


Scheme 31

an arrangement *anti* to the R group. Conversion to the carbocation **57** was then accomplished in 16% (R = Me$_2$Bu^{t}Si) to 68% (R = Ph) yield, through reaction with strong acid and acetic anhydride or trifluoromethanesulfonic anhydride. These carbocations were shown to adopt (as expected) the least sterically hindered conformation **58**, and this was proved by hydrolysis to alcohol **59**. In most cases, these cations acted as efficient catalysts in the Diels–Alder reaction between cyclopentadiene and methacrolein. Unfortunately, the product mixtures were shown to be racemic. Further investigations using these versatile cations are being undertaken and these should reveal other opportunities for asymmetric synthesis.

7.2 η^5-Iron complexes

As part of a continuing programme to explore the scope of transition metal–diene complexes in organic synthesis,[60] Knölker *et al.* have recently published a high yielding, convergent synthesis of the marine alkaloid hyellazole (**Scheme 32**).[61] The key step in this sequence required the electrophilic aromatic substitution of an appropriately substituted arylamine with the tricarbonyliron-complexed cyclohexadienylium cation **60**, to provide a substituted iron complex in almost quantitative yield. Subsequent oxidation with ferricenium hexafluorophosphate provided the target alkaloid in 59% yield. Complex **61**, which was formed as a side product during this oxidation, could also be readily converted to hyellazole *via* a demetallation–*O*-methylation sequence. This approach provided an extremely short (three steps) and efficient (83% overall yield based on **60**) method for the synthesis of carbazole alkaloids.



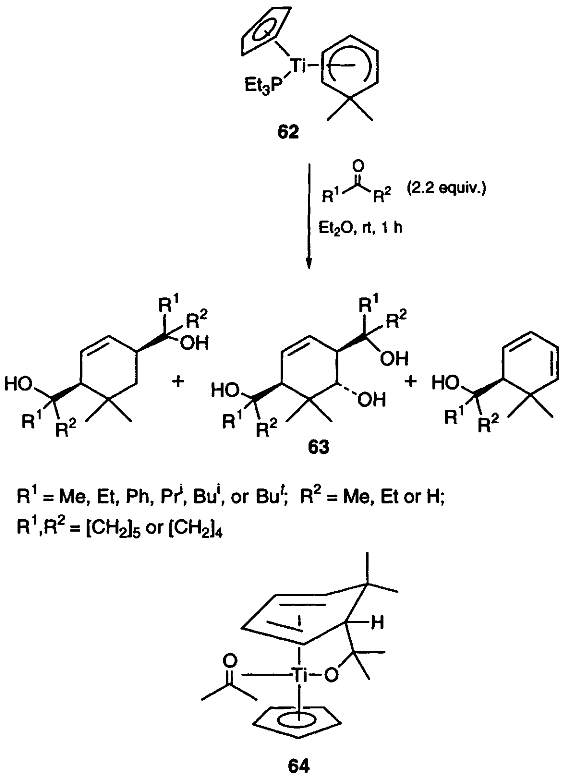
Scheme 32

7.3 η^5-Titanium complexes

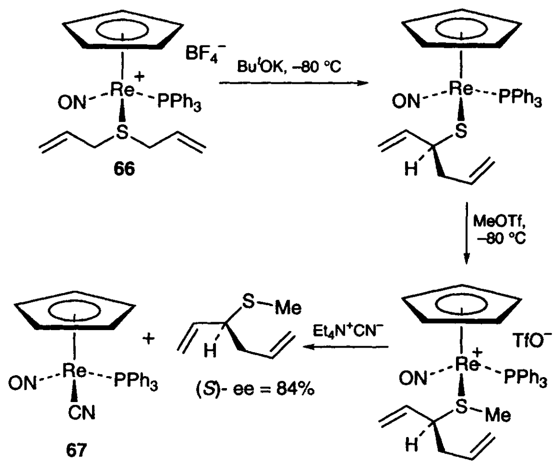
A recent communication by Ernst *et al.* has highlighted the discovery of a new class of coupling reactions, involving the reaction of a novel half-open titanocene complex **62** with aldehydes and ketones (**Scheme 33**).[62] The reaction proceeded with unusual 1,4-*syn* addition of the ketone or aldehyde, and was used to create up to five new stereocentres with very high or complete stereoselectivity. Simple modification of the reaction conditions, through exposure to air after addition of the substrate, resulted in formation of the triol **63**, in which the third hydroxy group was orientated *anti* to the existing 1,4-substituents. The origin of the stereochemistry has been rationalised through the generation of an η^4-diene complex **64** in which the second ketone initially coordinates to titanium prior to coupling. The exceptional regio- and stereo-control exhibited by this reaction bodes well for its application to the synthesis of polyoxygenated carbocycles.

7.4 η^5-Rhenium complexes

The application of rhenium complexes to the asymmetric synthesis of organosulfur compounds has recently been investigated by Gladysz (**Scheme 34**).[63] The key reaction proceeded *via* the [2,3] rearrangement of ylides derived from di(allyl) and di(prop-2-ynyl) sulfide complexes. Thus, treatment of the di(allyl) sulfide complex **66** with potassium *tert*-butoxide gives the rearranged complex, which was then methylated and decomplexed to provide the chiral (*S*) sulfide and rhenium complex **67** [this may be recycled in three steps to the di(allyl) sulfide



Scheme 33



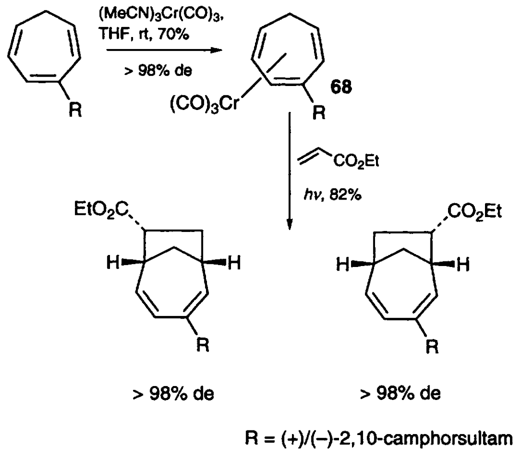
Scheme 34

66]. The starting material for this desymmetrisation process is prepared from commercially available $Re_2(CO)_{10}$, using a resolution. The ready availability of starting materials, coupled with the air stability of all the compounds depicted in **Scheme 34**, provided an ideal process for the synthesis of chiral sulfides on a multi-gram scale.

8 η^6-Complexes

8.1 η^6-Chromium complexes

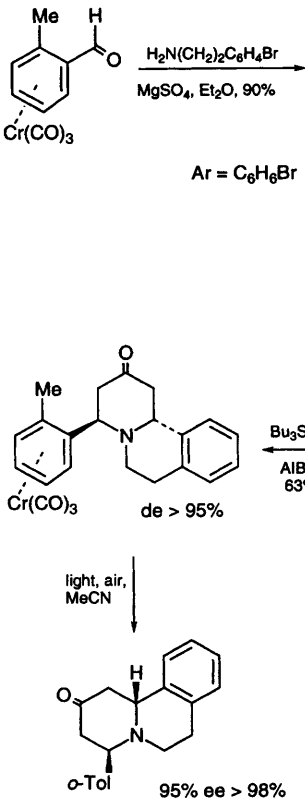
Much effort has been focused on the use of chromium(0) complexes in higher order cycloadditions.[64] This type of reaction has been shown to provide efficient routes to highly substituted polycyclic compounds, which may otherwise prove difficult to construct. Rigby has developed this methodology to encompass the generation of optically active cycloadducts using diastereoisomerically enriched tricarbonyl(cycloheptatriene)chromium(0) complexes **68** (**Scheme 35**).[65] Reaction of these complexes with ethyl acrylate gave the expected cycloadducts as a 1 : 1 mixture of regioisomers in diastereoisomerically pure form. Further examples have confirmed the complete stereocontrol exhibited by this reaction in a variety of [6π + 4π] and [6π + 2π] cycloadditions.



Scheme 35

Planar tricarbonylchromium complexes have also been used to good effect in stereoselective hetero-Diels–Alder and 1,3-dipolar cycloadditions.[66] One recent example involved the synthesis of indolizidines and quinolizidines (**Scheme 36**).[67] In this sequence, the chiral aldimine complex **69** underwent a smooth aza-Diels–Alder reaction with Danishefsky's diene, in the presence of tin(IV) chloride, to provide diastereoisomerically pure 2,3-dihydropyridin-4-one. Simple tributyltin mediated radical cyclisation proceeded with excellent stereoselectivity, which was accounted for in terms of a transition state conformation that minimised $A^{[1,3]}$-strain between the aryl methyl group and the dihydropyridinone ring.[67]

The use of η^6-chromium complexes in the synthesis of natural products and their derivatives has been of substantial interest.[68] One recent (formal) synthesis of the antileukaemic lactone (–)-steganone by Uemura *et al.*, employed a stereoselective cross-coupling of a planar chiral (arene)-chromium complex (**Scheme 37**).[69] The success of this sequence relied on two key transformations. Initially, *ortho*-lithiation of complex **70**, proceeded in a diastereoselective manner, allowing access to the chiral intermediate **71**. Subsequent reduction, followed by palladium catalysed cross-coupling with 2-formyl-4,5-methylenedioxyphenylboronic acid **72**,



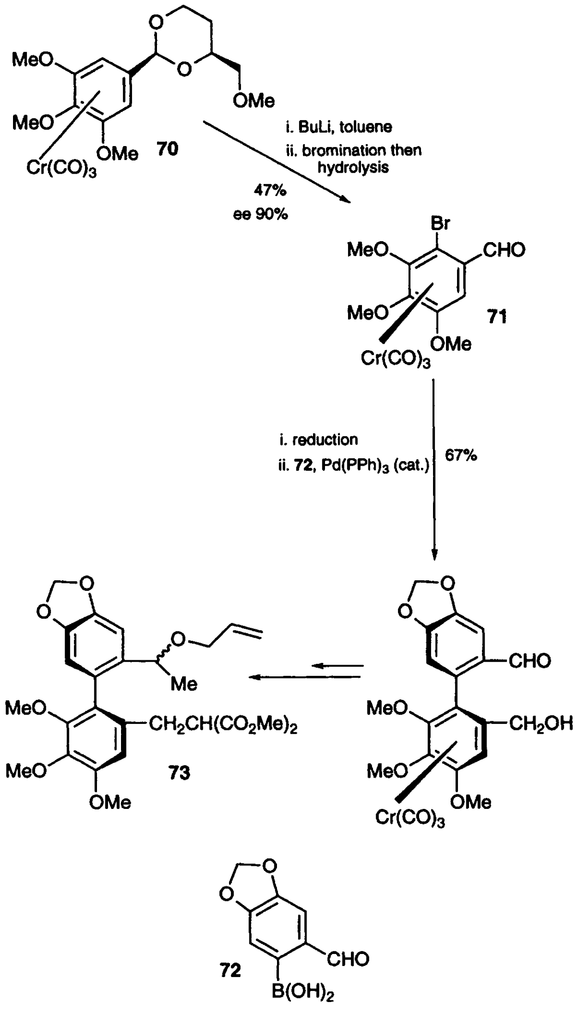
Scheme 36

gave a single biaryl product, the stereochemistry of which was assigned on the basis of previous results reported by this group.[70] Further elaboration gave the demetallated product **73**.

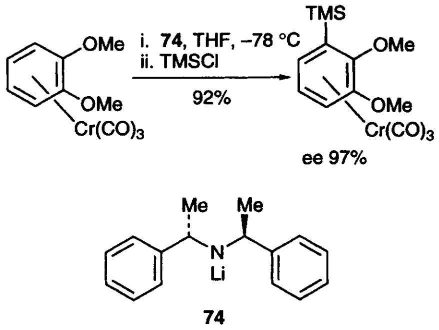
Efficient access to chiral tricarbonylchromium(0) complexes is of prime importance if they are to be utilised in asymmetric synthesis. One method by which this may be achieved involves the enantioselective deprotonation of a prochiral complex using a chiral base, followed by quenching with an appropriate electrophile.[71] Schmalz has described the enantioselective deprotonation–silylation of mono- and 1,2-dimethoxybenzene(tricarbonyl)chromium derivatives, using the chiral lithium amide **74** (**Scheme 38**).[72] As expected, best results were obtained when an *in situ* quench was employed, providing the silylated products in high enantiomeric purity.

8.2 η^6-Iron complexes

η^6-Iron complexes have recently been used in the synthesis of polyhydroxylated nortropane derivatives (**Scheme 39**).[73] Interest in this area was stimulated by the discovery of a new class of natural products (the calystegines), possessing the 1-hydroxynortropane structure. The approach described here relies on efficient formation of the substituted cycloheptadiene **75**, using the method originally described by Pearson.[74] Subsequent hetero-Diels–Alder reaction of this cycloheptadiene with the appropriate acyl nitroso compound, occurred with complete stereoselectivity. Further transformations provided the target 1-hydroxynortropane. This route should provide ready access to the calystegines and derivatives possessing similar bicyclic structures.



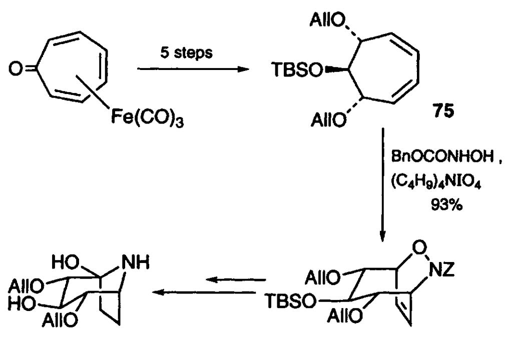
Scheme 37



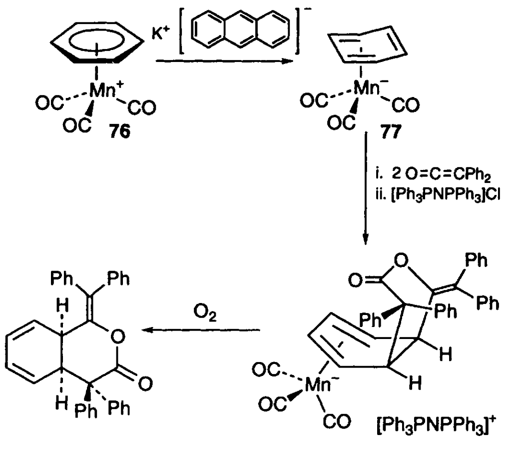
Scheme 38

8.3 η^6-Manganese complexes

It has been shown previously that the benzene ring in the η^6-manganese complex **76** (**Scheme 40**), can



Scheme 39

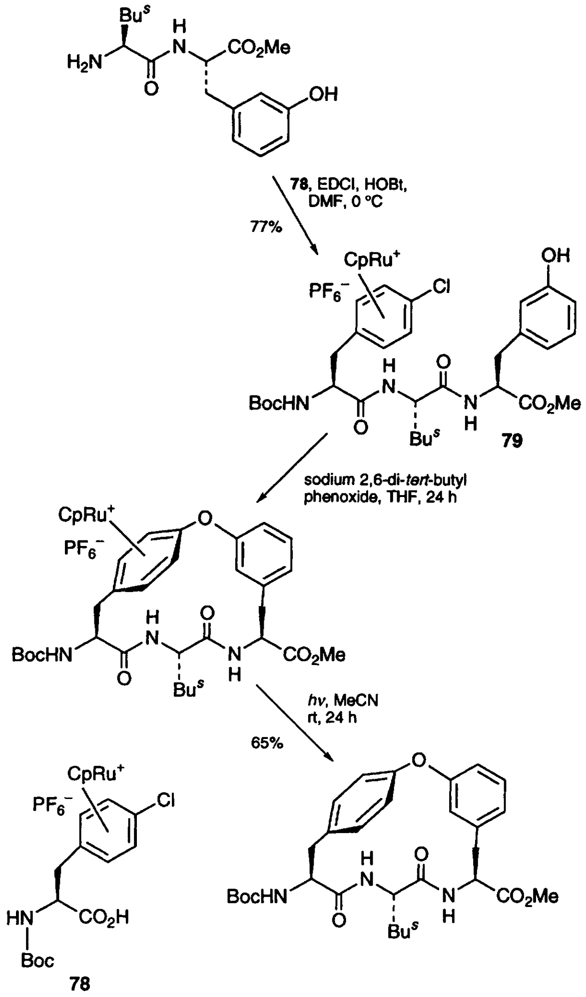


Scheme 40

undergo reductive activation with naphthalenide, thus allowing further functionalistion of the aromatic ring.[75] The chemistry of this system has now been extended to include an interesting [2+2+2] addition with diphenylketene.[76] Reduction of **76** with potassium anthracenide provided the postulated 18-electron transition metal complex **77** which, by virtue of the uncoordinated double bond, underwent a formal [2+2+2] cycloaddition with two equivalents of diphenylketene, and gave the bicyclic lactone complex. Oxidative decomplexation gave the highly functionalised dihydroisochroman-3-one. Further investigation should uncover other applications for this unusual cycloaddition.

8.4 η^6-Ruthenium complexes

Recent interest in the area of arene–ruthenium chemistry has been primarily concerned with the synthesis of cyclic biphenyl ethers as they form a key structural element in many biologically important peptides, including piperanomycin, bouvardin and the vancomycin family of antibiotics.[77] Rich has developed a macrocyclisation procedure for the synthesis of these cyclic biphenyl ether peptides (**Scheme 41**).[78] This protocol constructs the biphenyl ether linkage as one of the final synthetic steps, after initial formation of the peptide skeleton. The ruthenium π-complex of the Boc-protected amino acid **78** was initially converted to the tripeptide **79**, using standard peptide chemistry. Macrocyclisation was then achieved *via* an intramolecular S_NAr reaction of this activated π-complex. Subsequent photolysis gave the target cyclic tripeptide in 65% overall yield. This method should allow for the generation of diverse libraries of variously substituted aromatic peptides.

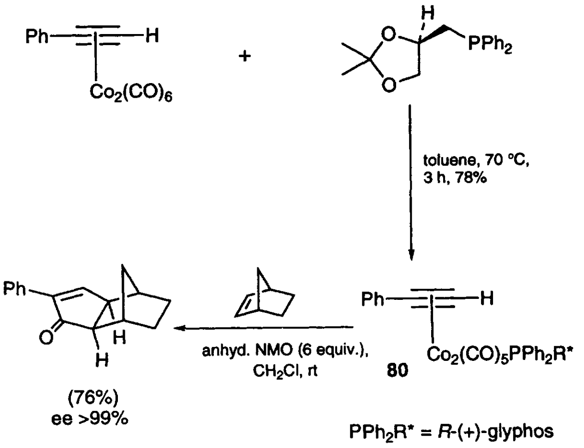


Scheme 41

9 Transition metal mediated cycloadditions

9.1 Pauson–Khand type reactions

Application of the Pauson–Khand reaction to the synthesis of enantiomerically enriched cyclopentenones has been investigated recently by Kerr.[79] Although the use of brucine *N*-oxide as a chiral promoter of this reaction provided cyclised products with moderate enantioselectivity, much greater success was achieved using the optically pure (alkyne)pentacarbonyldicobalt complexes **80** (**Scheme 42**) and anhydrous *N*-methylmorpholine *N*-oxide (NMO). These complexes, containing the chiral ligand (*R*)-(+)-glyphos, were readily prepared from the corresponding cobalt alkyne complex and

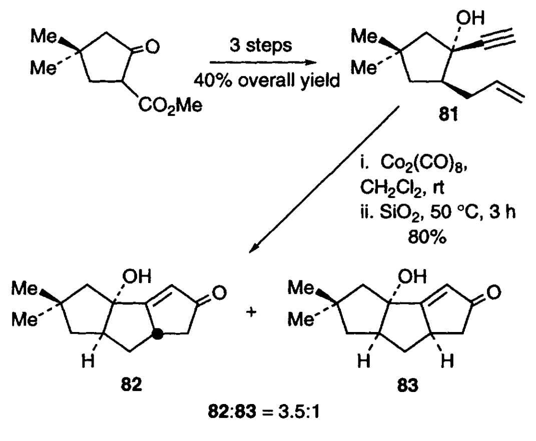


Scheme 42

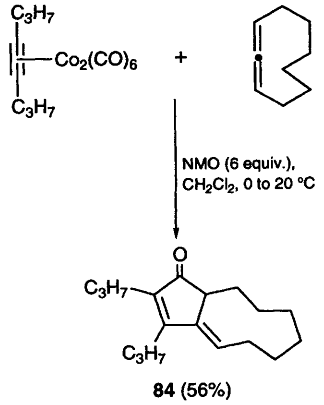
the individual diastereisomers separated by HPLC. Reaction with norbornene in the presence of anhydrous NMO prevents racemisation of the chiral cobalt complexes, giving the cyclopentenones in good yield (65–90%) and in good to excellent enantioselectivity (ees range from 64 to 99%).

A stereoselective Pauson–Khand cyclisation has been used as the key step in the synthesis of linearly fused triquinanes (**Scheme 43**).[80] The hirsutene type skeleton was constructed using the monocyclic precursor **81**, which was formed in three steps and 40% overall yield from the known cyclopentanone. Conversion into the corresponding dicobalt hexacarbonyl complex used conventional procedures, and this was followed by an intramolecular [2+2+1] cycloaddition which gave the required tricyclic compounds. The yields of the diastereoisomers **82** and **83** were found to depend heavily on the conditions employed for the cyclisation process, which included thermolysis in solution and oxidative initiation in the presence of NMO.

The advent of mild methods for promotion of the Pauson–Khand reaction has led to the development of a novel procedure for the intermolecular co-cyclisation of alkynes and allenes, resulting in formation of 4-alkylidenecyclopent-2-enones



Scheme 43

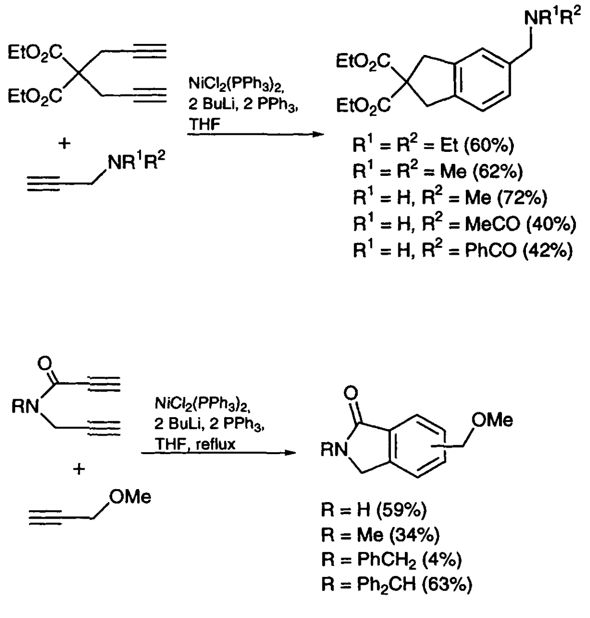


Scheme 44

(**Scheme 44**).[81] Use of an allene as the *ethylenic* partner, with NMO as promoter, gave cyclised products such as the enone **84** in good yield. The generality of this reaction was also demonstrated through the successful use of aromatic and silylated allenes. Use of the Pauson–Khand reaction in this manner provided a much improved alternative to the previously described $Fe_2(CO)_9$ mediated reaction.[82]

9.2 Nickel promoted [2+2+2] cyclotrimerisations

It has been shown that nickel(0) promotes a host of co-cyclisation reactions between α,ω-diynes and monoynes to provide bicyclic aromatics.[83] However, reports regarding the use of nitrogen-containing alkynes in such reactions are limited. This deficiency of information has prompted Smith to undertake an in-depth investigation of the reactivity of alkynylamines and alkynylamides (**Scheme 45**).[84] It was

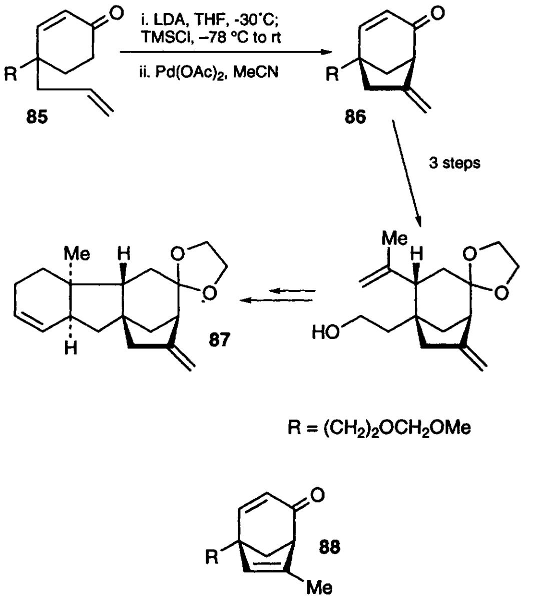


Scheme 45

found that both secondary and tertiary amino groups, in the monoyne or diyne unit, were amenable to cyclisation, whilst amides in the diyne required heating to effect reaction. Unfortunately, the cyclisation of medium length diynes under these conditions proved unsuccessful, probably as a consequence of an unfavourable entropic effect.

9.3 Palladium promoted cycloalkenylation

The stereoselective construction of the complex skeleton of an important family of plant growth regulators, known as the gibberellins, has been achieved using a palladium promoted cycloalkenylation (**Scheme 46**).[85] Treatment of the corresponding silyl enol ether of enone **85** with palladium(II) acetate, gave the required enone **86** as the sole product in 92% yield. Application of semiempirical Hamiltonian calculations subsequently showed that this *exo*-olefin ($\Delta H_f = -93.99$ kcal mol^{-1}; 1 cal = 4.184 J) was more stable than the corresponding *endo*-olefinic enone **88** ($\Delta H_f = -92.61$ kcal mol^{-1}). The enone **86** was transformed to the pentacyclic compound **87**, which may be used as a key intermediate in the preparation of the gibberellin GA_{12}.



Scheme 46

Acknowledgements

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10 References

1 T. J. Donohoe, *Contemp. Org. Synth.*, 1996, **3**, 1.
2 L. F. Tietze and W. Buhr, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1366.
3 T. Takahashi, M. Kotora and Z. Xi, *J. Chem. Soc., Chem. Commun.*, 1995, 1503.
4 S. Kim and K. H. Kim, *Tetrahedron Lett.*, 1995, **36**, 3725.
5 X. Huang and L.-S. Zhu, *J. Chem. Soc., Perkin Trans. 1*, 1996, 767.
6 B. Zheng and M. Srebnik, *Tetrahedron Lett.*, 1995, **36**, 5665.
7 T. Luker and R. J. Whitby, *Tetrahedron Lett.*, 1995, **36**, 4109. For reactions of the C–Zr bond with other electrophiles see: G. D. Probert, R. J. Whitby and S. J. Coote, *Tetrahedron Lett.*, 1995, **36**, 4113; D. F. Taber and Y. Wang, *Tetrahedron Lett.*, 1995, **36**, 6639; S. Pereira, B. Zheng and M. Srebnik, *J. Org. Chem.*, 1995, **60**, 6260; T. Takahashi, D. Y. Kondakov, Z. Xi and N. Suzuki, *J. Am. Chem. Soc.*, 1995, **117**, 5871; J. Barluenga, R. Sanz and F. J. Fañanás, *J. Chem. Soc., Chem. Commun.*, 1995, 1009.
8 A. J. Clark, I. Kasujee and J. L. Peacock, *Tetrahedron Lett.*, 1995, **36**, 7137.
9 M. B. Roe, M. Whittaker and G. Procter, *Tetrahedron Lett.*, 1995, **36**, 8103.
10 D. J. Critcher, S. Connolly and M. Wills, *Tetrahedron Lett.*, 1995, **36**, 3763.
11 N. A. Petasis and S.-P. Lu, *Tetrahedron Lett.*, 1996, **37**, 141.
12 N. A. Petasis, J. P. Staszewski and D.-K. Fu, *Tetrahedron Lett.*, 1995, **36**, 3619.
13 N. A. Petasis, Y.-H. Hu and D.-K. Fu, *Tetrahedron Lett.*, 1995, **36**, 6001.
14 S.-H. Kim, M. V. Hanson and R. D. Rieke, *Tetrahedron Lett.*, 1996, **37**, 2197.
15 G. Cahiez and S. Marquais, *Tetrahedron Lett.*, 1996, **37**, 1773.
16 R. W. Bates. T. Rama-Devi and H.-H. Ko, *Tetrahedron*, 1995, **51**, 12939.
17 K. H. Dötz and J. Pfeiffer, *Chem. Commun.*, 1996, 895; J. Barluenga, F. Aznar and S. Barluenga, *J. Chem. Soc., Chem. Commun.*, 1995, 1973; A. Rahm and W. Wulff, *J. Am. Chem. Soc.*, 1996, **118**, 1807; see also A. D. Reed and L. S. Hegedus, *J. Org. Chem.*, 1995, **60**, 3787.
18 J. E. Painter, P. Quayle and P. Patel, *Tetrahedron Lett.*, 1995, **36**, 8089.
19 J. Barluenga, F. Aznar, A. Martín and J. T. Vázquez, *J. Am. Chem. Soc.*, 1995, **117**, 9419.
20 J. G. Meyer and R. Aumamm, *Synlett*, 1995, 1011.
21 B. L. Flynn, F. J. Funke, C. C. Silveira and A. de Meijere, *Synlett*, 1995, 1007.
22 N. Ochifuji and M. Mori, *Tetrahedron Lett.*, 1995, **36**, 9501.
23 P. Quayle, S. Rahman and J. Herbert, *Tetrahedron Lett.*, 1995, **36**, 8087.
24 B. Schmidt, P. Kocienski and G. Reid, *Tetrahedron*, 1996, **52**, 1617; see also F. E. McDonald, C. C. Schultz and A. K. Chatterjee, *Organometallics*, 1995, **14**, 3628.
25 C. T. Baker, M. N. Mattson and P. Helquist, *Tetrahedron Lett.*, 1995, **36**, 7015.
26 J. Barluenga, P. L. Berna Jr., J. M. Concellón, *Tetrahedron Lett.*, 1995, **36**, 3937; see also B. C. Söderberg, D. C. York, E. A. Harriston, H. J. Caprara and A. H. Flurry, *Organometallics*, 1995, **14**, 3712.
27 D. K. Hill and J. W. Herndon, *Tetrahedron Lett.*, 1996, **37**, 1359.
28 Y. Wang and M. G. Finn, *J. Am. Chem. Soc.*, 1995, **117**, 8045.
29 A. Kasatkin, T. Nakagawa and F. Sato, *J. Am. Chem. Soc.*, 1995, **117**, 3881.
30 K. Harada, H. Urabe and F. Sato, *Tetrahedron Lett.*, 1995, **36**, 3203: see also Y. Gao, K. Harada and F. Sato, *Chem. Commun.*, 1996, 533; Y. Gao, K. Harada and F. Sato, *Tetrahedron Lett.*, 1995, **36**, 5913; Y. Hori-

kawa, T. Nomura, M. Wantanbe, I. Miura, T. Fujiwara and T. Takeda, *Tetrahedron Lett.*, 1995, **36**, 8835.

31 H. Urabe, T. Hata and F. Sato, *Tetrahedron Lett.*, 1995, **36**, 4621.

32 H. Urabe, T. Takeda and F. Sato, *Tetrahedron Lett.*, 1996, **37**, 1253; see also P. K. Zubaidha, A. Kasatkin and F. Sato, *Chem. Commun.*, 1996, 197.

33 V. Chaplinski and A. de Meijere, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 413; see also A. Kasatkin and F. Sato, *Tetrahedron Lett.*, 1995, **36**, 6079; A. Kasatkin, S. Okamoto and F. Sato, *Tetrahedron Lett.*, 1995, **36**, 6075.

34 O. G. Kulinkovich, S. V. Sviridov, D. A. Vasilevski and T. S. Prityskaya, *Zh. Org. Khim*, 1989, **25**, 2245; see ref 33.

35 D. Enders, S. von Berg and B. Jandeleit, *Synlett*, 1996, 18.

36 For a review, see: C. Mukai and M. Hanaoka, *Synlett*, 1996, 11.

37 C. S. Vizniowski, J. R. Green, T. L. Breen and A. V. Dalacu, *J. Org. Chem.*, 1995, **60**, 7496.

38 J. M. Palazón and V. S. Martín, *Tetrahedron Lett.*, 1995, **36**, 3549; see also E. Tyrrell, S. Claridge, R. Davis, J. Lebel and J. Berge, *Synlett*, 1995, 714.

39 G. G. Melikyan, M. A. Khan and K. M. Nicholas, *Organometallics*, 1995, **14**, 2170.

40 S. Legoupy, C. Crévisy, J.-C. Guillemin and R. Grée, *Tetrahedron Lett.*, 1996, **37**, 1225.

41 J. Szymoniak, D. Felix, J. Besançon and C. Moïse, *Tetrahedron*, 1996, **52**, 4377.

42 S. V. Ley and G. Meek, *J. Chem. Soc., Chem. Commun.*, 1995, 1751.

43 S. V. Ley and L. R. Cox, *Chem. Commun.*, 1996, 657.

44 S. V. Ley and G. Meek, *Chem. Commun.*, 1996, 317.

45 S. D. R. Christie, C. Cosset, D. R. Hamilton, W. J. Kerr and J. M. O'Callaghan, *J. Chem. Soc., Chem. Commun.*, 1995, 2051.

46 S. A. Benyunes, S. E, Gibson (née Thomas) and J. A. Stern, *J. Chem. Soc., Perkin Trans. 1*, 1995, 1333.

47 S. E. Gibson (née Thomas) and G. J. Tustin, *J. Chem. Soc., Perkin Trans. 1*, 1995, 2427.

48 K. Nunn, P. Mosset, R. Grée and R. W. Saalfrank, *J. Org. Chem.*, 1992, **57**, 3359; C. Tao and W. Donaldson, *J. Org. Chem.*, 1993, **58**, 2134.

49 W. A. Donaldson and L. Shang, *Tetrahedron Lett.*, 1996, **37**, 423.

50 A. McKillop, G. R. Stephenson and M. Tinki, *Synlett*, 1995, 669.

51 M.-C. P. Yeh, L.-W. Chuang, C.-C. Hwu, J.-M. Sheu and L.-C. Row, *Organometallics*, 1995, **14**, 3396.

52 I. Ripoche, J. Gelas, B. Grée, R. Grée and Y. Troin, *Tetrahedron Lett.*, 1995, **36**, 6675.

53 P. W. Jolly, *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. Stone and E. W. Abel, Pergamon, New York, 1982, vol. 8, p 613.

54 Y. Sato, M. Takimoto, K. Hayashi, T. Katsuhara, K. Takagi and M. Mori, *J. Am. Chem. Soc.*, 1994, **116**, 9771.

55 Y. Sato, M. Takimoto and M. Mori, *Tetrahedron Lett.*, 1996, **37**, 887.

56 R. Noyori, *Asymmetric Catalysis in Organic Synthesis*, Wiley, New York, 1994.

57 L. Schwink and P. Knochel, *Tetrahedron Lett.*, 1996, **37**, 25.

58 D. Lambusta, G. Nicolosi, A. Patti and M. Piatelli, *Tetrahedron Lett.*, 1996, **37**, 127.

59 S. Taudien, O. Riant and H. B. Kagan, *Tetrahedron Lett.*, 1995, **36**, 3513.

60 H.-J. Knölker, M. Bauermeister, J.-B. Pannek and M. Wolpert, *Synthesis*, 1995, 397.

61 H.-J. Knölker, E. Baum and T. Hopfmann, *Tetrahedron Lett.*, 1995, **36**, 5339.

62 A. M. Wilson, F. G. West, A. M. Arif and R. D. Ernst, *J. Am. Chem. Soc.*, 1995, **117**, 8490.

63 P. C. Cagle, O. Meyer, K. Weickhardt, A. M. Arif and J. A. Gladysz, *J. Am. Chem. Soc.*, 1995, **117**, 11730.

64 J. H. Rigby, *Acc. Chem. Res.*, 1993, **26**, 579; J. H. Rigby, S. Scribner and M. J. Heeg, *Tetrahedron Lett.*, 1995, **36**, 8569.

65 J. H. Rigby, P. Sugathapala and M. J. Heeg, *J. Am. Chem. Soc.*, 1995, **117**, 8851.

66 C. Baldoli, P. Del Buttero, M. Di Ciolo, S. Maiorana and A. Papagni, *Synlett*, 1996, 258; C. Baldoli, P. Del Buttero, E. Licandro, S. Maiorana and A. Papagni, *Tetrahedron: Asymmetry*, 1995, **6**, 1711.

67 E. P. Kündig, L. H. Xu, P. Romanens and G. Bernardinelli, *Synlett*, 1996, 270. For radical additions to (η^6-arene)(tricarbonyl)chromium complexes mediated by samarium(II) iodide see H.-G. Schmalz, S. Siegel and J. W. Bats, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2383.

68 T. Watanabe, K. Kamikawa and M. Uemura, *Tetrahedron Lett.*, 1995, **36**, 6695.; H.-G. Schmalz, A. Majdalani, T. Geller, J. Hollander and J. W. Bats, *Tetrahedron Lett.*, 1995, **36**, 4777.

69 M. Uemura, A. Daimon and Y. Hayashi, *J. Chem. Soc., Chem. Commun.*, 1995, 1943.

70 M. Uemura and K. Kamikawa, *J. Chem. Soc., Chem. Commun.*, 1994, 2697.

71 E. L. M. Cowton, S. E. Gibson (née Thomas), M. J. Schneider and M. H. Smith, *Chem. Commun.*, 1996, 839.

72 H.-G. Schmalz and K. Schellhaas, *Tetrahedron Lett.*, 1995, **36**, 5515.

73 J. Soulié, J.-F. Betzer, B. Muller and J.-Y. Lallemand, *Tetrahedron Lett.*, 1995, **36**, 9485.

74 A. J. Pearson and K. Srinivasan, *J. Org. Chem.*, 1992, **57**, 3965.

75 R. L. Thompson, S. Lee, A. L. Rheingol and N. J. Cooper, *Organometallics*, 1991, **10**, 1657.

76 S. Lee, S. J. Geib and N. J. Cooper, *J. Am. Chem. Soc.*, 1995, **117**, 9572.

77 A. J. Pearson and K. Lee, *J. Org. Chem.*, 1995, **60**, 7153; A. J. Pearson and G. Bignan, *Tetrahedron Lett.*, 1996, **37**, 735.

78 J. W. Janetka and D. H. Rich, *J. Am. Chem. Soc.*, 1995, **117**, 10585.

79 A. H. May, W. J. Kerr, G. G. Kirk and D. Middlemiss, *Organometallics*, 1995, **14**, 4986; W. J. Kerr, G. G. Kirk and D. Middlemiss, *Synlett*, 1995, 1085.

80 A. L. Veretenov, D. O. Koltun, W. A. Smit and Y. A. Strelenko, *Tetrahedron Lett.*, 1995, **36**, 4651.

81 M. Ahmar, F. Antras and B. Cazes, *Tetrahedron Lett.*, 1995, **36**, 4417.

82 R. Aumann and H. J. Weidenhaupt, *Chem. Ber.*, 1987, **120**, 23.

83 P. Bhatarah and E. H. Smith, *J. Chem. Soc., Perkin Trans. 1*, 1992, 2163; E. C. Colthup and L. S. Meriwether, *J. Org. Chem.*, 1961, **26**, 5169.

84 D. M. Duckworth, S. Lee-Wong, A. M. Z. Slawin, E. H. Smith and D. J. Williams, *J. Chem. Soc., Perkin Trans. 1*, 1996, 815.

85 M. Toyota, T. Wada, Y. Nishikawa, K. Yanai, K. Fukumoto and C. Kabuto, *Tetrahedron*, 1995, **51**, 6927