Available online at www.sciencedirect.com
SCIENCE DIRECT®
Coordination Chemistry Reviews 243 (2003) 3–81
COORDINATION CHEMISTRY REVIEWS
www.elsevier.com/locate/ccr

The chemistry of the carbon-transition metal double and triple bond: annual survey covering the year 2001[1]

James W. Herndon *

Department of Chemistry and Biochemistry, New Mexico State University, MSC 3C, Las Cruces, NM 88003, USA

Received 9 September 2002; accepted 11 September 2002

Contents

* Tel. +505-646-2487; fax: +505-646-2649.
E-mail address: jherndon@nmsu.edu (J.W. Herndon).

[1] For 2000, see Ref. [1].

0010-8545/03/$ - see front matter
doi:10.1016/S0010-8545(02)00276-X

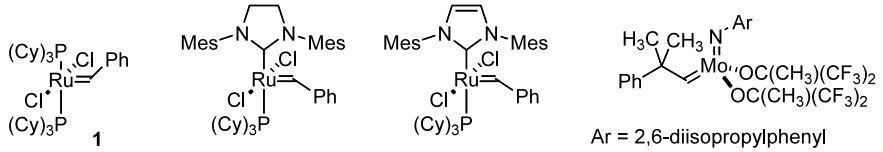
Abstract

This is a review of papers published in the year 2001 that focus on the synthesis, reactivity, or properties of compounds containing a carbon-transition metal double or triple bond.

Keywords: Carbon-transition metal double bond; Carbon-transition metal triple bond; Carbene/carbyne complex

1. Introduction

This survey is intended to be a comprehensive summary of articles that report on the synthesis, reactivity, or properties of compounds featuring a multiple bond between carbon and a transition metal. Reactions that employ metal carbene complexes as transient intermediates generated through well-established routes are not covered, unless there is some effort to characterize the carbene complex intermediate; several reviews on this area appeared in 2001 [2–8]. Although a determined effort has been made to include patents, in general only patents that are listed in or at the end of the Organometallics section of *Chemical Abstracts* (Section 29) are included; patents which appeared in Chemical Abstracts in the year 2001 have been included. In general, only patents that focus on the carbene/carbyne complex have been included. Only compounds that feature a multiple bond between one carbon atom and one transition metal are discussed in this survey, thus bridging carbene and carbyne complexes are not covered unless there is a multiple bond to at least one transition metal. The complexes of stable *N*-heterocyclic carbenes with transition metals have not been included; since the π-donation component of these complexes is minimal, they contain no formal carbon–metal multiple bond [9,10]. Several reviews in this area appeared in 2001 [11–14]. This survey has been divided into two sections, metal carbene (or alkylidene) complexes and metal carbyne (or alkylidyne) complexes; the carbene complex section represents the vast majority of this article, and articles that report on both carbene and carbyne complexes are most likely in the metal–carbyne section. The metal carbene section has been organized according to metal, starting from the left side of the Periodic Table. The Ionic Model [15] has been employed for the discussion of oxidation states and ligand electron count throughout this survey. A special section focusing on alkene metathesis has been included prior to the discussion of carbene complexes of individual metals. The metal carbyne section has been organized according to reaction type. One publication addresses calculation



1 2 3 4

Fig. 1. Structures of alkene metathesis catalysts **1**–**4**.

of structures for a wide variety of carbene and carbyne complexes for different metals, and does not fit in any one section [16].

Abbreviations (see also the front of issue #1 of the *Journal of Organic Chemistry* [17])

ROMP	ring opening metathesis polymerization
RCM	ring closing metathesis
ADMET	acyclic diene metathesis
Grubbs catalyst I	Structure **1** (Fig. 1)
Grubbs catalyst II	Structure **2** (Fig. 1)
Nolan catalyst	Structure **3** (Fig. 1)
Schrock catalyst	Structure **4** (Fig. 1)

2. Metal–carbene or metal–alkylidene complexes

2.1. Review articles

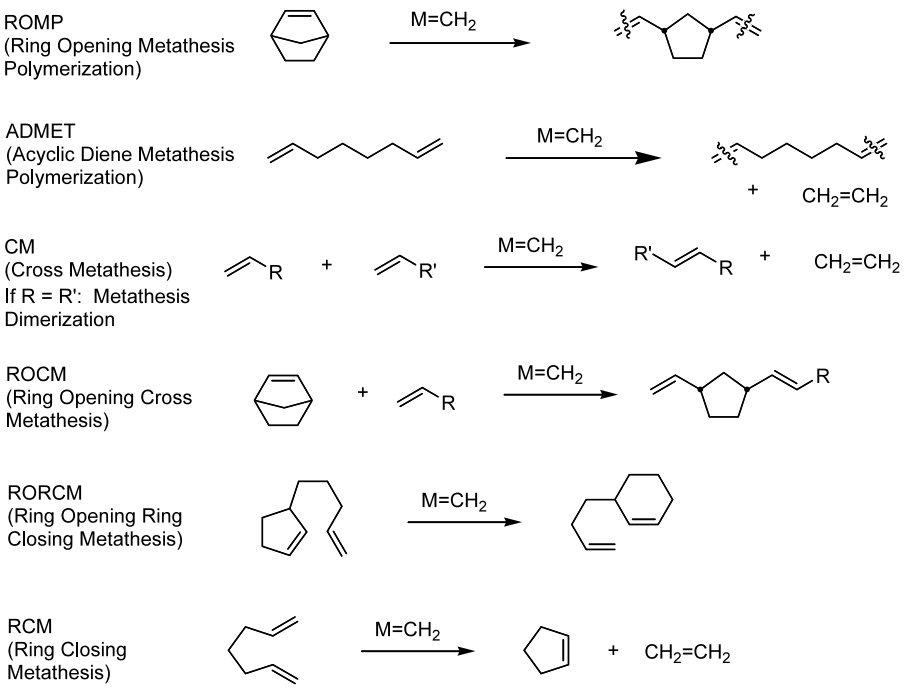
Several reviews covering aspects of metal–carbene complex chemistry appeared in 2001. Many reviews focusing on some aspect of olefin metathesis were published, including the following specific subjects: (1) metathesis catalysts featuring a heterocyclic carbene ligand [18]; (2) asymmetric alkene metathesis [19]; (3) formation of chelating ligands through RCM [20]; (4) ring closing metathesis [21]; (5) a general review of metathesis [22]; (6) olefin metathesis catalysts [23]; and (7) development of ruthenium carbene alkene metathesis catalysts [24]. Although not focusing directly on metathesis, some review articles featured a heavy metathesis component. Specific reviews in this category were reported for the following subjects: (1) polymer supported catalysts in synthetic organic chemistry [25]; (2) use of tartrates in the synthesis of natural products [26]; (3) use of combinatorial methods for catalyst discovery and optimization [27]; (4) traceless linkers [28]; (5) supported catalysts [29]; (6) synthesis of saturated oxygen heterocycles [30]; (7) β-turn mimetic based library syntheses [31]; (8) use of heterocyclic carbene complexes in organic synthesis [32]; and (9) organometallic catalysis in organic synthesis [33]. Reviews about other aspects of carbene complex chemistry include the following subjects: (1) metal vinylidene complexes and complexes of higher cumulenes [34]; (2) titanium carbene complexes [35]; (3) carbene complexes containing carbohydrate substituents [36]; (4) carbene complexes of Group IV elements featuring pincer ligands [37]; (5) carbene complexes prepared from lithiated heterocycles [38]; (6) chelated oxazolidinone- and imidazolidinone-containing Group VI carbene complexes [39]; (7) addition of carbon nucleophiles to Fischer carbene complexes [40]; (8) cyclopropanation reactions of ruthenium and molybdenum vinylidene complexes [41]; (9) luminescent platinum and rhenium carbene complexes [42]; (10) aminocarbene complexes derived from nucleophilic addition to isocyanide ligands [43]; and (11) reaction of d(0) alkylidene and amide complexes with silanes [44]. Although not focusing exclusively on carbene complexes, other reviews devote a large portion to this subject. Specific subjects covered include: (1) stoichiometric use of transition metals in organic synthesis [45]; (2) total synthesis of deoxy sugars, which frequently uses metathesis and metal–vinylidene based approaches [46]; (3) synthesis of β-lactams [47]; (4) complexes containing metal–carbon σ-bonds to metals in the iron, cobalt, and nickel groups [48]; (5) metal–carbon bond functionalities attached to an oxo surface modeled by calixarenes [49]; and (6) the chemistry of hydrido-chlorobis(triisopropylphosphine)osmium(II) and related compounds [50].

2.2. Alkene metathesis

Alkene metathesis was the most common reaction process reported for metal–carbene complexes in 2001, and this special section is devoted to papers that focus on this process. Many examples of both polymerization [mostly ring opening metathesis polymerization (ROMP)] reactions and small-molecule syntheses appeared. Only metathesis reactions initiated by a discrete transition metal–carbene complex, or metathesis reactions that discuss the carbene complex intermediates of this reaction have been included here. Distinct modes of alkene metathesis are depicted in Scheme 1.

2.2.1. General studies of alkene metathesis catalysts

Several mechanistic studies related to alkene metathesis appeared in 2001. A detailed mechanistic study was undertaken in order to better understand the enhanced level of activity of Grubbs catalyst II (**2**, Scheme 2) relative to Grubbs catalyst I (**1**) [51]. The mechanistic picture for one cycle of the metathesis reaction is depicted in Scheme 2. Catalyst **1** actually undergoes phosphine dissociation nearly twice as fast as catalyst **2**. The enhanced rate of metathesis for catalyst **2** was attributed to the rate of reaction of intermediate **5** with alkenes vs. reaction with phosphine to regenerate the starting complex (i.e. the k_2/k_{-1} ratio). Several other factors were observed to increase the rate of phosphine dissociation but did not necessarily lead to better metathesis catalysts: (1) replacement of PCy_3 by PPh_3 in catalyst **2**, (2) replacement of chlorines by iodines, and (3) presence of a large and electron-donating group at the carbene carbon [52]. Preparation of a fluorinated analog of Grubbs catalyst II (**7**) was reported [53]. Coupling of catalyst **2** with 1,1-difluoroethylene led to a mixture of carbene complex **7** and **8**. A mixture of the two complexes was obtained at room temperature

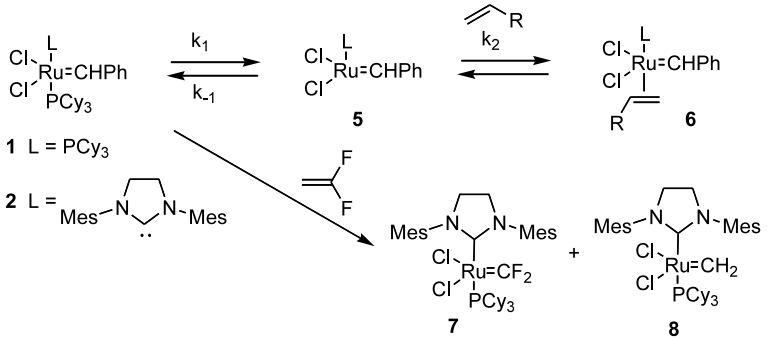


Scheme 1.

however the reaction at 60 °C led to nearly exclusive formation of the fluorinated complex. The fluorinated complex was a poor ROMP catalyst, however its activity could be enhanced by adding HCl.

A series of cationic ruthenium–carbene catalysts were synthesized in situ and their activity in ROMP was evaluated by electrospray ionization tandem mass spectrometry [54]. Four structural features of the catalyst $[\{R_2P(CH_2)_nPR_2\}XRu=CHR']^+$ were evaluated: (1) the halogen ligand, (2) the diphosphine bite-angle, (3) the steric bulk of the phosphine, and (4) the carbene ligand. The most reactive complex in acyclic olefin metathesis features chloride ligands and the phosphine $Cy_2PCH_2PCy_2$; variation of the carbene moiety CHR′ had only a modest influence. The rate-determining step in the gas phase was metallacyclobutane formation. In ROMP reactions, intramolecular carbene–alkene coupling in living polymeric species had a profound influence on the overall rate. The reactivity trends were determined in the gas phase parallel solution-phase reactivity. The rate in solution was affected by dimer/monomer preequilibrium; the active catalyst is produced after facile dissociation of the dimeric species.

Numerous attempts to develop new catalysts for alkene metathesis were reported in 2001; some representative examples are depicted in Fig. 2. Several derivatives of the catalysts depicted in Fig. 2 were synthesized and tested in their ability to undergo various metathesis processes, including: (1) ruthenium complexes that feature a chelating di(*t*-butyl)phosphine ligand, which require the addition of TMSOTf to function as a ROMP catalyst [55]; (2) ruthenium complexes featuring a chelating triarylphosphine ligand, which are less active than Grubbs Catalyst I [56]; (3) allenylidene–ruthenium complexes [57] and analogs featuring a heterocyclic carbene ligand (e.g. **9**) [58]; (4) heteroatom-stabilized ruthenium carbene complexes



Scheme 2.

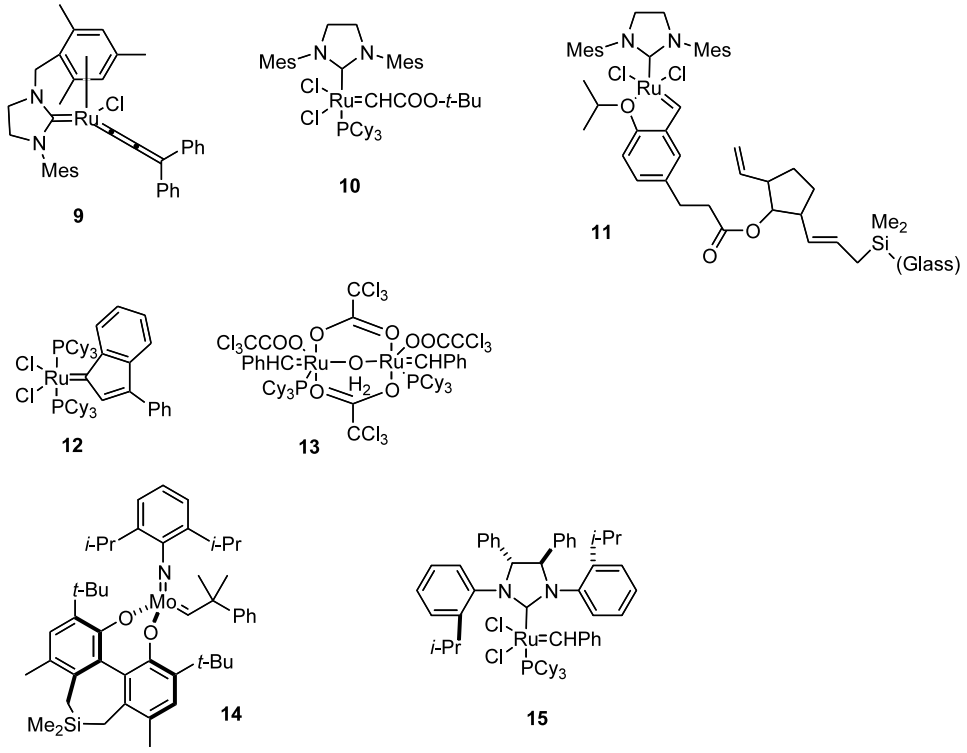


Fig. 2. Representative examples of new catalysts for alkene metathesis.

that feature a hydride ligand and related carbyne complexes [59]; (5) ester-substituted ruthenium carbene complexes (enoic carbene complexes) (e.g. **10**), which are excellent catalysts for cross-metathesis involving α,β-unsaturated ester components [60]; (6) in situ generated ruthenium vinylidene complexes that feature a heterocyclic carbene ligand [61]; (7) recoverable and reusable phosphine-free ruthenium catalysts (e.g. **11**) [62,63]; (8) a recoverable ruthenium phosphine catalyst [64]; (9) ruthenium carbene complexes that feature a heterocyclic carbene ligand connected to alkene, ester, or nitrile functionality [65]; (10) an easily-prepared indenylidene analog of Grubbs catalyst I (**12**) [66]; (11) carboxylate-bridged dimeric analogs of Grubbs catalyst I (e.g. **13**) [67]; (12) a ruthenium–arene complex featuring a stable carbene ligand [68]; (13) an in situ generated vanadium carbene complex [69]; (14) an in situ generated tungsten carbene complex [70]; (15) analogs of Grubbs catalyst I featuring polymer-bound phosphine ligands [71]; (16) monolithic-supported alkene metathesis catalysts [72]; (17) a polymer bound analog of Grubbs catalyst I [73]; and (18) ferrocenyl-substituted analogs of the Schrock catalyst, which might function as redox-tunable metathesis catalysts [74]. Several patents were issued for the synthesis and development of metal–carbene containing olefin metathesis catalysts [75–79]. Several examples of catalysts designed to effect asymmetric alkene metathesis were reported in 2001, including: (1) molybdenum carbene complexes that feature a silicon-bridged chiral biphenyl ligand (e.g. **14**) [80]; (2) molybdenum carbene complexes featuring chiral aryl-substituted binaphthol ligands, which would react with ethylene to produce an isolable metallacyclobutane [81]; (3) molybdenum carbene complexes that feature aryl-substituted binaphthol ligands, which catalyze six-membered ring-forming RORCM (see Scheme 1) with a high degree of enantioselectivity [82]; (4) molybdenum carbene complexes featuring binaphthol ligands where the unsubstituted ring is hydrogenated; these complexes efficiently catalyze enantioselective ring opening cross metathesis (ROCM), enantioselective ring closing metathesis for compounds that contain enantiotopic alkenes, and enantioselective ring closing metathesis through kinetic resolution [83]; and (5) a chiral analog of Grubbs Catalyst II (e.g. **15**), which is effective for enantioselective RCM reactions [84].

Other general studies of alkene metathesis where carbene complexes were discussed include: (1) a survey of metathesis reactions conducted in supercritical CO_2 [85]; (2) a survey of metathesis reactions in ionic liquids [86]; (3) evaluation of a series of ruthenium catalysts that feature one *N*-heterocyclic carbene ligand; emphasis is on structural variations within the *N*-heterocyclic carbene ligand [87]; (4) a method to remove ruthenium containing byproducts from metathesis reactions using triphenylphosphine or DMSO [88]; and (5) a kinetic study of the ROMP of oxanorbornene derivatives substituted with dendritic diester groups [89].

A theoretical paper concerning the tungsten mediated alkene metathesis appeared in 2001 [90]. Formation of

secondary and primary carbene complexes from tertiary metal carbene complexes is a slow process with high activation energy. The rate-determining step in the metathesis sequence was dissociation of the alkene from the metal carbene–alkene complex. Low *E*/*Z* stereoselectivity was attributed to similar activation and binding energies for the intermediate leading to each alkene isomer, and the fact that *cis–trans* isomerization occurs under the reaction conditions. A theoretical paper concerning metathesis using alumina-bound molybdenum carbene complexes was also reported [91].

2.2.2. Polymerization reactions

Initiation of the ROMP (see Scheme 1) reaction using carbene complexes remains a very active area of investigation. The strained alkene norbornene, norbornene derivatives, and copolymerization involving a norbornene derivative and another alkene accounted for a large fraction of all reports of the ROMP reaction in 2001 (Fig. 3). Examples of ROMP using metal carbene complexes include: (1) ROMP of norbornene derivatives containing chelating pyridine ligands (e.g. **16**) [92]; (2) ROMP of norbornene derivatives connected to oligopeptides for the design of fibronectin cell adhesion inhibitors [93]; (3) attachment of polynorbornene "brushes" to electrode surfaces via ROMP of electrode-bound norbornene derivatives [94]; (4) ROMP of norbornene derivatives connected to the 1,4,7-triazacyclonane ligand [95]; (5) formation of polymer-bound allylboronates through ROMP of norbornene diol derivatives in the presence of dicyclopentadiene (for cross linking) followed by conversion of the diols to the boronate ester [96]; (6) formation of a polymer bond Mosher ester derivative through ROMP of an oxanorbornene derivative fused to an *N*-acyloxysuccinimide ring (**17**) [97]; (7) preparation of a polymer bound version of tosylmethyl isocyanide through ROMP of sulfonylmethyl formamide-containing norbornene derivatives, followed by dehydration [98]; (8) preparation of polymer-bound α-bromoesters through ROMP of norbornenes containing α-bromoester functionality [99]; (9) ROMP of norbornene **18** for the purpose of immobilizing a bromo-alkene radical cyclization substrate [100]; (10) ROMP of norbornene-type β-amino acids [101]; (11) ROMP of norbornene in an emulsion using a water-soluble analog of Grubbs catalyst I [102]; (12) ROMP of phosphazene-containing norbornenes (e.g. **19**) [103,104]; (13) ROMP of norbornenyl polyphosphazenes [105]; (14) ROMP of ionic cyclooctatetraene derivatives using a tungsten carbene complex catalyst [106]; (15) ROMP of norbornene derivatives connected to various compounds with anticancer activity (e.g. **20**) [107]; (16) synthesis of photochromic polymers via ROMP of norbornene derivatives connected to benzoquinones [108]; (17) synthesis of "polymacromonomers" by ROMP of norbornene-containing ethers, followed by treatment of the living polymers with norbornene-containing esters or acid chlorides [109]; (18) frontal ROMP of dicyclopentadiene [110]; (19) ROMP of tricyclic derivatives of general structure **21** [111]; (20)

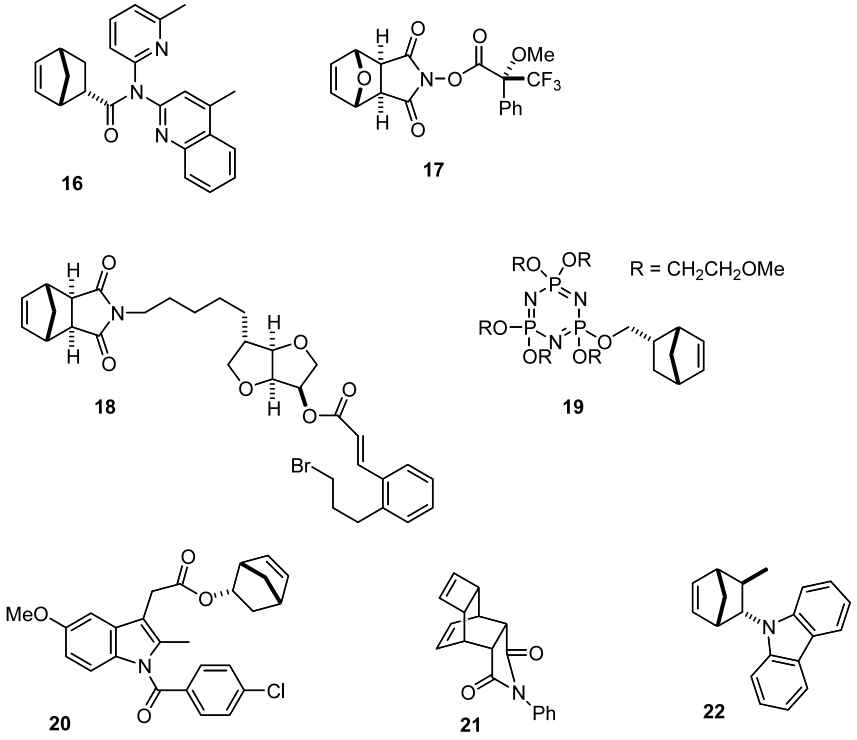


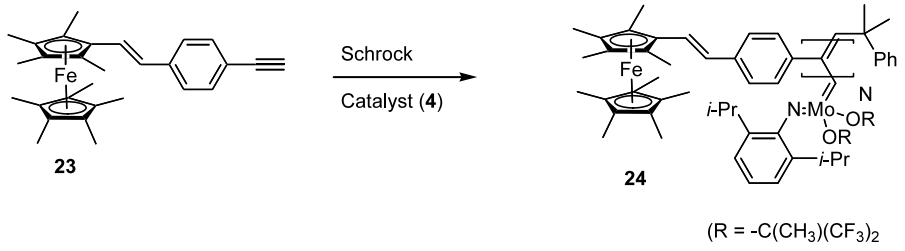
Fig. 3. Representative substrates for the ROMP reaction.

ROMP of deuterated norbornene derivatives and study of the resulting polymers by neutron scattering techniques [112]; (21) synthesis of end-functionalized polynorbornenes through ROMP of norbornene in the presence of allyl acetate [113]; (22) increased initiation efficiency in ROMP reactions through use of Grubbs catalyst I in the presence of excess phosphine [114]; (23) ROMP using chelating analogs of Grubbs catalyst I; the catalyst appears to be more reactive than Grubbs catalyst I but is more prone to decomposition [115]; (24) synthesis of C-linked polysaccharides through ROMP of oxanorbornene diols followed by dihydroxylation of the resulting ring opening metathesis polymer [116]; (25) ROMP of nucleobase-containing norbornene derivatives [117]; and (26) ROMP of norbornene derivatives substituted with carbazole and other electron-rich moieties (e.g. **22**) [118].

The use of carbene complexes for the synthesis of poly(ferrocenium)-based silica supports was reported (Scheme 3) [119]. In one phase of these studies, living polymers (e.g. **24**) were synthesized through the reaction of the Schrock carbene complex (**4**) with various ferrocene derivatives (e.g. **23**). The resulting living polymer was then treated with surface-bound norbornene derivatives, followed by quench with ferrocenecarboxaldehyde to effect a ring-opening metathesis of the surface-bound norbornenes and net attachment of the alkyne polymeric unit of **24**.

Several examples using carbene complexes to initiate acyclic diene metathesis (ADMET) (see Scheme 1) polymerization reactions were reported in 2001 (see Fig. 4), including: (1) polymerization of end-of-chain dienes (e.g. general structure **25**) in the presence of monosubstituted alkene-containing phthalimide derivatives (e.g. **26**) [120]; (2) synthesis of stacked phthalocyanine polymers through ADMET polymerization of octaene derivatives of general structure **27** [121]; (3) ADMET polymerization of end-of-chain dienes that are substituted at sp^3 carbons by polyether derivatives of a hydroxymethyl group (e.g. **28**) [122]; and (4) ADMET polymerization of end-of-chain dienes substituted by amino acids (e.g. **29**) [123].

Other studies involving the use of carbene complexes in polymer chemistry were also reported. Metathesis reactions were employed to effect depolymerization of styrene–butadiene and styrene–isoprene copolymers [124]. Efforts to obtain spectral information on carbene



Scheme 3.

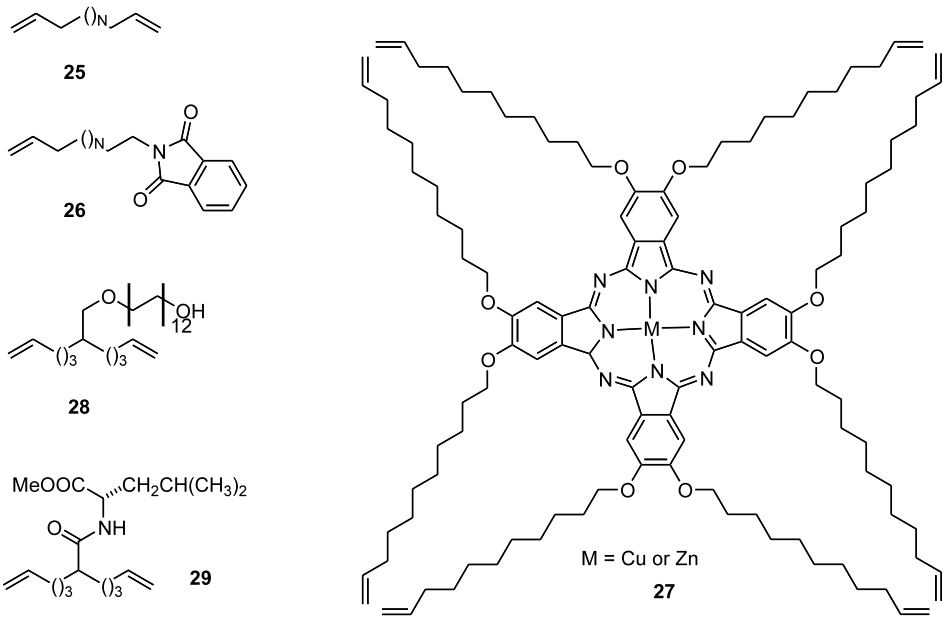
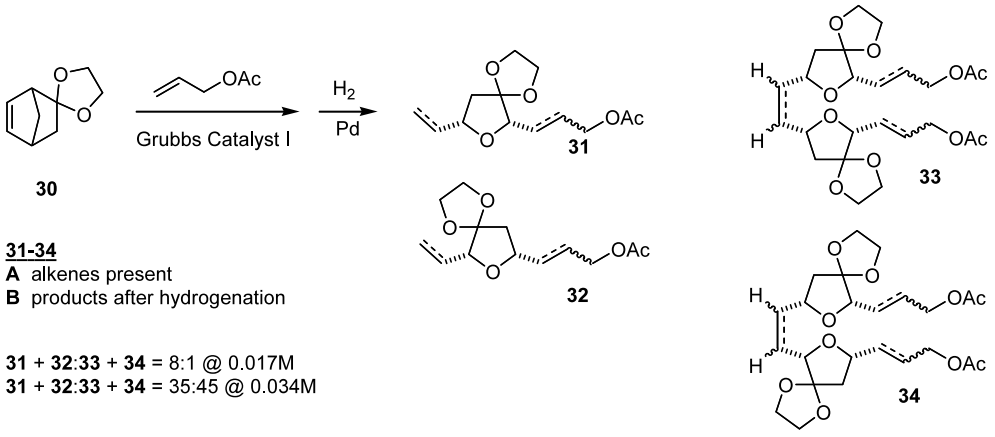


Fig. 4. Representative substrates for the ADMET polymerization reaction.



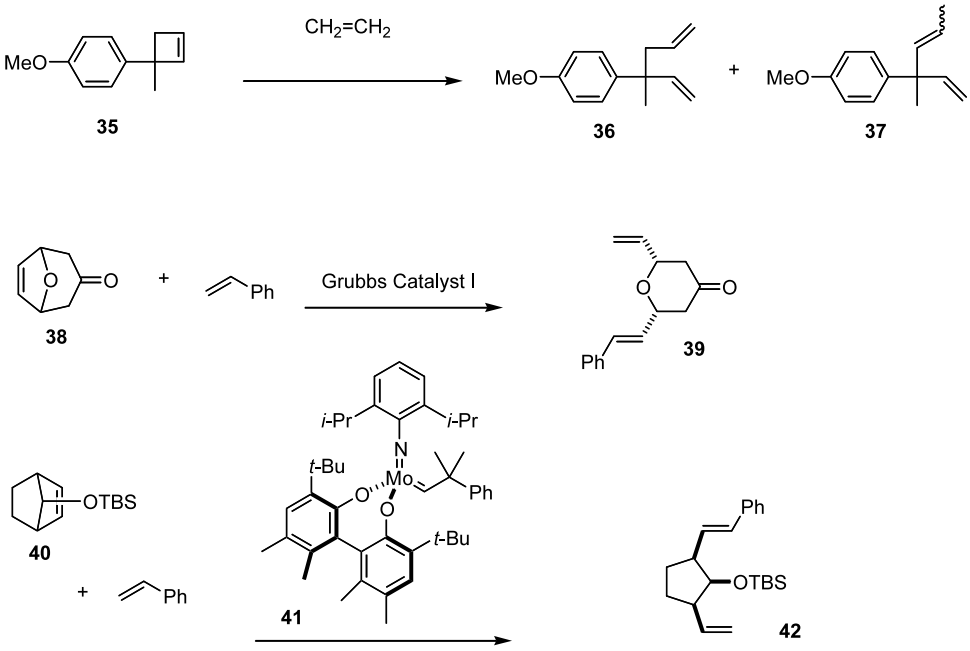
Scheme 4.

intermediates in the ROMP employing $H_2Os_3(CO)_{12}$ failed [125].

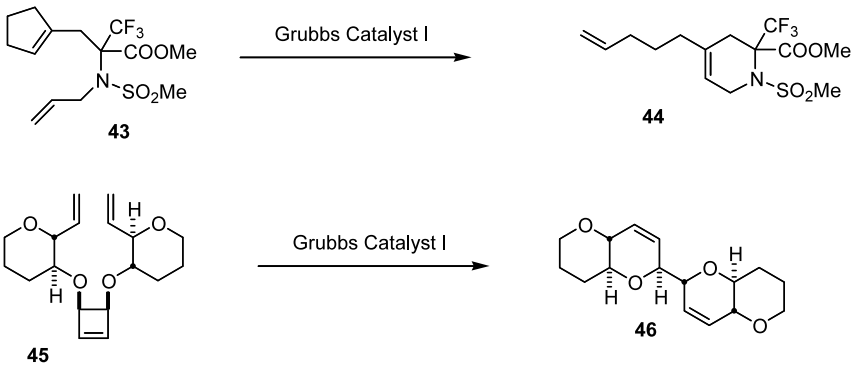
2.2.3. Nonpolymer-forming ring opening metathesis reactions

Several examples of ROCM (see Scheme 1) were reported in 2001. Cometathesis of norbornenone ketal **30** (Scheme 4) and allyl acetate led to mixtures of ring-opening cross metathesis products **31A** and **32A** and the products **33A** and **34A** arising from metathesis dimerization or cross metathesis of the products **31A** and **32A** [126]. More dilute solutions led to an increase in the proportion of the simple cometathesis products **31A** and **32A**. The evaluation of the ratios of **31**–**34** was conducted after hydrogenation of the alkene substituents. Cometathesis of cyclobutene derivative **35** (Scheme 5) with ethylene also led to the expected ring opening product **36**, accompanied by the double bond isomerization product **37** [127]. Successful cometathesis of oxabicyclo[3.2.1]octenone derivatives (e.g. **38**) and various monosubstituted alkenes was reported [128]. A related process was demonstrated for cometathesis of six- and seven-membered alkenes with electron-deficient alkenes using the phosphine-free catalyst ruthenium–carbene complex [129]. Asymmetric ROCM was demonstrated for a variety of meso norbornene derivatives (e.g. **40**) and styrene using an optically active molybdenum carbene complex catalyst **41** [130].

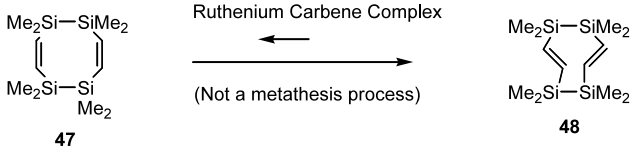
Some examples of ring opening ring closing metathesis (RORCM) (see Scheme 1), were reported in 2001. Treatment of acyclic amine derivatives (e.g. **43**, Scheme 6) with Grubbs catalyst I led to RORCM products,



Scheme 5.



Scheme 6.



Scheme 7.

cyclic amino acids (e.g. **44**) [131]. A double RORCM sequence was observed when cyclobutene derivative **45** was treated with Grubbs catalyst II [132].

The ruthenium–carbene complex catalyzed *cis–trans* isomerization of tetrasilacyclooctadiene derivatives (e.g. **47**, **48**, Scheme 7) was found to occur by a reversible metal hydride addition process and not via an alkene metathesis mechanism [133,134].

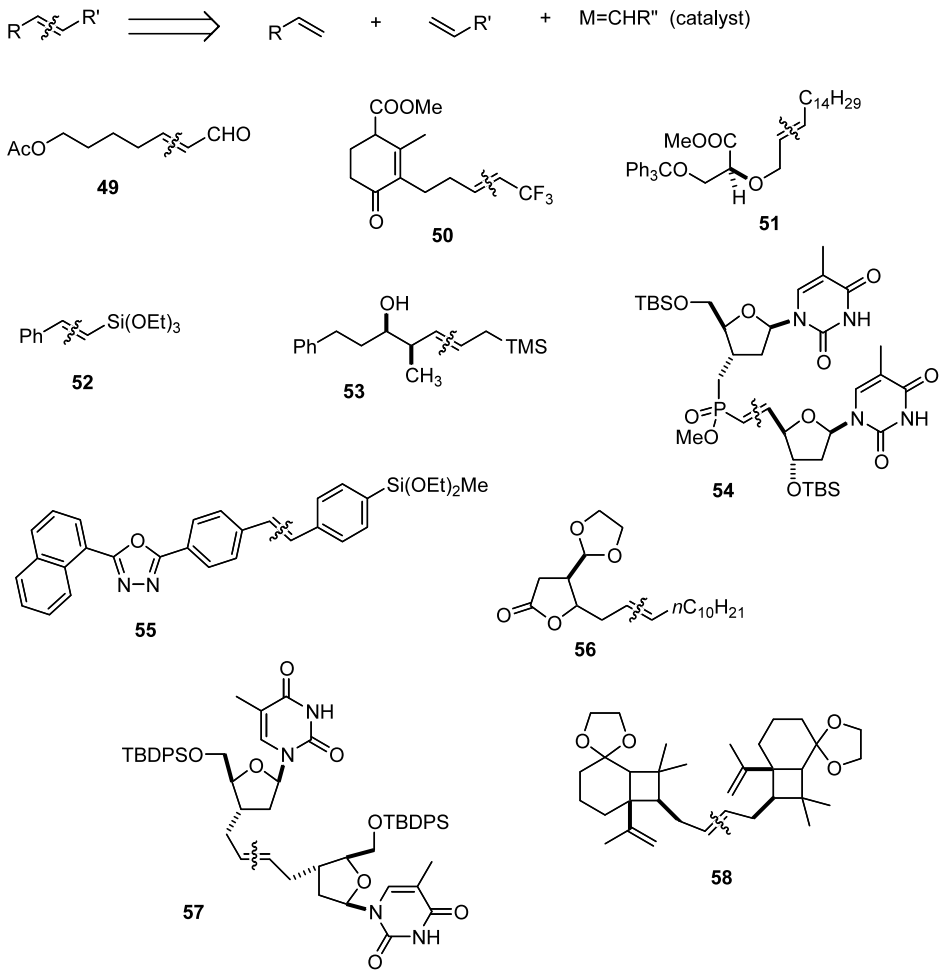
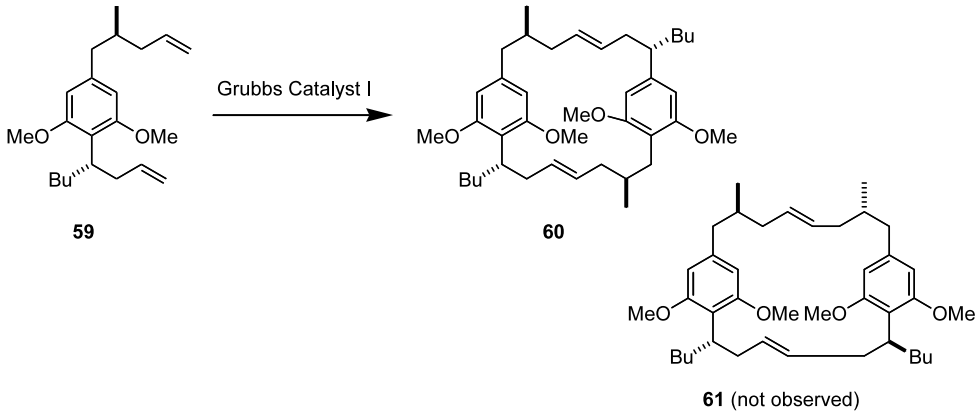


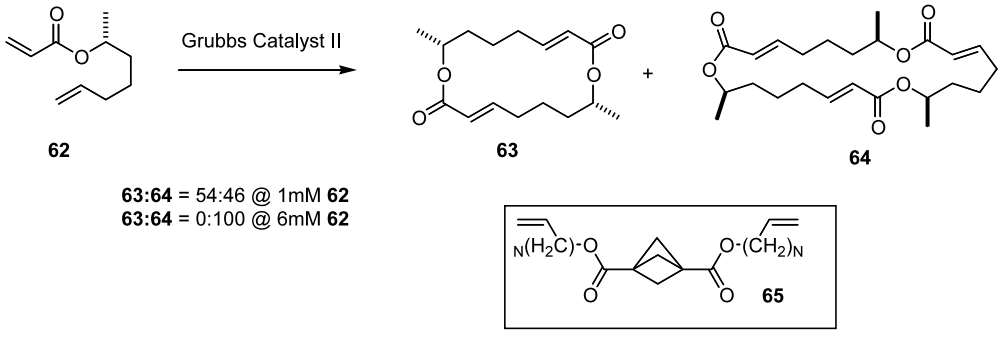
Fig. 5. Representative examples of compounds prepared through cross metathesis and metathesis dimerization.



Scheme 8.

2.2.4. Cross metathesis, metathesis-dimerization, and metathesis cyclodimerization reactions

The cross metathesis reaction of various dissimilar monosubstituted alkenes was investigated (Fig. 5) including: (1) formation of α,β-unsaturated aldehydes (e.g. **49**) and esters through cross metathesis of various monosubstituted alkenes with acrolein or acrylate derivatives [135–137]; (2) formation of α,β-unsaturated amides through cross metathesis of monosubstituted alkenes with *N*-methoxyacrylamide derivatives [138]; (3) synthesis of fluorinated alkenes (e.g. **50**) through cross metathesis of simple fluorinated alkenes with various monosubstituted alkenes [139]; (4) synthesis of C-allylic glycosides through cross metathesis of a C-allyl glycoside with an allylic amine [140]; (5) synthesis of α-alkoxy ester derivatives (e.g. **51**) through cross metathesis of α-allyloxy esters with monosubstituted alkenes [141]; (6) synthesis of alkenylsiloxanes (e.g. **52**) through cross metathesis of vinyl siloxanes with monosubstituted alkenes [142]; (7) synthesis of alkenyl sulfones through cross metathesis of monosubstituted alkenes with phenyl vinyl sulfone [143]; (8) synthesis of complex 2-allylated phenol derivatives through cross metathesis of 2-allylphenol derivatives with styrene derivatives [144]; (9) synthesis of allylsilane derivatives (e.g. **53**) through cross metathesis of homoallylic alcohols with allyltrimethylsilane [145]; (10) synthesis of a phosphonate linked dinucleotide (e.g. **54**) through cross metathesis of nucleoside vinylphosphonate with a 5-vinylnucleoside derivative [146]; (11) synthesis of alkenyl phosphonates through cross metathesis of monosubstituted alkenes with vinyl phosphonates [147]; (12) synthesis of α,β-unsaturated nitriles through cross metathesis of monosubstituted alkenes with acrylonitrile [148]; (13) preparation of an intermediate for prosophylline total synthesis through cross metathesis of a homoallylic amine with undec-10-en-3-one [149]; (14) cross metathesis of polymer-bound allylic ethers or *N*-allyl amides with various mono- and disubstituted alkenes [150]; (15) synthesis of 5-(4-alkenylphenyl)-1,3,4-oxadiazole derivatives (e.g. **55**) through cross metathesis of 5-(4-vinylphenyl)-1,3,4-oxadiazole with *p*-silylstyrene derivatives [151]; (16) cross metathesis of vinylferrocenes with various vinylarene derivatives [152]; (17) preparation of an intermediate for roccallaric acid synthesis (**56**) through cross metathesis of an allyl-lactone derivative with 1-dodecene [153]; and (18) formation of carbon-linked disaccharides [154]. Several examples of dimerization via metathesis were reported in 2001, including: (1) dimerization of vancomycin derivatives [155]; (2) synthesis of dinucleotide analogs (e.g. **57**) via dimerization of 3-allylnucleoside derivatives [156]; and (3) preferential formation of metathesis dimer **58** over an RCM product [157].



Scheme 9.

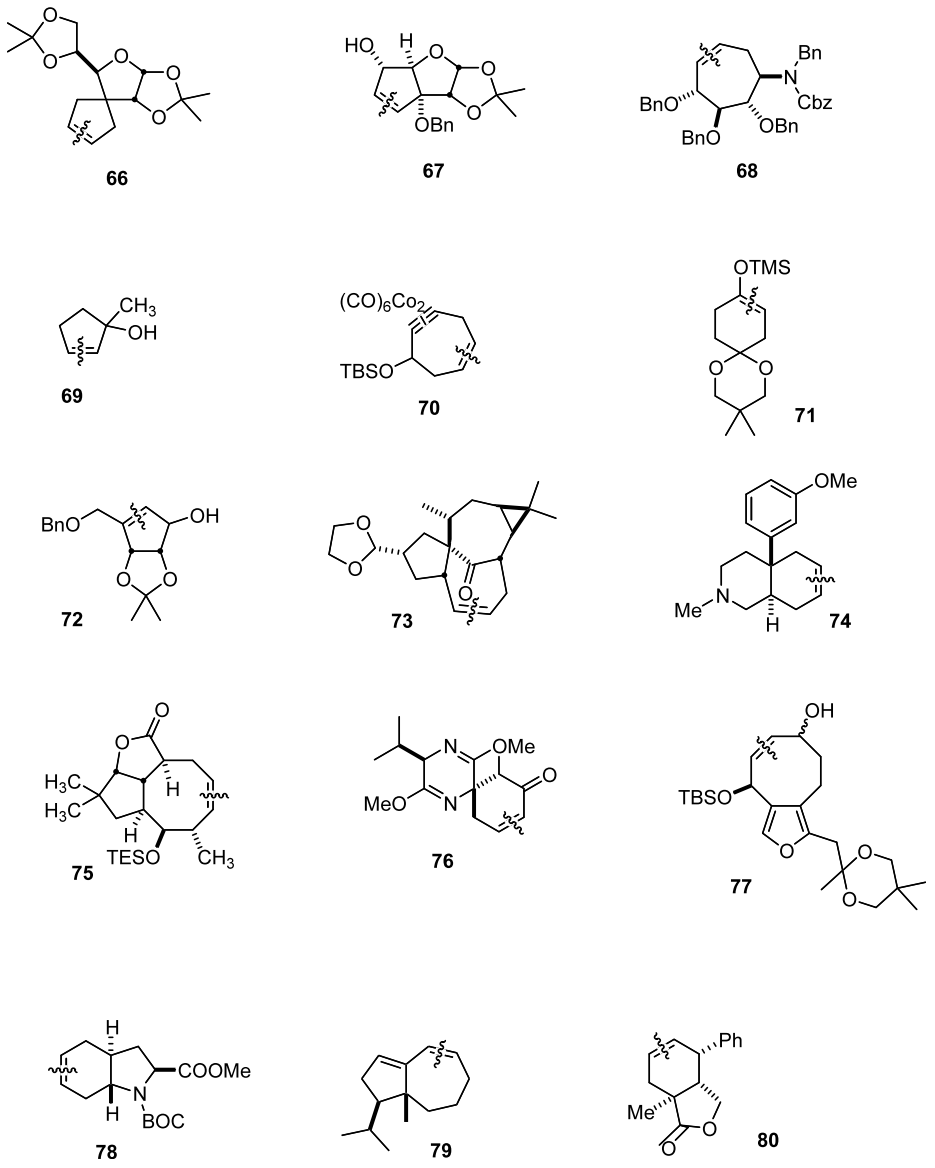


Fig. 6. Representative carbocycles produced through an RCM reaction (bond constructed through RCM indicated).

A tandem metathesis dimerization–RCM procedure was employed as a key step in the total synthesis of cylindrocyclophane derivatives (e.g. **60**, Scheme 8) [158]. The reaction was completely selective with formation of the head-to-tail isomer **60**. The selectivity was attributed to thermodynamic control; the head-to-head dimer **61** is considerably less stable [159]. In an effort to synthesize pyrenophorin derivatives (Scheme 9), the formation of cyclic dimers (e.g. **63**) and trimers (e.g. **64**) from treatment of acrylate ester–alkene derivatives of general structure **62** with various ruthenium metathesis catalysts was examined [160,161]. The product distribution was very time and concentration dependent. A similar process was observed for esters of general structure **65**, where mixtures of cyclic dimer and trimer were produced when $n = 4$ or 5 [162]. An RCM product was formed using longer chain analogs of **65**.

Cross metathesis of polymer-bond carbohydrates, linked to the resin through an alkene linkage, and ethylene was used as a method to free the carbohydrate derivative from the resin [163,164]. This step was an important component in an automated solid-phase oligosaccharide synthesis.

2.2.5. Ring closing metathesis

The ring-closing metathesis reaction (RCM) (see Scheme 1) has emerged as a very important method for organic synthesis. Many examples forming diverse ring sizes have been reported, including macrocycles and medium-size rings, as well as the traditional five- and six-membered ring-forming reactions.

The RCM reaction has been employed for the synthesis of a variety of carbocyclic ring systems (Fig. 6, the indicated bond was formed via the RCM

reaction). Examples include: (1) synthesis of six-membered rings fused to the bicyclo[2.2.2]octane ring system [165]; (2) formation of ten-membered ring ketones [166]; (3) synthesis of five-membered rings spiro-fused to furanose sugars (e.g. **66**) [167]; (4) synthesis of five- and six-membered rings fused to furanose sugars (e.g. **67**) [168]; (5) synthesis of six- and seven-membered rings *trans* fused to the cyclohexane ring system [169]; (6) synthesis of cyclic enones (conjugated and unconjugated) spiro fused to five-membered rings [170]; (7) synthesis of highly functionalized seven-membered rings (e.g. **68**) [171,172]; (8) RCM of linalool (formation of **69**) in the same reaction pot as a palladium-catalyzed isomerization of crotyl acetate [173]; (9) synthesis of five- to seven-membered rings fused to oxazolidinones [174]; (10) formation of cycloheptyne–cobalt complexes (e.g. **70**) through RCM [175,176]; (11) tandem RCM and dehydration for the synthesis of naphthalene derivatives [177]; (12) synthesis of cyanocyclohexenecarboxylic esters [178]; (13) use of RCM for the synthesis of cyclic silyl enol ethers (e.g. **71**) [179]; (14) preparation of highly oxygenated six-membered rings [180–182]; (15) synthesis of seven-membered rings fused to tetrahydrofuran rings [183]; (16) formation of highly oxygenated five-membered rings for carbocyclic nucleoside synthesis (e.g. **72**) [184–186]; (17) preparation of the A ring of previtamin D analogs [187]; (18) preparation of the trans bicyclo[4.3.1]decane ring system (e.g. **73**) present in ingenol [188]; (19) preparation of a cyclohexenone ring for fumagillol total synthesis [189]; (20) preparation of cyclohexene derivatives (e.g. **74**) for the synthesis of opiate derivatives [190]; (21) synthesis of cyclohexene rings for total synthesis of securinine [191]; (22) synthesis of functionalized cyclopentene derivatives [192,193]; (23) formation of cyclopentenes for the total synthesis of zizaene [194]; (24) formation of highly oxygenated eight-membered rings [195]; (25) synthesis of an eight-membered ring (**75**) for asteriscanolide total synthesis [196]; (26) formation of a five-membered ring for synthesis of the carbocyclic analog of arabofuranose [197]; (27) synthesis of spirocyclic five- and six-membered rings for total synthesis of acorenone [198]; (28) synthesis of five-membered rings spiro fused to lactones [199]; (29) formation of cyclohexene in a failed attempt to prepare cyclododecatetraene via alkene metathesis of 1,7-octadiene [200]; (30) formation of spiro-fused cyclohexanones (e.g. **76**) for the preparation of rigid homoserine analogs [201]; (31) formation of oligopeptides featuring carbocyclic amino acid residues [202]; (32) closure of one of the outer five-membered rings in the synthesis of the linear triquinane desoxyhypnophilin [203]; (33) formation of an eight-membered ring (**77**) for teubrevin H total synthesis [204]; (34) synthesis of a cyclohexene-fused proline analog (e.g. **78**) [205]; (35) synthesis of six-membered ring fused to the pyrrolidine ring system [206]; (36) formation of a seven-membered ring of the hydroazulene ring system (**79**) [207]; (37) formation of six-membered rings fused to γ-lactones (e.g. **80**) [208]; and (38) synthesis of the cyclodecene ring of sarcodictyin [209].

Numerous examples of the formation of nitrogen heterocycles using the RCM reaction (Fig. 7) were reported in 2001, including: (1) formation of tetrahydropyridine derivatives (e.g. **81**) [210,211]; (2) formation of nitrogen heterocycles that contain an ester and a trifluoromethyl group alpha to the nitrogen [212]; (3) synthesis of the piperidene ring of ergot alkaloids (**82**) [213]; (4) synthesis of five-membered ring nitrogen heterocycles fused to the azabicyclo[3.3.1]nonane ring system (e.g. **83**) [214]; (5) synthesis of nitrogen heterocycles fused to the oxazolidinone ring system [215–218]; (6) synthesis of cyclic conjugated α,β-unsaturated δ-lactams and lactones [219]; (7) formation of the dihydroquinoline ring system (e.g. **84**) [220,221]; (8) synthesis of lactams [222–225]; (9) synthesis of *N*-protected azepine derivatives (e.g. **85**) [226,227]; (10) synthesis of cyclic *N*-tosyl enamides (e.g. **86**) [228]; (11) simultaneous formation of nitrogen and oxygen heterocycles (e.g. **87**) from tetraene derivatives [229,230]; (12) synthesis of the indolizidine ring system (e.g. **88**) [231,232]; (13) synthesis of rings containing two nitrogens fused to the β-lactam ring system [233]; (14) synthesis of five-membered ring *N*-protected heterocycles [234]; (15) synthesis of cyclic amino acids [235,236]; (16) formation of a pyrrolizidine (**89**) for total synthesis of hyacinthacine A_2 via RCM of a protonated amine [237]; (17) synthesis of a bicyclic lactam for total synthesis of coniceine [238]; (18) synthesis of [5.3.0]-bicyclic lactams [239]; (19) synthesis of cyclic sulfonamides [240,241]; (20) synthesis of protected cyclic amine **90** for total synthesis of anatabine [242]; (21) synthesis of bicyclic lactams [243]; (22) synthesis of an eight-membered ring protected amine (**91**) for mitosane total synthesis [244]; and (23) synthesis of ten-membered ring cyclic amides (e.g. **92**) [245].

Many examples of oxygen heterocycle synthesis using the RCM reaction were reported in 2001 (Fig. 8), including: (1) formation of α,β-unsaturated six-membered ring lactones (e.g. **93**) [246–250]; (2) formation of ribose derivatives annulated through the 2- and 5-carbons (e.g. **94**) [251]; (3) formation of eight-membered ring cyclic ethers [252]; (4) formation of nine-membered ring cyclic ether **95** for total synthesis of isolaurallene [253]; (5) formation of six- to nine-membered ring systems (e.g. **96**, **97**) of ciguatoxin/brevetoxin and related compounds [254–260]; (6) synthesis of selenium-containing lactones [261]; (7) *E*-selective 10-membered ring lactone synthesis [262]; (8) synthesis of oxygen heterocycles spiro fused to highly oxygenated cyclohexane derivatives (e.g. **98**) [263]; (9) synthesis of oxygen heterocycles in the presence of arene tricarbonylchromium functionality [264]; (10) synthesis of dioxabicyclo[3.2.1]octane derivatives (e.g. **99**) for synthesis

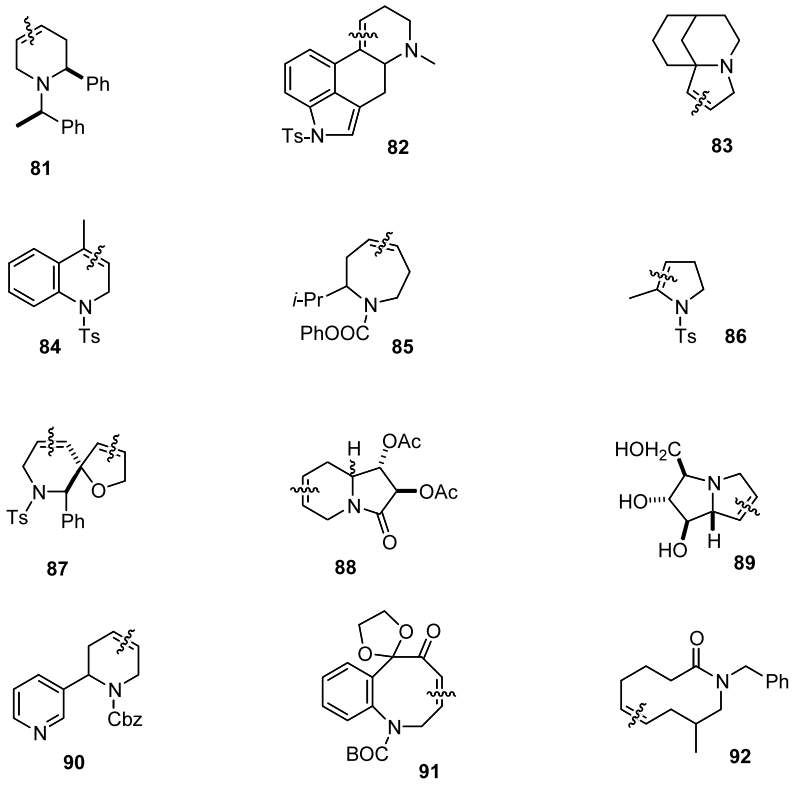


Fig. 7. Representative *N*-heterocycles produced through an RCM reaction (bond constructed through RCM indicated).

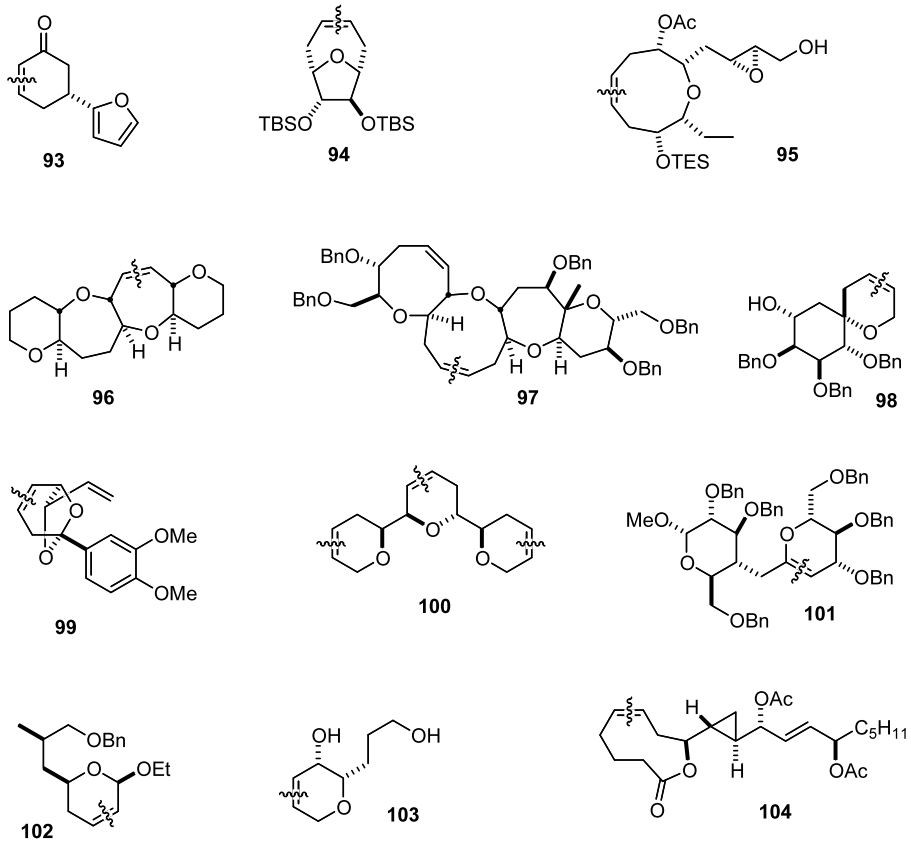


Fig. 8. Representative oxygen-heterocycles produced through an RCM reaction (bond constructed through RCM indicated).

of nanulosic acid [265,266]; (11) selective formation of oxygen heterocycles (e.g. **100**) over carbocycles in the RCM of a hexaene derivative [267]; (12) simultaneous formation of one [268] or two dihydrofuran rings [269]; (13) formation of six-membered ring oxygen heterocycles [270]; (14) formation of glycal derivatives (e.g. **101**) [271]; (15) formation of a seven-membered ring oxygen heterocycle fused to a highly oxygenated cyclohexane derivative [272]; (16) formation of a six-membered ring oxygen heterocycle (e.g. **102**) for synthesis of laulimalide [273–277]; (17) formation of six-membered ring oxygen heterocycle **103** for pseudomonic acid total synthesis [278]; and (18) synthesis of nine-membered ring lactone **104** for total synthesis of halicholactone [279].

Other heterocyclic compounds were also constructed via the RCM reaction (Fig. 9). Examples include: (1) formation of bridged ferrocene derivatives (e.g. **105**) through RCM of diallylferrocenes [280]; (2) formation of cyclic phosphate esters (e.g. **106**) [281]; (3) formation of cyclic phosphonate esters [282,283]; (4) formation of cyclic phosphonamides (e.g. **107**) [284,285]; (5) formation of cyclic thiophosphonates [286]; (6) formation of cyclic siloxanes (e.g. **108**) [287–290]; (7) formation of cyclic silanes from trienes in the presence of ethylene (both RCM and cross metathesis with ethylene occur)

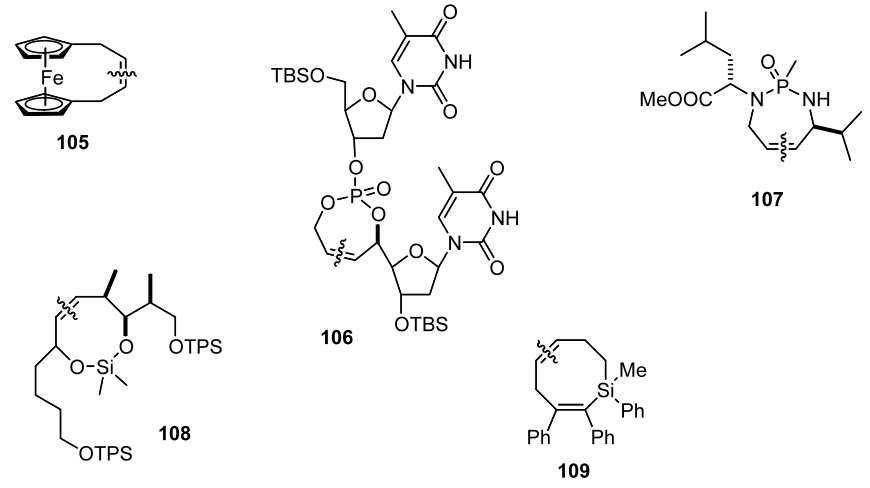


Fig. 9. Representative examples of other heterocycles prepared via the RCM reaction (bond constructed through RCM indicated).

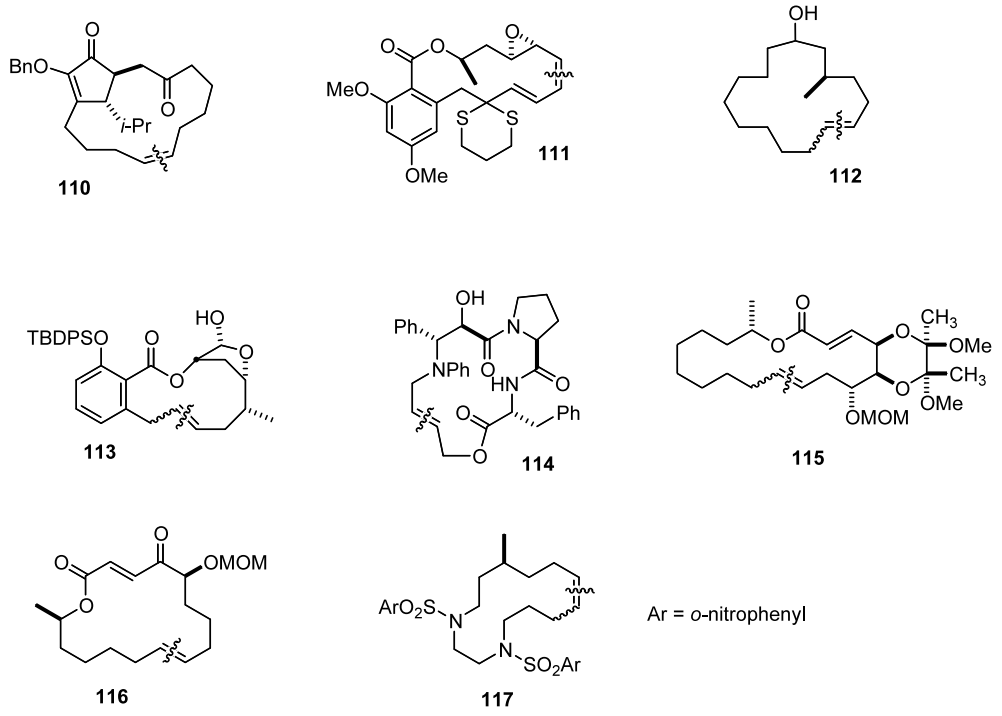
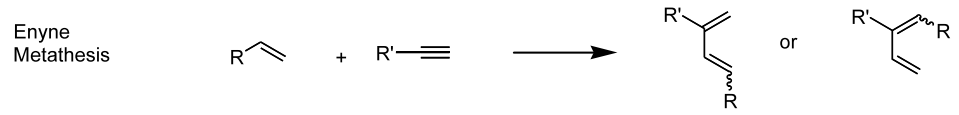


Fig. 10. Representative macrocycles (ring size >10) Prepared using the RCM reaction (bond constructed through RCM indicated).



Scheme 10.

[291]; (8) formation of silacyclooctadienes (e.g. **109**) [292]; and (9) formation of tetrahydrooxazepines bound to a polymer support [293].

Numerous examples of successful macrocyclic ring closure using the RCM reaction were reported in 2001 (Fig. 10), including: (1) synthesis of cyclopentenones bridged through the 3- and 5-positions (e.g. **110**) for roseophilin total synthesis [294]; (2) formation of pyrroles bridged through the 2- and 4-positions for roseophilin total synthesis [295]; (3) formation of macrocyclic esters (e.g. **111**) via RCM of a conjugated diene and a vinyl epoxides for total synthesis of radicicol and monocillin I [296]; (4) synthesis of macrocyclic alkenes (e.g. **112**) for total synthesis of muscone; this paper also notes that ruthenium metathesis catalysts can serve as hydrogenation catalysts [297]; (5) synthesis of macrocyclic lactones (e.g. **113**) for total synthesis of salicylhalamide [298–302]; (6) closure of the macrocyclic ring of epothilone [303]; (7) synthesis of macrocyclic peptide derivatives (e.g. **114**) [304–308]; (8) synthesis of polymer-bound macrocyclic carbamate esters and comparison with analogous solution phase macrocyclization reactions [309]; (9) synthesis of macrocyclic phthalate diesters [310]; (10) synthesis of macrocyclic esters in the presence of azide functionality [311]; (11) synthesis of macrocycle-bridged taxol analogues [312]; (12) synthesis of 18-membered ring derivative **115** for total synthesis of aspicilin [313]; (13) synthesis of macrocyclic ester **116** for total synthesis of A26771B [314]; (14) synthesis of catenane derivatives [315]; (15) synthesis of cored dendrimers [316]; (16) synthesis of macrocycle-bridged silsesquioxanes [317]; (17) synthesis of multicyclopropane-fused macrocyclic arrays [318]; (18) synthesis of various small, medium and large rings featuring a 1,2-diol derivative in the newly-formed rings [319]; (19) macrocyclic lactones bound to a solid support [320]; (20) formation of macrocyclic sulfonamides [321]; and (21) synthesis of the macrocyclic diamines (e.g. **117**) for total synthesis of the incorrect but proposed structure of haliclorensin [322] and for the revised correct structure [323].

2.2.6. *Alkene metathesis involving alkyne components*

Several examples of the synthesis of conjugated dienes through the intramolecular and intermolecular metathesis of enynes (Scheme 10) were reported in 2001. Examples of intermolecular enyne metathesis reactions (Fig. 11) include: (1) cometathesis of 3-butyn-1-ol tosylate and allylic ethers, resulting in synthesis of diene-ethers (e.g. **118**) [324] and (2) cometathesis of a porphyrin-bound alkyne and a disaccharide-bound alkene [325]. Examples of intramolecular enyne metath-

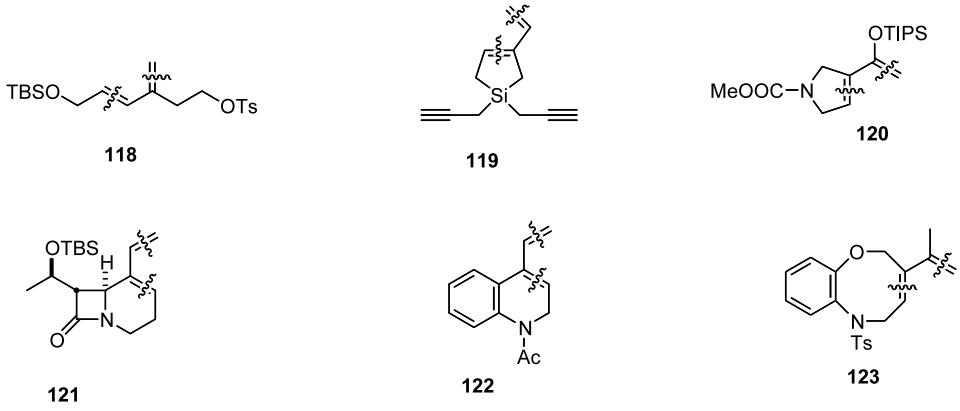
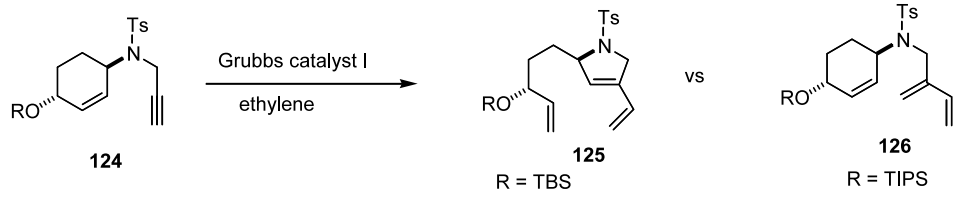
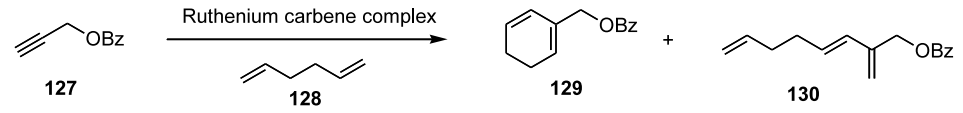


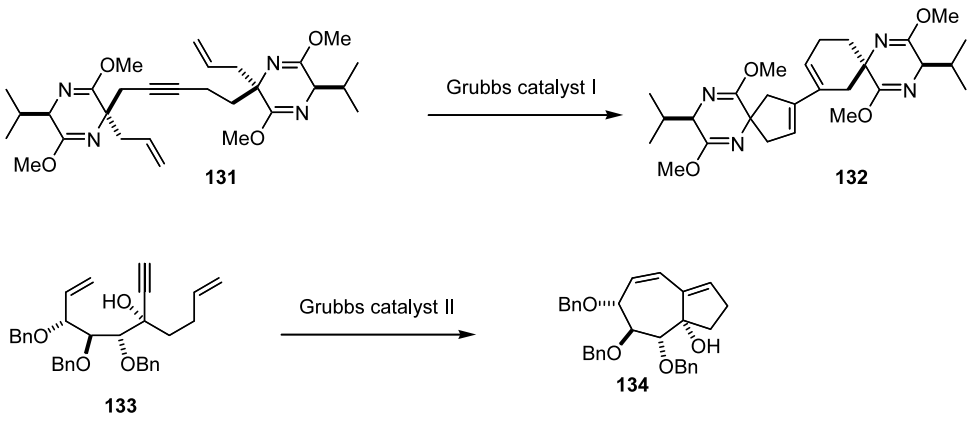
Fig. 11. Representative conjugated dienes prepared using an enyne metathesis reaction (bonds constructed through RCM indicated).



Scheme 11.



Scheme 12.



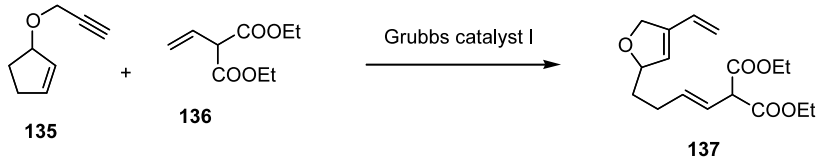
Scheme 13.

esis include: (1) formation of silacycles (e.g. **119**) using silanes containing allyl and propargyl groups, and also formation of silacycles using RCM of diallylsilanes [326]; (2) formation of cyclic siloxanes using a similar process [327]; (3) formation of dihydropyrroles (e.g. **120**) via enyne metathesis employing silyloxyalkynes [328]; (4) formation of carbocycles fused to the β-lactam ring system (e.g. **121**) [329]; (5) formation of carbocycles fused to the piperidine ring system [330]; (6) synthesis of various heterocycles fused to a benzene ring (e.g. **122**) [331]; (7) formation of various heterocyclic rings through enyne metathesis followed in situ capture of the resulting dienes by dienophiles [332]; (8) preparation of benzoxepin derivatives through tandem enyne metathesis-Diels–Alder reaction [333]; and (9) formation of eight- and nine-membered ring heterocycles (e.g. **123**) using enyne metathesis [334]. Enyne metathesis using a cyclic alkene component (e.g. **124**, Scheme 11) afforded isomerization product **125** using the *t*-butyldimethylsilyl ether. The triisopropylsiloxy analog of **124** underwent intermolecular enyne metathesis with ethylene to afford triene **126** and did not undergo the intramolecular metathesis [335].

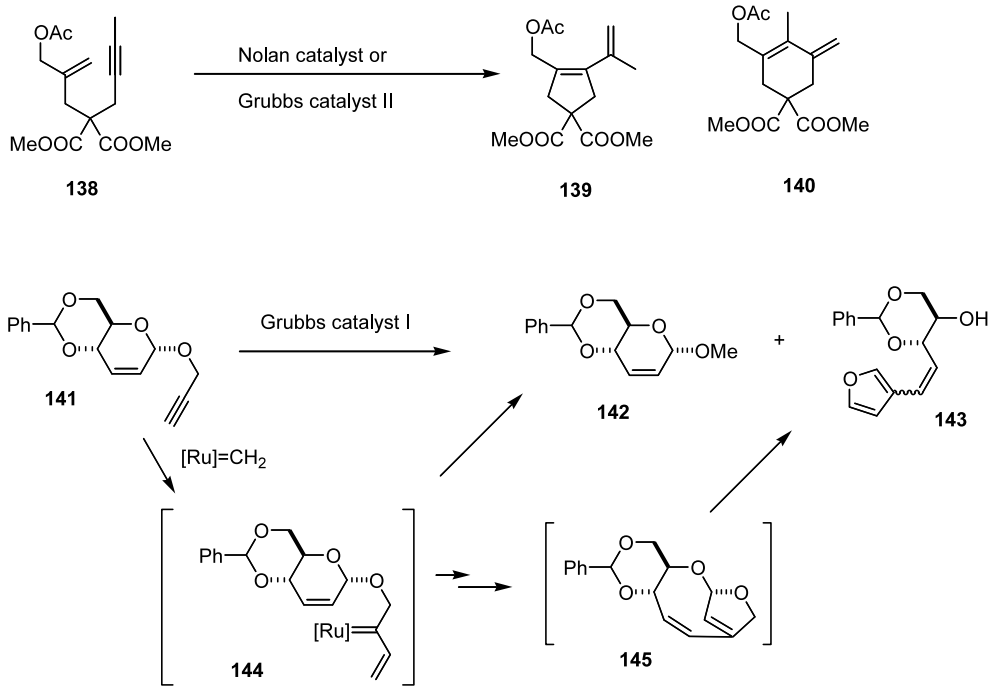
Cometathesis of alkynes and 1,5-hexadiene was reported (Scheme 12) [336]. The reaction leads to a mixture of cyclohexadienes (e.g. **129**) and acyclic trienes (e.g. **130**); the acyclic trienes were obtained as exclusively the *E* isomer. Presumably enyne metathesis initially produces a mixture of triene **130** and the analogous *Z* isomer. The *Z* isomer then undergoes a RCM to afford cyclohexadiene derivative **129**.

Several examples of enyne metathesis employing more than one alkene component were reported in 2001. A tandem enyne metathesis–RCM reaction was observed upon treatment of alkyne **131** (Scheme 13) with Grubbs catalyst I [337]. A similar process was reported for synthesis of cyclic siloxanes fused to cyclopentene rings [338]. A related process was employed for the synthesis of highly oxygenated compounds featuring the bicyclo[5.3.0]decane ring system (e.g. **134**) [339]. A variety of isomerizations of this type, in addition to several related examples involving only alkene metathesis, were also demonstrated [340]. A tandem enyne metathesis–cross metathesis was observed upon treatment of a mixture of enyne **135** (Scheme 14) and allylmalonate **136** with Grubbs catalyst I [341].

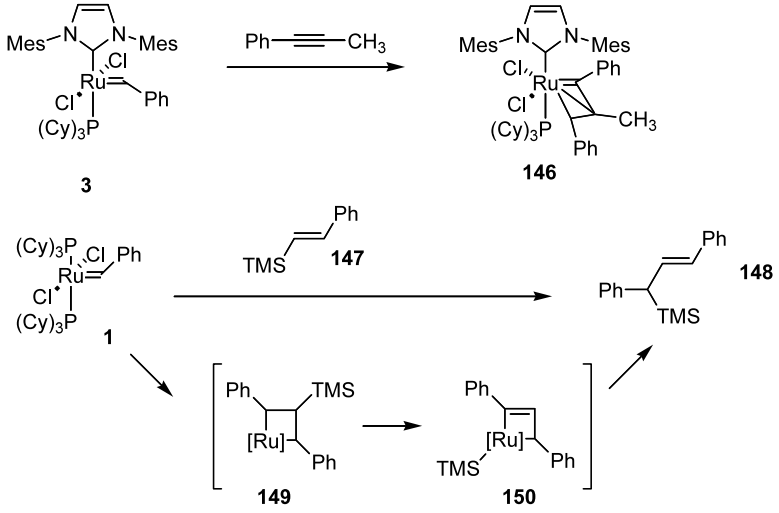
Both of the regioisomeric metathesis products **139** (Scheme 15) and **140** were observed in the enyne metathesis of compound **138** [342]. Compound **140** was proposed to arise through initial reaction of the methylene–ruthenium complex intermediate with the alkyne. The unsuccessful enyne metathesis of alkyne **141** resulted in the formation of the anomeric-exchange product **142** and the vinylfuran derivatives **143** [343].



Scheme 14.



Scheme 15.



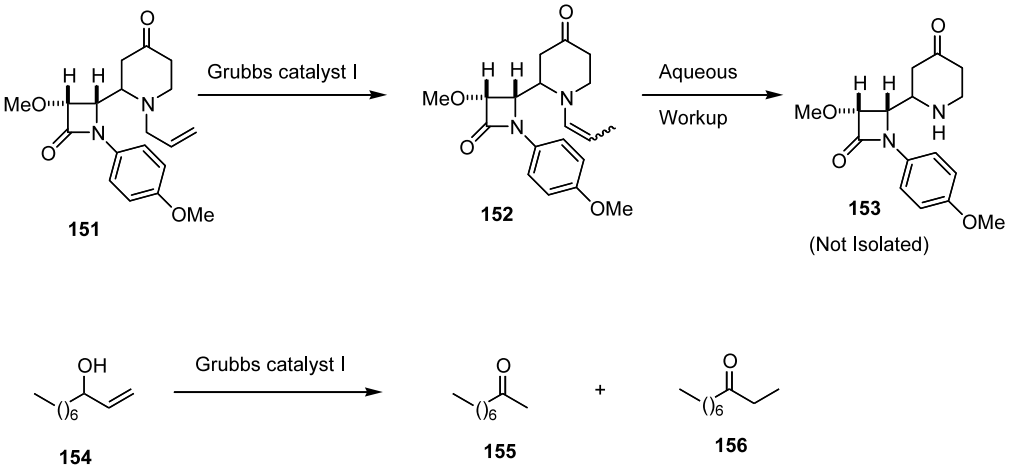
Scheme 16.

Compound **142** was proposed to arise through hydrogenolysis of the carbene complex–alkyne adduct **144**, while compounds **143** were suggested to arise by elimination of an alcohol from the dihydrofuran ring of hypothetical enyne metathesis product **145**.

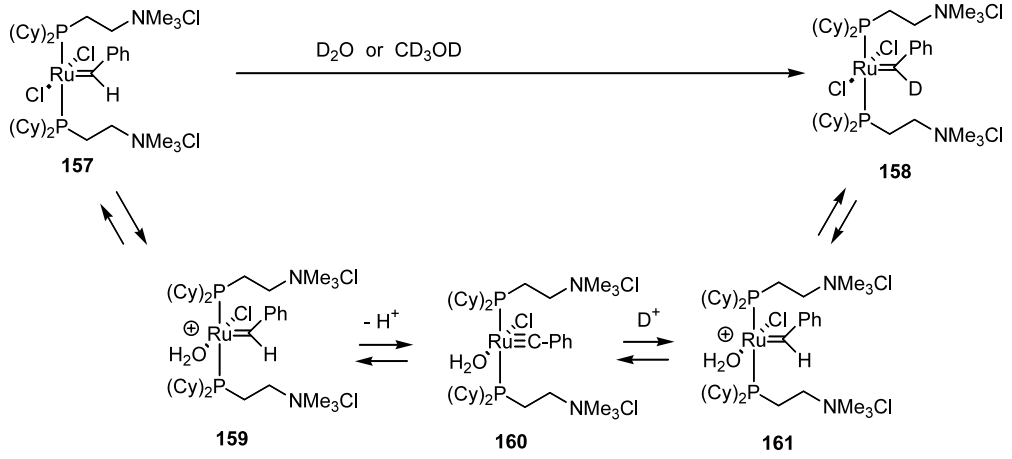
2.2.7. Non-metathesis reaction processes involving the ruthenium metathesis catalysts

The stoichiometric coupling of ruthenium metathesis catalysts with alkynes and alkenes was investigated (Scheme 16). The reaction of Grubbs catalyst II with alkynes leads to the formation of stable internally coordinated vinylcarbene complexes (e.g. **146**) with a high degree of regioselectivity [344]. The stoichiometric reaction of Grubbs catalyst I with vinylsilanes (e.g. **147**) led to allylsilane derivatives (e.g. **148**) where there is a net migration of silicon [345]. A mechanism involving regioselective formation of a metallacyclobutene (e.g. **149**), followed by β-silyl elimination to form a metallacyclobutene (e.g. **150**) and reductive elimination was proposed.

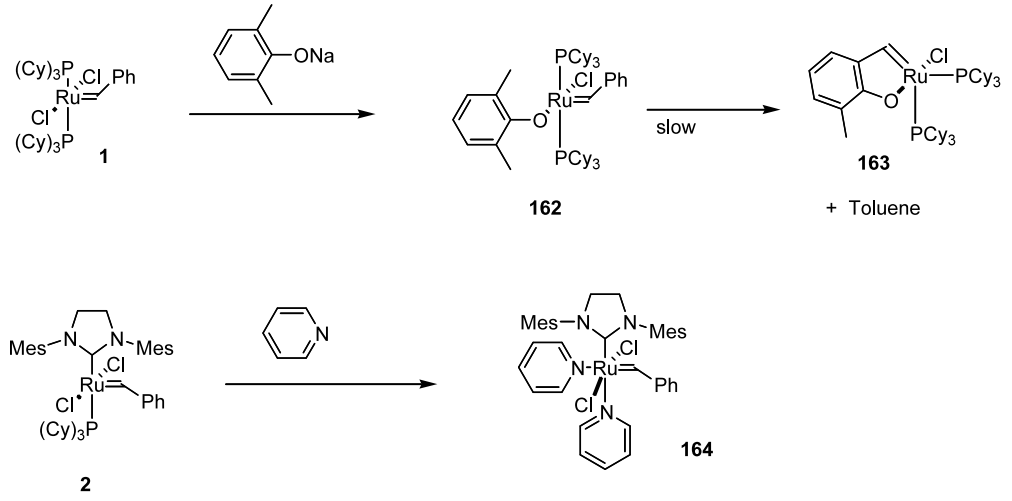
Conversion of allylamines (e.g. **151**, Scheme 17) to enamines (e.g. **152**) was accomplished using Grubbs catalyst I [346]. Treatment of allylamines with Grubbs catalyst I followed by enamine hydrolysis results in a net deallylation. Treatment of allylic alcohol derivatives



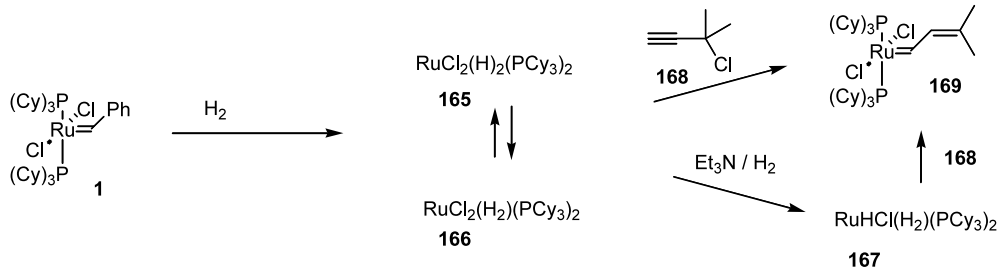
Scheme 17.



Scheme 18.



Scheme 19.

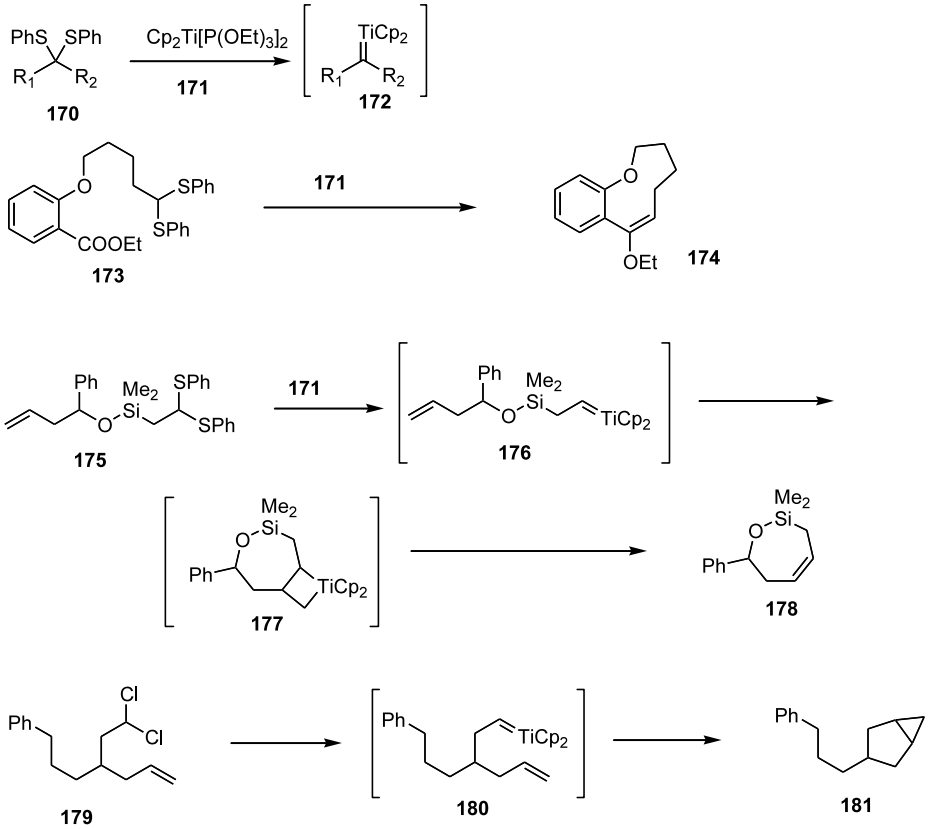


Scheme 20.

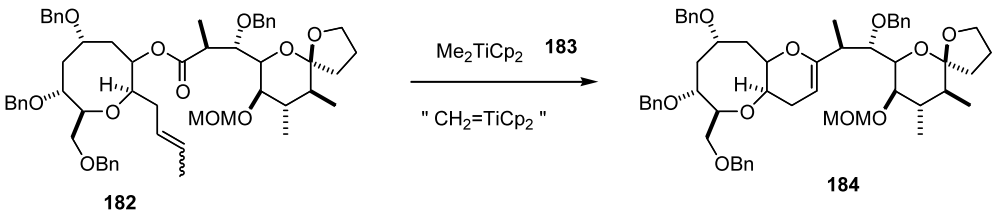
(e.g. **154**) with Grubbs catalyst I led to either the fragmentation product **155** or the isomerization product **156** [347]. The fragmentation product was major when a stoichiometric amount of catalyst was employed. Formation of the isomerization product was a general process when only catalytic amounts of Grubbs catalyst I were employed.

Water-soluble analogs of the Grubbs catalyst (e.g. **157**, Scheme 18) undergo hydrogen–deuterium exchange at the carbene carbon when dissolved in water or methanol [348]. The mechanism for the exchange process is depicted in Scheme 18. Exchange of a chloride ligand for water, followed by loss of a proton to form carbyne complex **160**, followed by protonation of the carbyne by a water molecule was proposed. Solvent and dielectric effects were consistent with this mechanism.

A variety of ligand exchange reactions were reported for ruthenium carbene metathesis catalysts (Scheme 19). An unusual carbene transposition was observed during attempted preparation of phenoxide analogs of Grubbs catalyst I (e.g. **162**) [349]. Rapid ligand exchange leading to complex **162** was observed upon treatment of Grubbs catalyst I with 2,6-dimethylphenoxide ion. A slower process, conversion to carbene complex **163**, was also observed. A mechanism involving oxidative addition into the benzylic C–H bond, followed by hydrogen transfer to the benzylidene ligand, followed by α-hydride elimination and reductive elimination of toluene was proposed. Formation of dipyridine complex **164** from Grubbs catalyst II and pyridine was reported [350]. A variety of ligand exchange processes were reported for complex **164**. Photolysis reactions of Grubbs catalyst I



Scheme 21.



Scheme 22.

were examined [351]. Upon ultraviolet irradiation, the primary photo process observed was ejection of a phosphine ligand. The photolysis reaction is initiated by a Ligand Field triplet state.

The hydrogenation of Grubbs catalyst I was reported [352]. Fluxional ruthenium dihydride/dihydrogen complexes (**165**, **166**, Scheme 20) were observed from the reaction with hydrogen gas. Treatment of the equilibrating complexes with triethylamine led to ruthenium complex **167**, which functions as a highly active hydrogenation catalyst. Reaction of any of the complexes **165**–**167** with 3-chloro-3-methyl-1-butyne (**168**) led to the ruthenium–alkenylcarbene complex **169**.

2.3. Individual carbene or alkylidene complexes classified according to metal

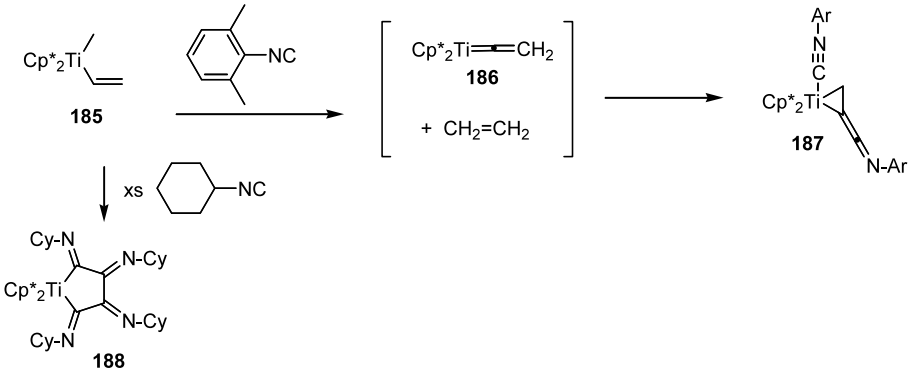
2.3.1. Group IV metal–carbene complexes

Both isolable titanium–carbene complexes and reactions that involve titanium alkylidene complexes are covered in this section. Routine uses of the Tebbe and Petassis reagents for carbonyl olefination are not covered in this article.

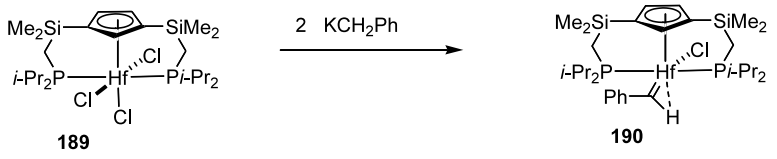
Several examples of the generation of titanium alkylidene intermediates (**172**, Scheme 21) from dithioacetals (**170**) and low-valent titanium (**171**) were reported in 2001. Formation of a variety of cyclic enol ethers (e.g. **174**) via a tandem carbene generation/carbonyl olefination process was observed upon treatment of ester–dithioacetals (e.g. **173**) with complex **171** [353]. Reaction of dithioacetal **175** with titanium complex **171** led to cyclic siloxane **178** [354]. In this reaction, the carbene intermediate **176** undergoes a ring closing metathesis reaction with the alkene functionality. The titanium carbene complex intermediate was also successfully generated from a 1,1-dichloro derivative (e.g. **179**) [355]. Treatment of dichloride **179** with titanium complex **171** led to the cyclopropane derivative **181**; cyclopropanation by intermediate carbene complex **180** was the key step in this reaction.

A related tandem carbonyl olefination–ring closing metathesis process was employed or the synthesis of cyclic ethers present in brevitoxin/ciguatoxin. For example, treatment of ester–alkene **182** (Scheme 22) with various titanium–carbene complex precursors (e.g. **183**) led to cyclic ether derivative **184** [356,357].

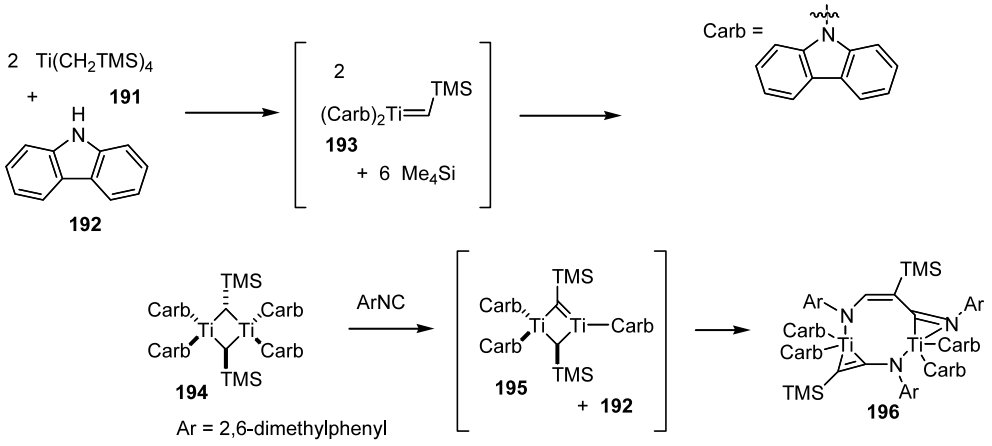
The reaction of titanium alkyls with isocyanides was studied (Scheme 23) [358]. Reaction of complex **185** with 2,6-dimethylphenylisocyanide led to the metallacyclopropane derivative **187**. A likely mechanism is formation



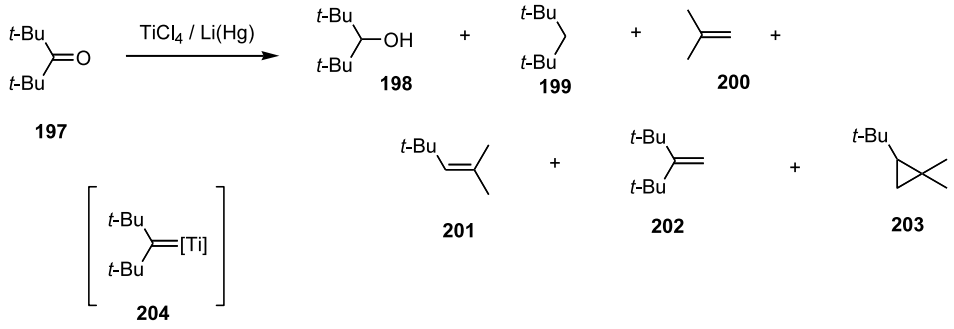
Scheme 23.



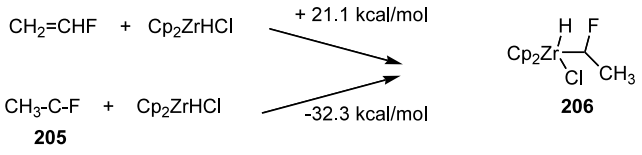
Scheme 24.



Scheme 25.



Scheme 26.

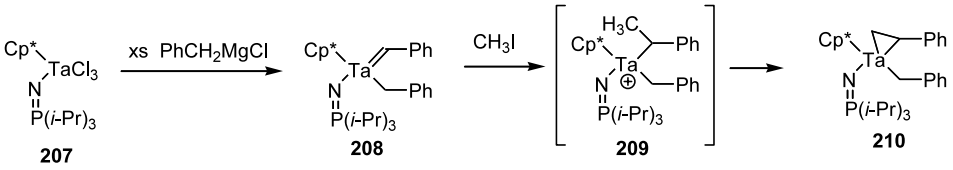


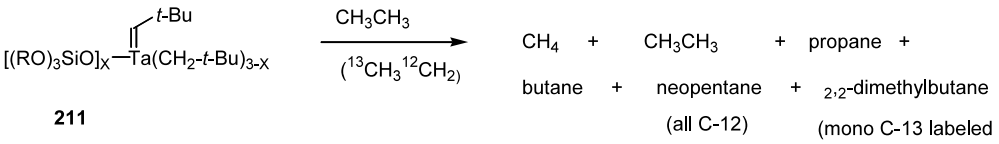
Scheme 27.

of a titanium vinylidene complex (**186**), followed by complexation with the isocyanide and insertion. The reaction with cyclohexyl isocyanide proceeded by a different course and produced a product (**188**) where none of the original alkyl groups are incorporated.

The hafnium–pincer carbene complex **190** (Scheme 24) was prepared from the hafnium trichloride derivative **189** and two equivalents of benzylpotassium [359]. A bis(pincer)carbene complex was also reported using a similar method [360].

Titanium carbene intermediates (e.g. **193**, Scheme 25) were proposed in the formation of bimetallic complex **194** from coupling of tetrakis(trimethylsilylmethyl)tita-





Scheme 28.

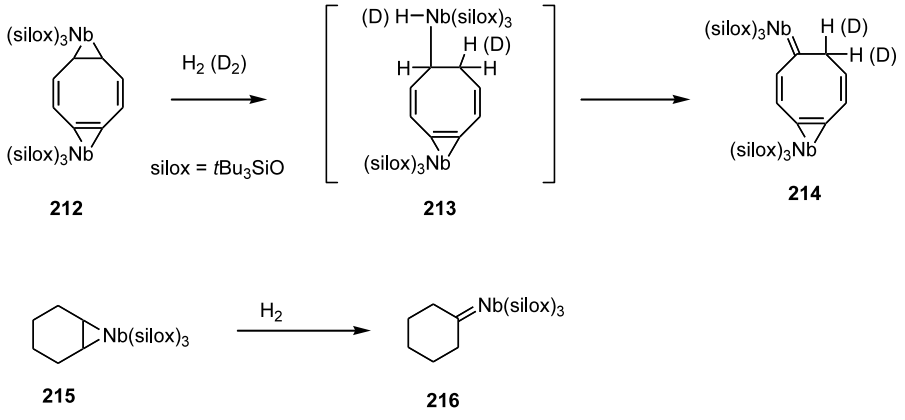
nium (**191**) with carbazole (**192**) [361]. Reaction of complex **194** with an isocyanide to form **196** was proposed to occur from bridging carbyne complex **195**.

Titanium carbenes (e.g. **204**, Scheme 26) were suggested as intermediates in the McMurry coupling [362,363]. The reaction of hindered ketone **197** with low valent titanium resulted in compounds **198**–**203**. The major product **199** was observed only if water was added to the reaction mixture and it likely results from protonation of di(*t*-butyl)carbene–titanium complex **204**.

Hypothetical zirconium(IV)–carbene complexes (e.g. **206**, Scheme 27), which cannot back bond, were studied by density functional theory [364]. Formation of carbene complex **206** from fluoroethylene and Cp_2ZrHCl is endothermic ($+21.1$ kcal mol^{-1}) while formation from the free carbene **205** is exothermic (-32.3 kcal mol^{-1}). There is some evidence of interaction between the chloride ligand and the carbene carbon in the energy-minimized structure for **206**.

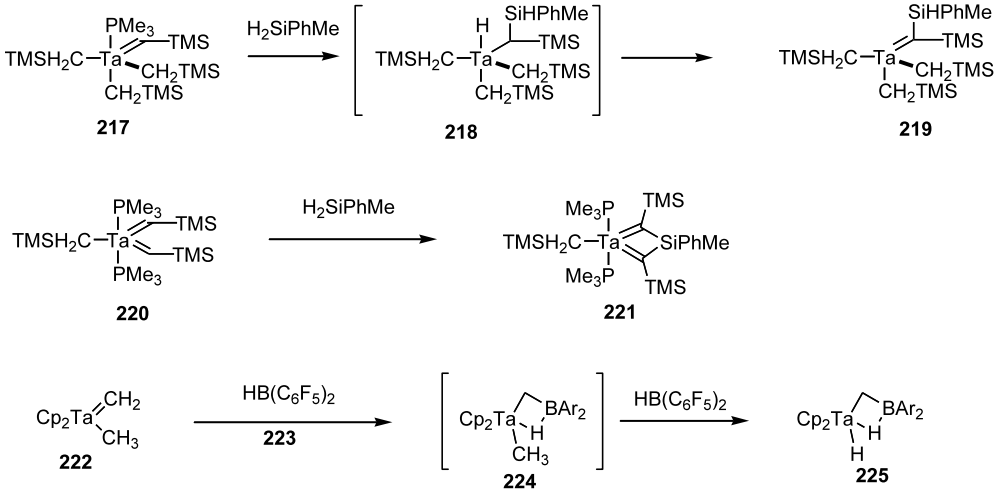
2.3.2. Group V metal–carbene complexes

Several papers reported on the synthesis of Group V metal carbene complexes through α-hydride elimination from Group V metal–alkyl complexes. Reaction of tantalum(V) complex **207** (Scheme 28) with excess benzylmagnesium chloride led to the stable tantalum–carbene complex **208** [365]. Reaction with iodomethane led to alkene complex **210** through addition of methyl iodide at the carbene carbon followed by β-hydride elimination and proton abstraction. The preparation and reactions of silica-bound tantalum–carbene complex (e.g. **211**) with alkanes were examined [366,367]. Alkane metathesis, resulting in a variety of low molecular weight alkenes, was observed upon exposure of ethane to carbene complex **211**. Two reaction pathways were considered: (1) addition of the C–C bond of ethane to the Ta–C double bond and (2) addition of the C–H bond of ethane to the Ta–C double bond. The second pathway was favored since there was more neopentane than 2,2-dimethylbutane. This was also consistent with a



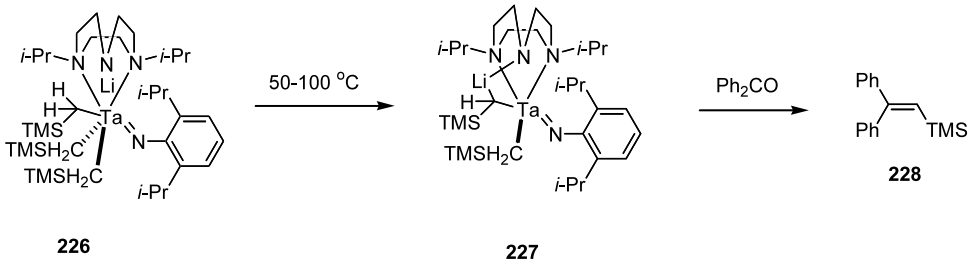
212 **213** **214** **215** **216**

Scheme 29.



217 **218** **219** **220** **221** **222** **223** **224** **225**

Scheme 30.



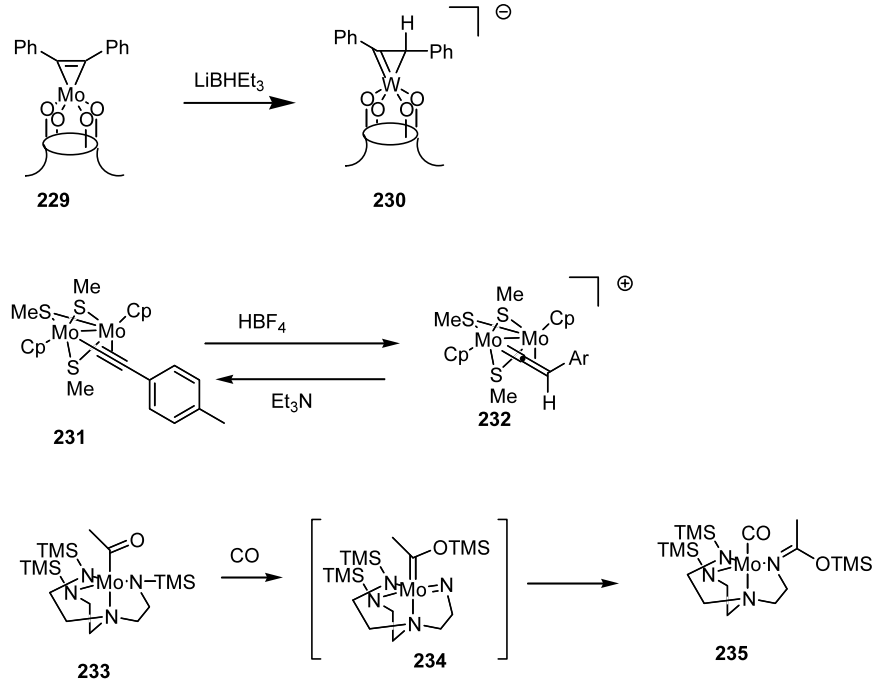
Scheme 31.

C-13 labeling experiment using ethane C-13_1. In this experiment, the neopentane produced was unlabeled, while 2,2-dimethylbutane was mono-labeled. Niobium–alkylidene complexes were generated in impure form through the coupling of $(ArO)_2NbCl_3$ complexes with 2–3 equiv. of $PhCH_2MgBr$ or $TMSCH_2MgCl$ [368]. A vanadium carbene complex intermediate was proposed in the binding of a trineopentylvanadium complex [(*t*-$BuCH_2)_3V{=}N$-*t*-Bu] to dehydroxylated silica [369].

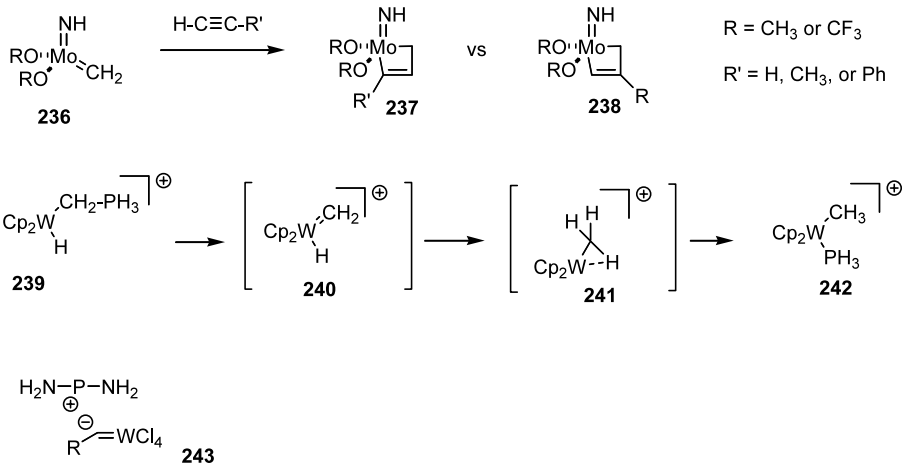
Reaction of alkyne–alkene diniobium complex **212** (Scheme 29) with hydrogen led to the alkyne–carbene diniobium complex **214** [370]. A deuterium labeling experiment revealed that one of the hydrogens from H_2 is incorporated into the product. The hydrogenation product **213** was suggested as an intermediate, which affords the carbene complex through α-hydride elimination and extrusion of hydrogen. This transformation was found to be general. Simpler niobium–alkene complexes (e.g. **215**) also transformed to carbene complexes upon treatment with hydrogen.

The reaction of tantalum(III) carbene complexes (e.g. **217**, Scheme 30) with silane derivatives was studied [371]. Replacement of carbene–hydrogens by silicons was noted in reactions with dihydrosilanes. A mechanism involving addition of the silicon hydride to the tantalum carbon double bond followed by α-hydride elimination and reductive elimination of hydrogen was proposed. Deuterium labeling studies support the proposed mechanistic pathway. Reaction of the bis(carbene) complex **220** with methyl(phenyl)dihydrosilane led to the dimetallacycle **221**. Hydroboration of tantalum carbene complex **222** led to tantalum alkyls featuring a bridging hydride ligand (e.g. **225**) [372].

The thermal decomposition of tris(trimethylsilylmethyl)tantalum(V) complex **226** (Scheme 31) led to tantalum–organolithium compound **227**, which is formally a tantalum carbene complex [373]. Tantalum carbenoid complex **227** afforded carbonyl olefination product **228** upon reaction with benzophenone and a ketene complex upon treatment with carbon monoxide [374].



Scheme 32.



Scheme 33.

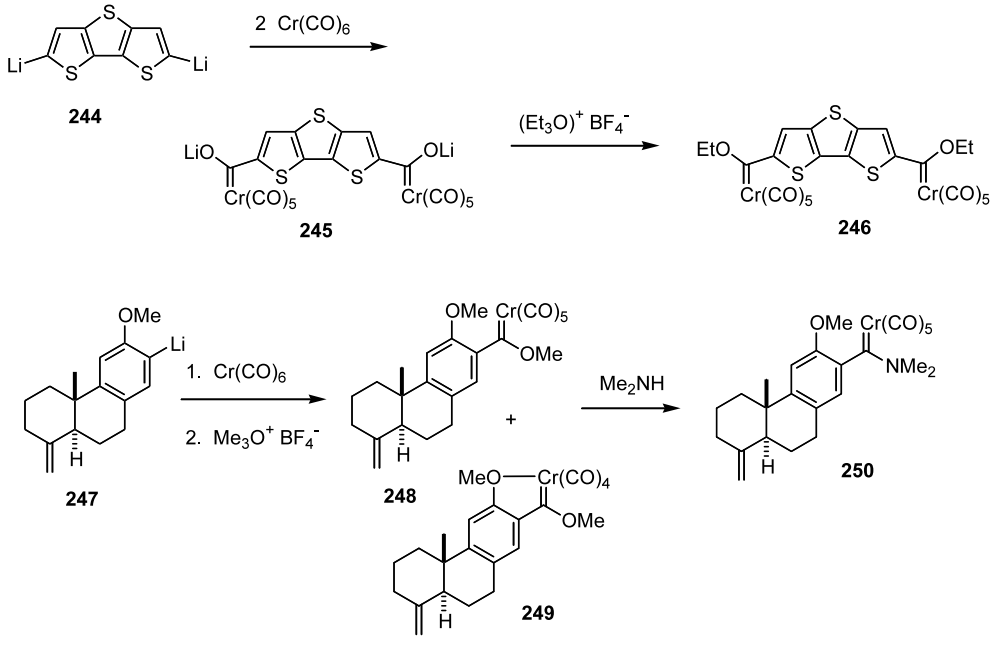
The insertion of ethylene into alkylniobium complexes was studied by density functional theory [375]. Among the mechanisms considered was the α-hydride elimination–reductive elimination to produce a niobium–carbene complex, followed by [2+2]-cycloaddition and ring opening through reductive elimination.

2.3.3. Group VI metal–carbene complexes (further classified according to structure and reaction type)

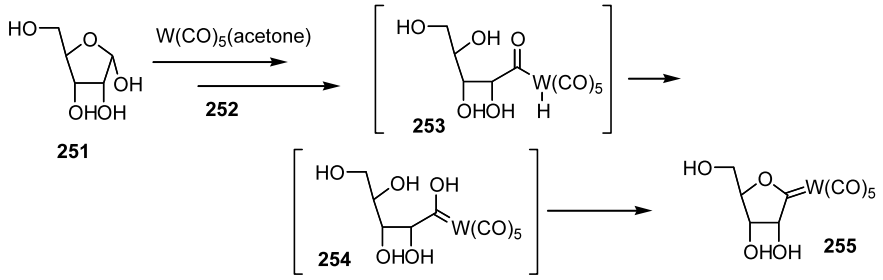
2.3.3.1. Schrock-type carbene complexes (oxidation state +3 or higher using the ionic model). A significant portion of this subject material has already been presented in the alkene metathesis section; the Schrock catalyst belongs to this class.

Several papers reported on the generation or intermediacy of compounds in this class. Molybdenum calixarene alkyne complexes (e.g. **229**, Scheme 32) were converted to the corresponding η^2-alkenyl complexes (e.g. **230**) by treatment with lithium triethylborohydride [376]. The formation of bimetallic molybdenum–vinylidene complexes (e.g. **232**) was observed upon protonation of the corresponding molybdenum–alkyne complexes [377]. Treatment of the vinylidene complexes with base resulted in regeneration of the alkyne complex. Molybdenum–carbene-imido complex **234** was proposed as intermediate in the transformation of molybdenum–acyl complex **233** to the carbonyl complex **235** [378].

Several papers reported on theoretical investigations of this category of carbene complex in 2001. The



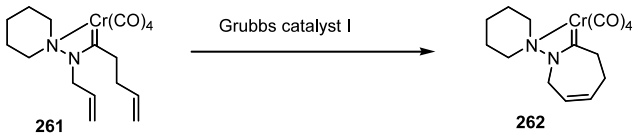
Scheme 34.



Scheme 35.

coupling of molybdenum(IV) carbene complex **236** (Scheme 33) with alkynes was studied by Density Functional Theory [379]. In the formation of the metallacyclobutenes (**237**, **238**) from reaction of complex **236** with acetylene, the reaction employing the trifluoromethoxy ligand occurs with a lower activation energy (2.3 kcal mol^{-1}) than the analogous complex featuring a methoxy group (10.3 kcal mol^{-1}). When terminal alkynes are employed, formation of regioisomer **237** is the lower energy pathway, however the energy difference between the two isomers is reduced when the reaction is conducted in the solution phase. The conversion of phosphorous ylide complex **239** to phosphine complex **242** was studied by density functional theory [380]. The first step in this transformation is dissociation of the phosphine to the carbene complex **240**, which is endothermic by 17 kJ mol^{-1}. A density functional theory study of tungsten carbene complexes that feature a carbanion at the carbene carbon (e.g. **243**) was conducted [381]. The complex to a phosphorus cation features a long carbon–phosphorus bond and a short carbon–tungsten bond. The complex appears to have substantial carbyne character.

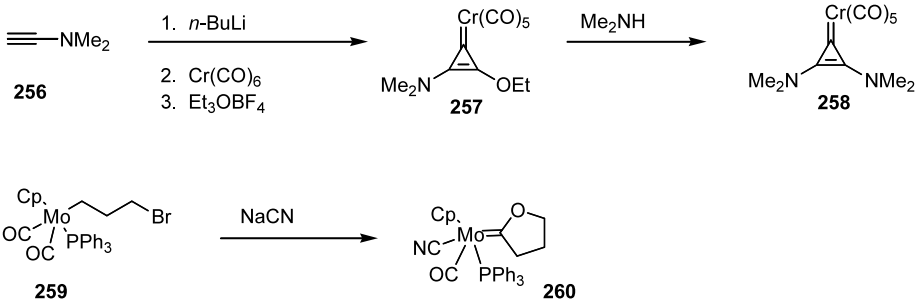
2.3.3.2. Publications focusing on synthesis or formation of Fischer carbene complexes of Group VI metals. The most common procedure used for the synthesis of Group VI metal–carbene complexes (e.g. **246**, Scheme 34) is the Fischer synthesis, which is illustrated by the example in Scheme 34. In this case coupling of a dicarbanion (**244**) with a Group VI metal carbonyl derivative, followed by alkylation of the resulting acylate (**245**) leads to the dicarbene complex [382,383].



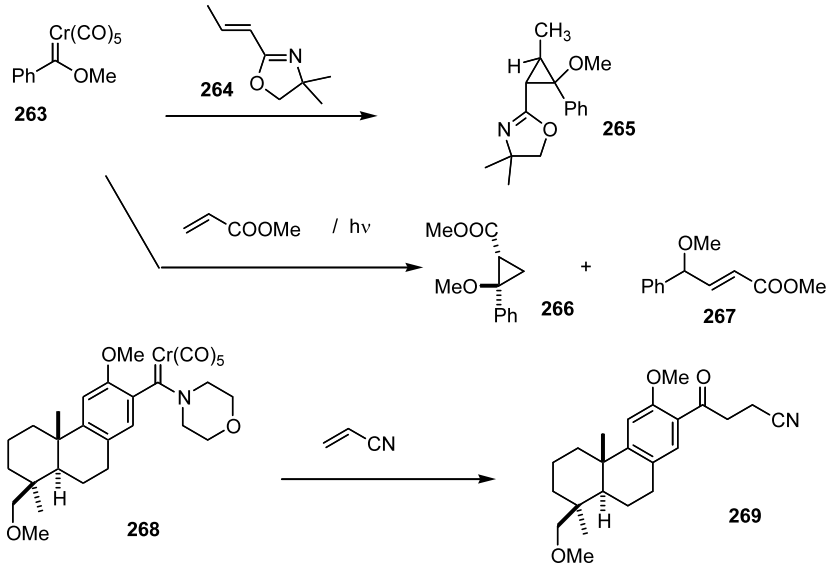
Scheme 37.

Various podocarpane-substituted alkoxycarbene complexes (e.g. **248**) were prepared, and subsequently converted to the aminocarbene complexes (e.g. **250**) through aminolysis [384].

Other synthetic routes to Group VI metal–carbene complexes were also reported in 2001. The direct formation of furanosylidene complex **255** (Scheme 35) from the carbohydrate **251** and the tungsten complex **252** was reported [385]. The carbene complex is generated in quantitative yield and does not require the addition of Lewis acids. Key steps in the proposed mechanism are formation of the hydrido acyl complex **253** from the aldehydic form of **251** and subsequent conversion of **253** to hydroxycarbene complex **254**, which cyclizes to the observed product **255**. The reaction was unique to ribose derivatives and this was attributed to a high concentration of the aldehydic form relative to pyranose sugars and the presence of the hydroxy group at the 2-position (the corresponding deoxyribose derivative failed to produce a carbene complex). Cyclopropenylidene–chromium complex **257** (Scheme 36) was produced from ynamine **256** [386]. Subsequent reaction with dialkylamines led to diaminocyclopropenylidene complexes (e.g. **258**). Cyclic molybdenum–carbene complexes (e.g. **260**) were prepared through



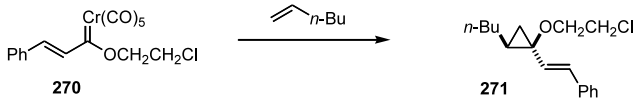
Scheme 36.



Scheme 38.

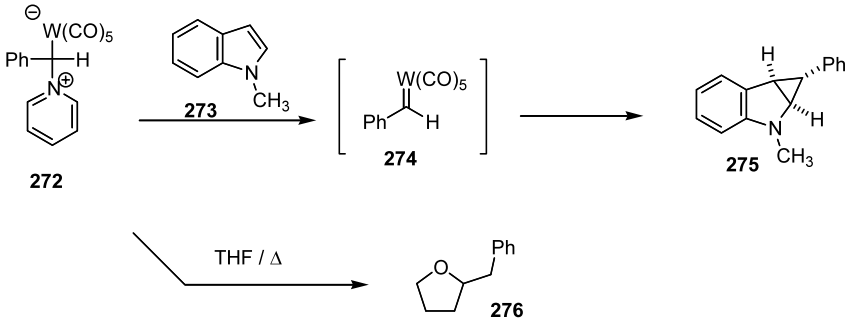
reaction of bromopropyl–molybdenum complex **259** with potassium cyanide or lithium iodide, presumably via formation of the anionic acyl complex followed by intramolecular *O*-alkylation [387]. A variety of hydrazinocarbene complexes (e.g. **262**, Scheme 37) were prepared through metathesis reactions of hydrazinocarbene complexes containing alkenyl substituents (e.g. **261**) [388].

2.3.3.3. Reaction of Group VI metal–carbene complexes with alkenes and dienes. This section focuses on reactions of Group VI metal–carbene complexes involving coupling with alkenes at the carbene–carbon. Other examples of the coupling of carbene complexes with alkenes where the reactive site is elsewhere can be found ahead under the heading: cycloaddition reactions occurring at the C–C π-bond of α,β-unsaturated metal–carbene complexes (Section 2.3.3.7). Cyclopropanation is a common reaction pathway for the coupling of Fischer carbene complexes with polarized alkenes.

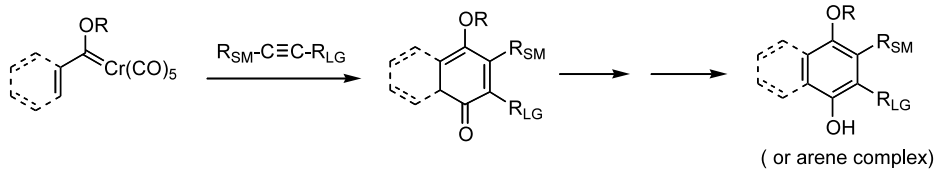


Scheme 39.

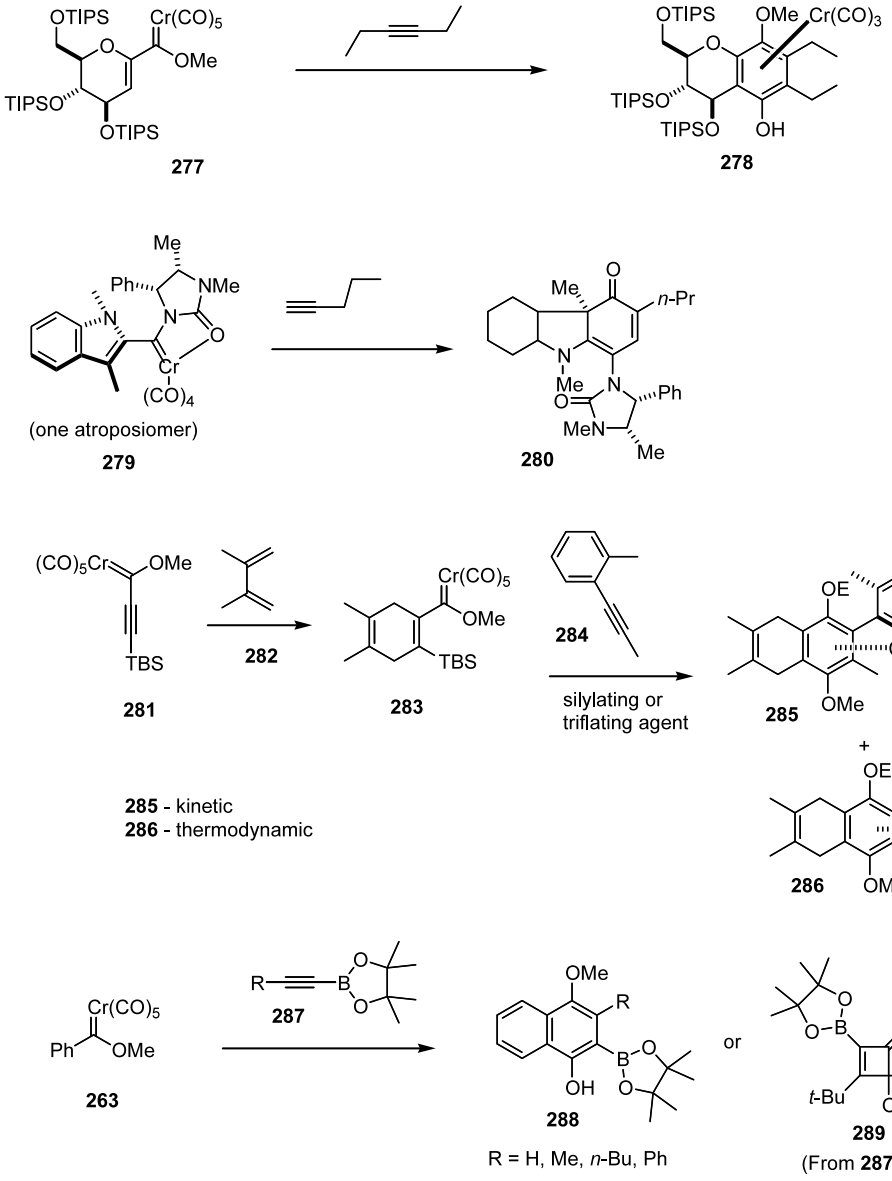
Cyclopropanation reactions of alkenyloximes (e.g. **264**, Scheme 38) by Fischer carbene chromium complexes were reported [389]. The reaction led to the indicated stereoisomer with a high degree of selectivity. The reaction using chiral oxime derivatives led to analogous compounds with a high degree of relative asymmetric induction. Room temperature photolysis-induced cyclopropanation of acrylate esters by phenylcarbene complex **263** was reported [390]. This reaction afforded mixtures of the cyclopropanes **266** and the ring opened products **267**. The reaction of electron-deficient alkenes with aminocarbene complexes fused to the podocarpane ring system (e.g. **268**) was reported [391]. Coupling with α,β-unsaturated carbonyl derivatives or acrylonitrile led to the γ-keto carbonyl derivatives of general structure **269**, presumably through formation of a cyclopropylamine followed by hydrolysis. Coupling with phenyl vinyl sulfone or sulfoxide led to the allylic amine derivatives (nitrogen analogs of **267**).



Scheme 40.



Scheme 41.



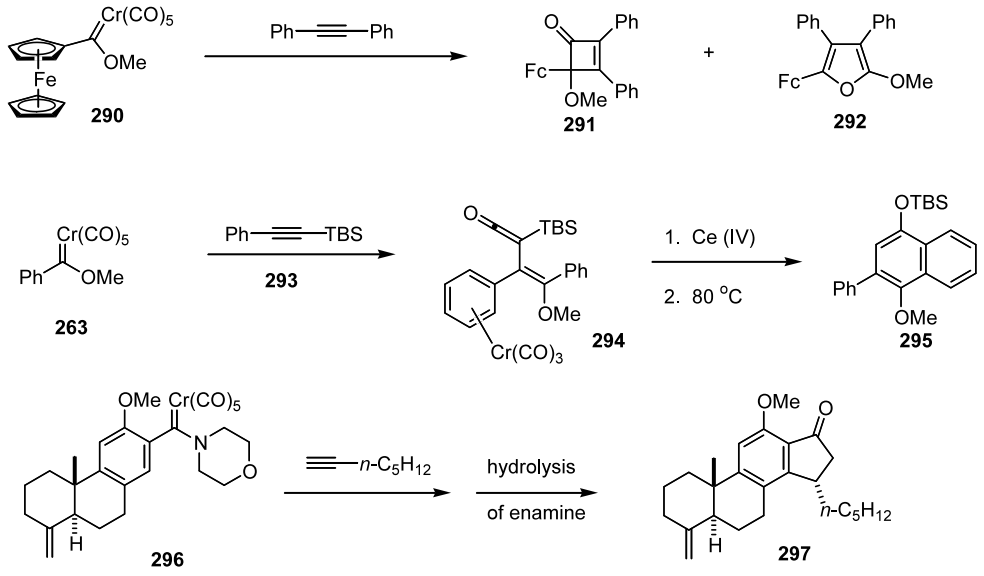
Scheme 42.

Successful cyclopropanation of unactivated alkenes (e.g. 1-hexene) was achieved using α,β-unsaturated chromium carbene complexes (e.g. **270**, Scheme 39). Chloroethylcarbene complex analogs (e.g. **270**) were noticeably more reactive and could successfull cyclopropanate norbornene, styrene, and 1-hexene [392].

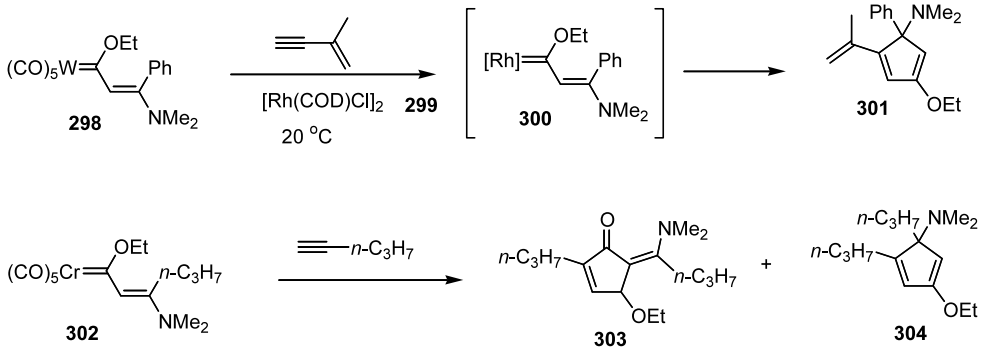
Thermolysis of pyridinium ylides (e.g. **272**, Scheme 40) in the presence of enamines (e.g. **273**) led to cyclopropanation products (e.g. **275**) [393]. The reaction proceeds through generation of the nonheteroatom-stabilized carbene complexes (e.g. **274**) followed by subsequent cyclopropanation. Thermolysis in THF or ether led to products resulting from net insertion of the

carbene complex intermediates into the α C–H bond (e.g. **276**).

2.3.3.4. Reaction of Group VI metal–carbene complexes with alkynes—benzannulation. Many examples of benzannulation using α,β-unsaturated chromium–carbene complexes (Scheme 41) and alkynes (commonly known as the Dötz reaction) were reported in 2001. Formation of benzo-fused carbohydrates (e.g. **278**, Scheme 42) was achieved through coupling α,β-unsaturated carbene complex **277** with alkynes [394]. The arene complex **278** was formed with a high degree of stereoselectivity. The use of chiral ancillaries in benzannulation reactions involving alkynes and Fischer carbene complexes was reported [395]. The best diastereoselectivities reported involve the coupling of atropoisomeric indolocarbene complexes (e.g. **279**) with terminal alkynes. An atroposelective benzannulation reaction was observed in the coupling of cyclohexenylcarbene complex **283** (obtained by Diels–Alder reaction of alkynylcarbene complex **281** with 2,3-dimethyl-1,3-butadiene) with *o*-tolylacetylene derivatives (e.g. **284**) [396]. A reagent for silylating or triflating the phenol group was added to the reaction to allow for isolation of the arene complex. Both of the expected isomers **285** and **286** were observed. However, either could be obtained as the major product depending on the timing of the addition of the phenol protecting group. The kinetic product **285** was obtained if the reaction was conducted in the presence of the silylating agent. The thermodynamic product **286** was obtained when the silylating agent was added later, or if a less bulky group like a triflate was attached to the phenol. An atroposelective benzannulation was also observed in a similar reaction used for the synthesis of colchicine derivatives [397]. The coupling of arylcarbene–chromium complexes with alkynylboranes (e.g. **287**) was reported [398]. Most alkynes afforded benzannulation products, naphthylboranes (e.g. **288**), with a high degree of regioselectivity, however the *t*-butylacetylene derivative led to a cyclobutenone (e.g. **289**). A successful Dötz reaction was demonstrated for a selenium-containing alkyne for synthesis of a naphthoquinone natural



Scheme 43.

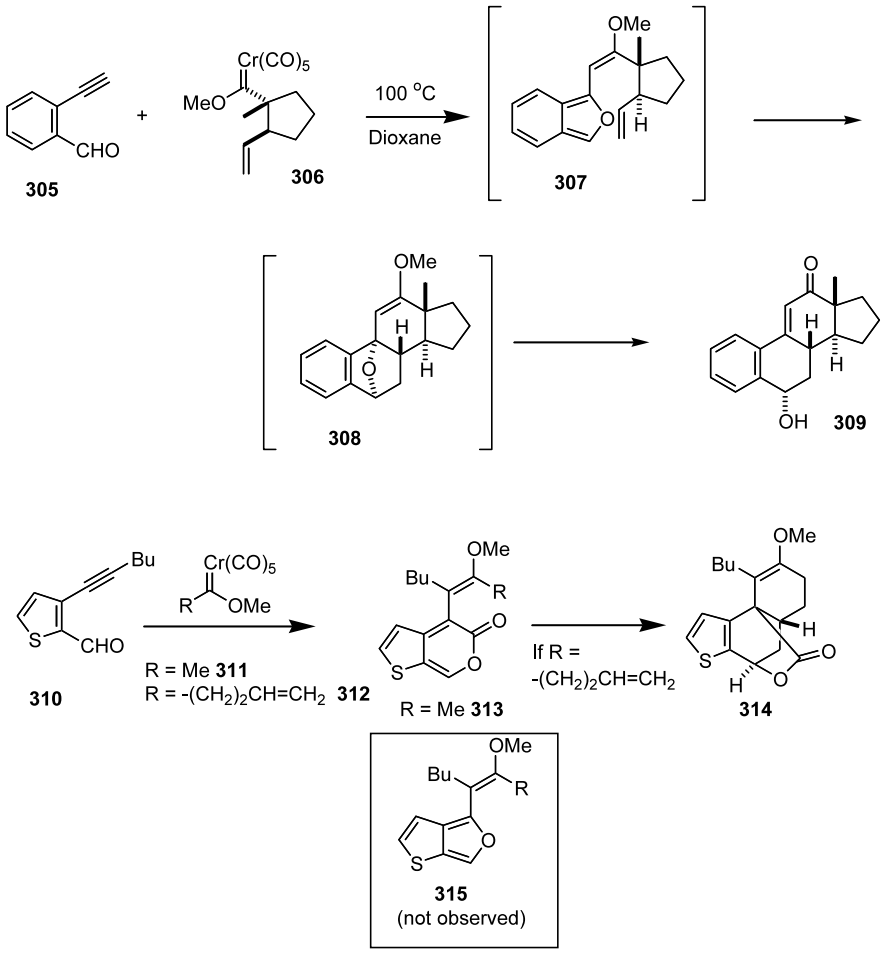


Scheme 44.

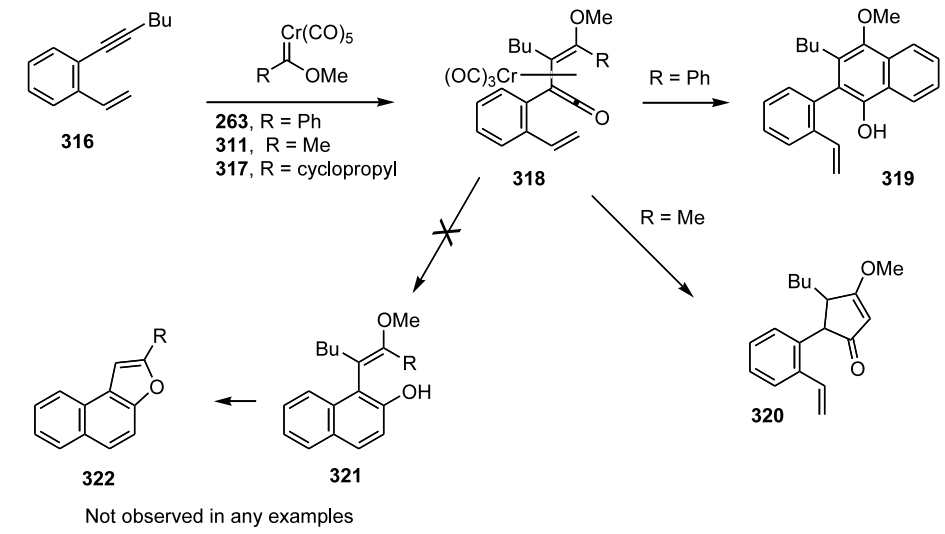
product [399]. The dry state adsorption technique afforded superior yields of benzannulation product. Coupling of an arylcarbene–chromium complex with 2-butyne-1,4-diol derivatives led to highly oxygenated naphthalene derivatives [400].

2.3.3.5. Nonbenzannulation reactions of Group VI metal–carbene complexes with alkynes. In addition to benzannulation products, the coupling of alkynes with α,β-unsaturated carbene complexes often leads to other coupling products, including furans, cyclobutenones, ketenes, and cyclopentenones. Examples of these reaction processes are depicted in Scheme 43. Coupling of ferrocenylcarbene complex **290** with alkynes led to predominantly cyclobutenones (e.g. **291**) and furans (e.g. **292**) and not benzannulation products [401]. The product distribution was highly dependent on the metal and on the number of equivalents of alkyne employed. The furan products were more prevalent when the reaction was conducted at high concentration. Formation of ketene complexes (e.g. **294**) was observed in the coupling of phenylcarbene complex **263** with sterically hindered silyl phenyl acetylenes (e.g. **293**) [402]. Formation of the stable ketene–arene complex was initially observed, and treatment of the complex with photolysis or cerium (IV) followed by thermolysis of the resulting free ketenes at 80 °C led to the benzannulation products (e.g. **295**). Cyclopentannulation reactions involving the coupling of alkynes and aminocarbene complexes fused to podocarpane rings (e.g. **296**) were reported [403]. The products from these couplings (e.g. **297**) feature the basic skeleton of the steroid ring system. Related cyclopentannulation reactions involving complexes where the alkyne is tethered to the carbene complex through nitrogen were also reported [404].

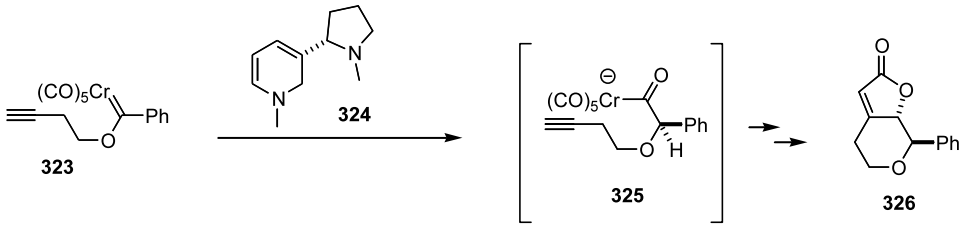
The coupling of β-aminoalkenylcarbene–tungsten complexes (e.g. **298**, Scheme 44) with conjugated acetylenes in the presence of various rhodium complexes (e.g. **299**) was examined [405]. The coupling proceeded at 20 °C to provide the cyclopentadiene derivatives (e.g. **301**). A mechanism involving initial carbene transfer from tungsten to rhodium was proposed. Related cyclopentannulation reactions were observed in the coupling of β-amino-α,β-unsaturated chromium carbene complexes (e.g. **302**) with terminal alkynes [406]. This coupling reaction can provide either the analogous five-



Scheme 45.



Scheme 46.



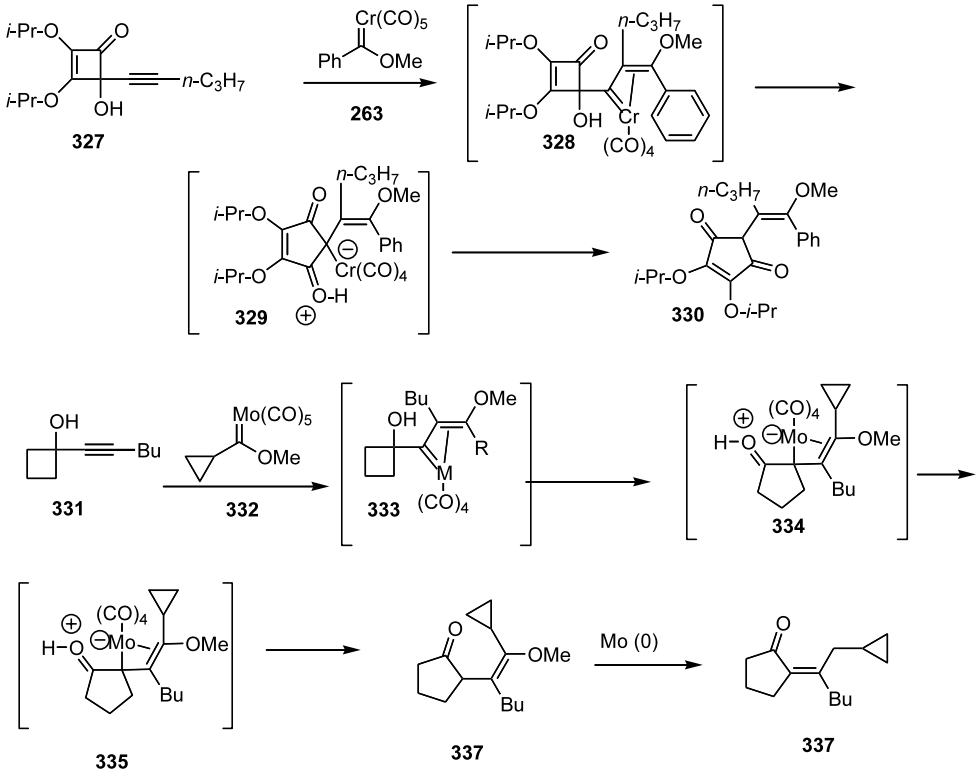
Scheme 47.

membered ring derivative (e.g. **304**) or a five-membered ring product resulting from CO insertion (e.g. **303**). The distribution of **303** and **304** was very dependent upon the substrate and the reaction conditions. The formation of the simple cyclopentannulation product **304** was maximized for analogs of **302** featuring small amino groups and electron-donating β-alkyl groups, and also maximized when the reaction was performed in the presence of ligand additives and in highly coordinating solvents.

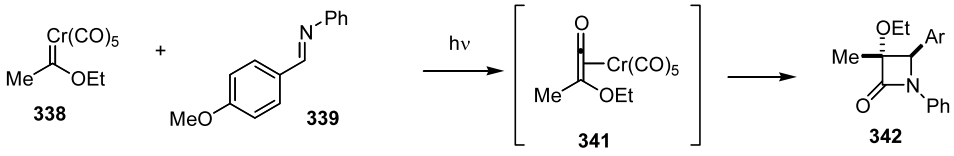
Coupling of γ,δ-unsaturated carbene complexes (e.g. **306**, Scheme 45) with *o*-alkynylbenzaldehyde derivatives (e.g. **305**) led to the formation of steroid derivatives (e.g. **309**) in a single pot [407]. A mechanism involving generation of an isobenzofuran (**307**), followed by intramolecular Diels–Alder reaction and oxanorbornene ring opening was proposed. The reaction proceeded with a very high degree of relative asymmetric induction. Coupling of furan and thiophene analogs of **304** (e.g. **310**) led to the *o*-quinoidal-like pyrone ring systems **313** [408]. The products derived from **310** incorporate a molecule of CO relative to those derived from **304**. The differences for heteroaromatic carboxaldehyde substrates (e.g. **310**) relative to arene analogs (e.g. **304**) were attributed to the enhanced ring strain in the unobserved furan derivatives **315**. The reaction employing γ,δ-unsaturated carbene complexes led to the intramolecular Diels–Alder adducts **314**.

Coupling of Fischer carbene complexes with 2-alkynylstyrene (e.g. **316**, Scheme 46) or related 2-alkynylbiphenyl derivatives was reported [409]. In both cases, a vinylketene intermediate (e.g. **318**) was expected to cyclize to provide enyne-derived benzannulation products (e.g. **321** or **322**), however this was never more than a minor reaction pathway. In all cases, reaction with phenylcarbene complex **263** led to a Dötz benzannulation product (e.g. **319**). Reactions with methylcarbene complex **311** proceeded primarily through C–H activation and resulted in cyclopentenone derivatives (e.g. **320**). The same cyclopentenone derivatives were produced in higher yield using the cyclopropylcarbene complex **317**.

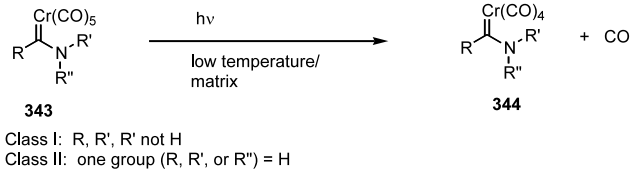
Treatment of alkyne–carbene complexes (e.g. **323**, Scheme 47) with dihydronicotine (**324**) led to the bicyclic derivatives (e.g. **326**) with a moderate degree of enantioselectivity [410]. This process incorporates three of the carbon monoxide molecules originating from chromium hexacarbonyl. A mechanism was proposed involving hydride addition, followed by CO insertion (affording acylate **325**), alkyne insertion, and a second CO insertion, followed by intramolecular attack of the ketone on the metal acyl.



Scheme 48.

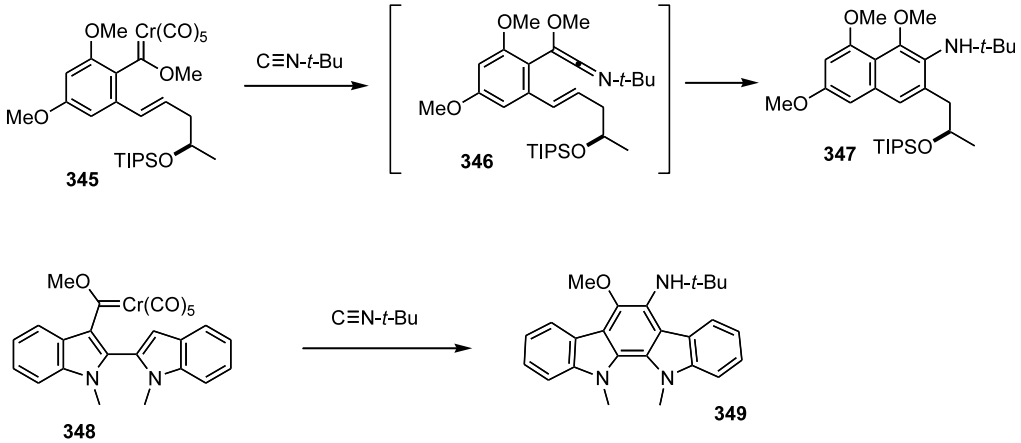


Scheme 49.



Scheme 50.

The coupling of 1-alkynyl cyclic alcohols (e.g. **327**, **331**, Scheme 48) with carbene complexes was reported [411]. Alkynols derived from cyclobutenediones (e.g. **327**) underwent clean ring expansion to afford 2-alkenyl-4-cyclopenten-1,3-dione derivatives (e.g. **330**). Less strained analogs (e.g. **331**) generally did not



Scheme 51.

undergo a ring expansion reaction upon treatment with chromium carbene complexes, however treatment with molybdenum carbene complexes (e.g. **332**) did result in ring expansion products (e.g. **337**). A mechanism involving pinacol-like ring expansion from vinylcarbene complex intermediates (e.g. **328**, **333**) was proposed.

2.3.3.6. Photolysis reactions of Group VI metal–carbene complexes and conversion of carbene complexes to ketenes or ketimines. Several publications concerning the formation of chromium ketene complexes (e.g. **341**, Scheme 49) through photolysis of Fischer carbene–chromium complexes appeared in 2001 [412]. The coupling of chromium carbene-derived ketenes and imines generally affords β-lactam derivatives (e.g. **342**). The photolytic coupling of imines with carbene complexes that feature the podocarpane ring system (e.g. complex **248** in Scheme 34) was also reported [413]. Ferrocenyl-substituted β-lactams were produced through photolytic coupling of carbene complexes and imines derived from ferrocenecarboxaldehyde [414].

The photolysis of various aminocarbene–chromium complexes in a matrix at low temperature was reported [415]. Complexes were divided into two classes of general structures **343** (Scheme 50). A ketene intermediate was not observed for any of the photolyses; CO loss was the only photo process observed. Class II complexes were reactive to nitrogen, ethylene, or CO present in the matrix, whereas Class I complexes did not couple with these species. The reactivity differences were attributed to blocking of a face by the more sterically bulky intermediate in the tetracarbonyl complex **344**.

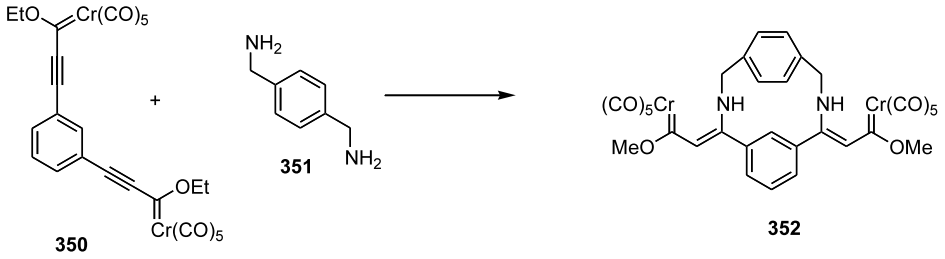
Related ketimine complexes (e.g. **346**, Scheme 51) can be produced through treatment of Fischer carbene complexes with isocyanides. Treatment of carbene complex **345** with *t*-butyl isocyanide led to aminonaphthalene derivative **347** [416]. This reaction proceeds via conversion to ketimine **346**, which cyclizes to afford the observed product. This reaction is a key step in the synthesis of calphostin derivatives. Indolocarbene complexes (e.g. **348**) were prepared and either treated with isocyanides or subjected to photolysis [417]. Upon treatment with *t*-butyl isocyanide, ketimine generation and cyclization occurred to afford arylamine derivative **349**. The photochemically generated ketene complex underwent a similar cyclization to afford the analogous phenol derivative.

2.3.3.7. Reactions occurring at the conjugated C–C π-bond of α,β-unsaturated Group VI metal–carbene complexes. Numerous reaction processes were reported in 2001 where a carbene complex activates a π-bond for nucleophilic addition or cycloaddition reactions (i.e. the carbene complex is a surrogate for an "activated ester").

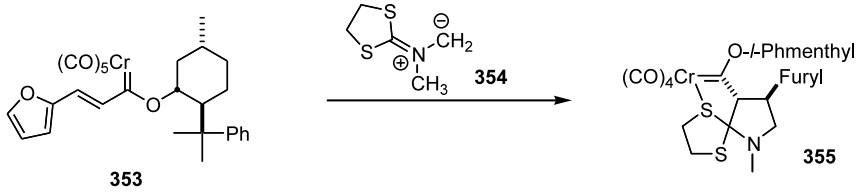
Various meta cyclophane derivatives (e.g. **352**, Scheme 52) were formed through the double Michael addition of aromatic diamines (e.g. **351**) to bis(carbene) complexes (e.g. **350**) [418]. Addition of amines to simpler alkynyl aminocarbene complexes led to β-aminoalkenylcarbene complexes [419].

Highly diastereoselective 1,3-dipolar addition processes were observed in the reaction of α,β-unsaturated phenylmenthyloxycarbene complexes (e.g. **353**, Scheme 53) with azomethine ylides (e.g. **354**) [420]. The products readily undergo loss of a CO ligand to form a chelate complex with one of the sulfur atoms. This reaction was used as a key step in the enantioselective synthesis of rolipram.

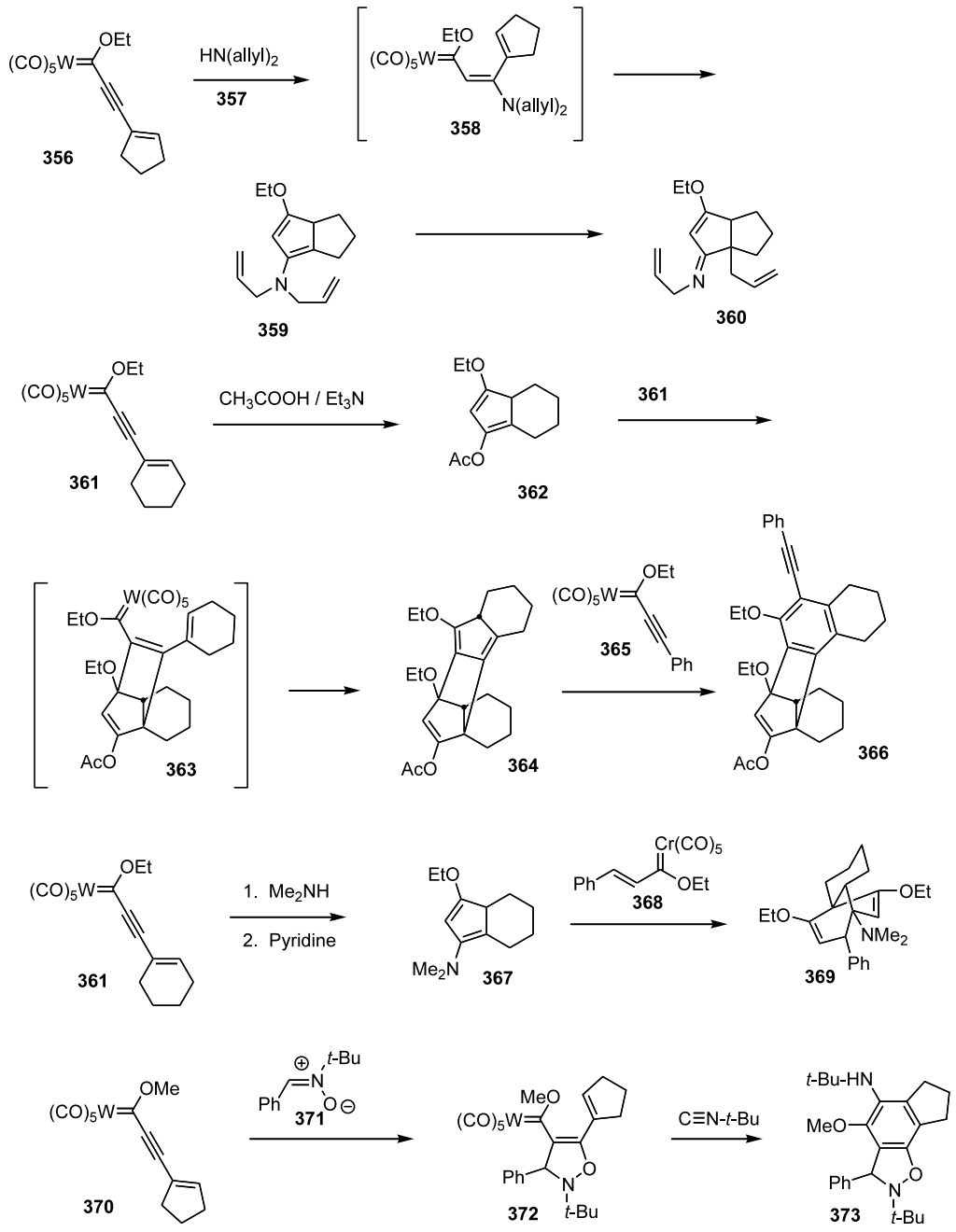
In numerous cases, either nucleophilic addition or cycloaddition to the triple bond of an enynylcarbene complex or arylalkynylcarbene complex is followed by a secondary cyclization process of the resulting α,β,γ,δ-unsaturated carbene complex (often referred to as a 1-metallahexatriene); examples are depicted in Scheme 54.



Scheme 52.

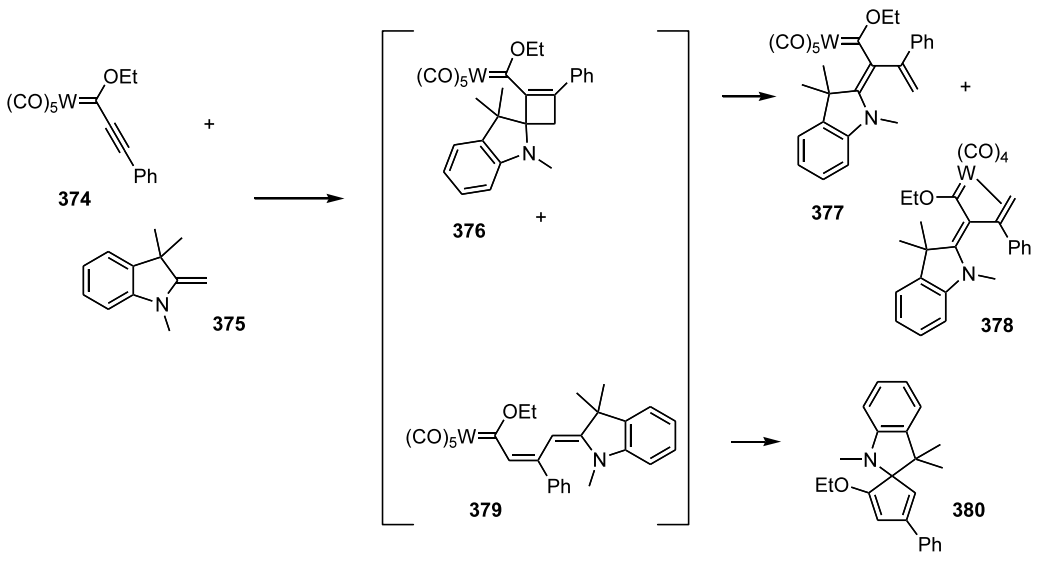


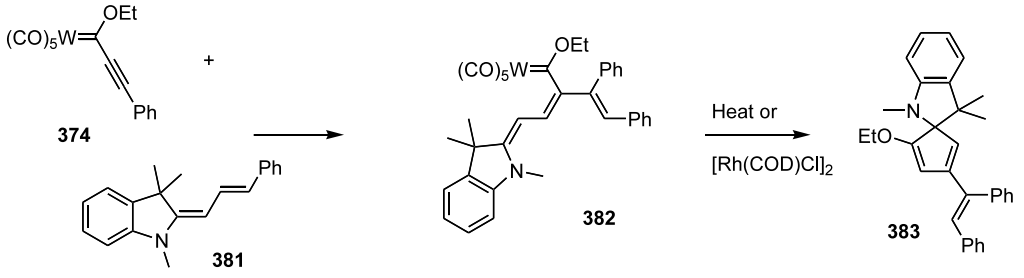
Scheme 53.



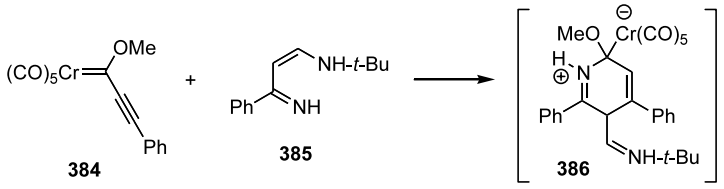
Scheme 54.

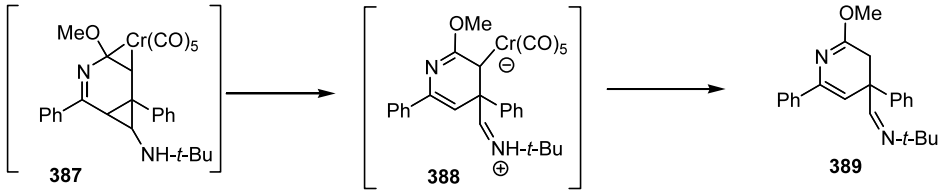
Cyclopentannulation reactions were reported for the coupling of enynylcarbene complexes (e.g. **356**, Scheme 54) with allylamines [421]. In these cases, after cyclopentannulation (forming **359**), an amino-Claisen rearrangement occurred to give the C-allylated products (e.g. **360**). Reaction of enynylcarbene complexes with β-aminoenones also proceeded via Michael addition followed by cyclization to the expected cyclopentadiene derivatives [422]. Addition of carboxylate anions to enynylcarbene complexes led to the expected cyclopentadiene derivatives (e.g. **362**), however these very rapidly underwent a Diels–Alder reaction with the starting carbene complex to afford compounds **364** after secondary cyclization [423]. A "trimeric" product **366** could also be isolated which likely occurs via cyclopropanation of **364** followed by ring opening and ethanol elimination. Thermolysis of β-amino-α,β,γ,δ-unsaturated carbene complexes (prepared by reaction of enynylcarbene complexes with amines) also afforded cyclopentannulation products, which underwent Diels–Alder reactions when thermolysis was performed in the presence of alkynes [424]. A similar process using electron-deficient dienophiles was also reported [425], however use of α,β-unsaturated carbene complexes in



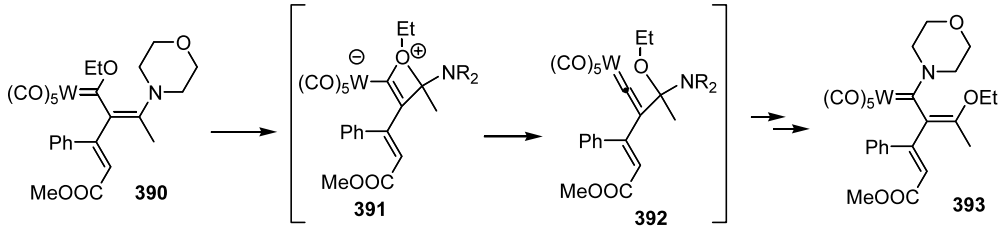


Scheme 55.

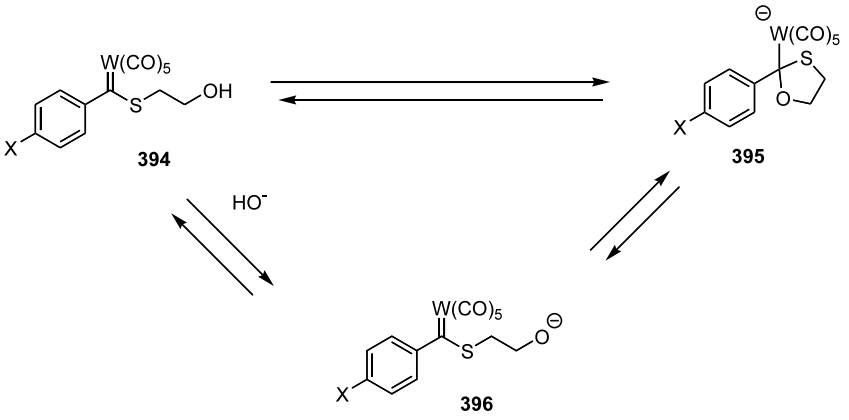




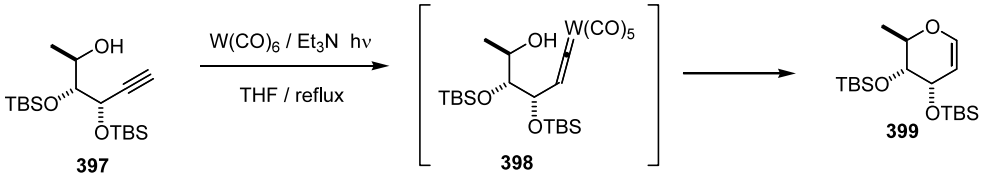
Scheme 56.



Scheme 57.



Scheme 58.



Scheme 59.

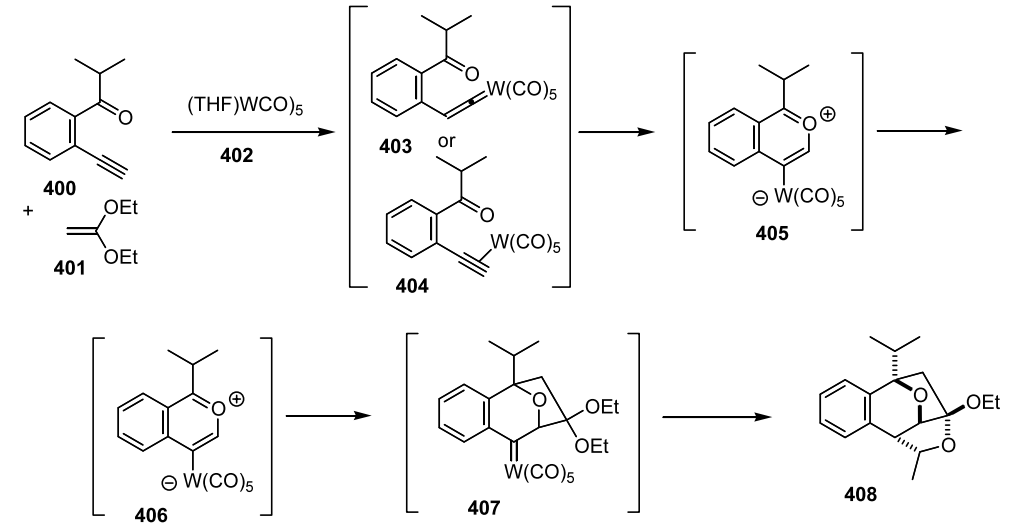
the final cycloaddition step led to [4+3] cycloaddition products (e.g. **369**). Tandem 1,3-dipolar addition of nitrones (e.g. **371**) to the triple bond of enynylcarbene complexes followed by reaction with isonitriles led to the formation of benzisoxazole derivatives (e.g. **373**) [426]. The tandem process can also be performed as a one-pot reaction. The reaction of alkynylcarbene–tungsten complexes with various enamines (e.g. **374**, Scheme 55) was examined [427]. The initial coupling proceeded via dual reaction pathways: (1) [2+2]-cycloaddition followed by ring opening of the resulting cyclobutene to afford dienylcarbene complexes (e.g. **377** and **378**), or (2) Michael addition followed by cyclization to afford a cyclopentadiene derivative (e.g. **380**). The reactions using dienamines (e.g. **381**) led to metallahexatrienes (e.g. **382**) through [2+2]-cycloaddition and ring opening, which also transformed to the corresponding cyclopentadienes (e.g. **383**) [428]. Conversion of the metallahexatriene to the cyclopentadiene could be accelerated by transforming the tungsten–carbene complex to a rhodium–carbene complex, which underwent a more rapid cyclization reaction.

The synthesis of dihydropyridine derivatives (e.g. **389**, Scheme 56) through the coupling of alkynylcarbene complexes (e.g. **384**) with β-amino-α,β-unsaturated imines (e.g. **385**) was reported [429]. The proposed mechanism for this transformation involves Michael addition of the enamine and subsequent proton transfer, followed by addition of the imine nitrogen to the carbene carbon to afford heterocyclic intermediate **386**. A 1,2-shift of the metal and nucleophilic addition to the imine leads to bicyclic compound **387**, which undergoes ring opening to afford iminium salt **388**. Protonation of the carbon–metal bond then affords the observed product.

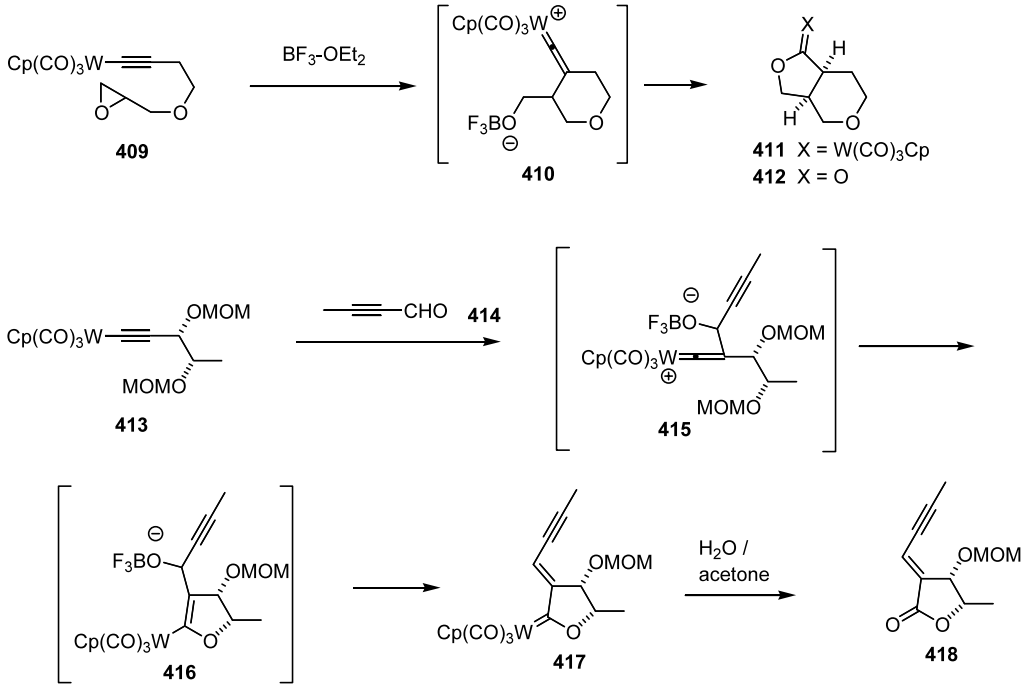
The isomerization of β-amino alkoxycarbene complexes (e.g. **390**, Scheme 57) to β-alkoxy aminocarbene complexes (e.g. **393**) was reported [430]. This reaction was unique to morpholino complexes. A mechanism involving nucleophilic addition of the carbene oxygen, resulting in intermediate **391**, followed by conversion to the vinylidene aminal **392**, followed by nucleophilic addition of nitrogen to the carbene carbon and ring opening was proposed.

2.3.3.8. Physical organic chemistry of Group VI Fischer carbene complexes. Kinetic and thermodynamic values for the base-induced cyclization of thiocarbene complexes of general structure **394** (Scheme 58) were determined [431]. The favored mechanism is that depicted in Scheme 58, involving reversible deprotonation of the alcohol followed by cyclization. Electron-withdrawing groups lead to an enhancement in the portion of **395** at equilibrium, however the carbene complex is the major species at equilibrium in all cases. The observed electronic effect has been attributed to destabilization of the carbene complex by electron withdrawing X groups.

2.3.3.9. Synthesis and reactivity of Group VI metal–vinylidene complexes, and reactions that involve vinylidene–metal complexes as intermediates. The cyclization of hydroxy acetylenes (e.g. **397**, Scheme 59) by tungsten pentacarbonyl sources led to glycal derivatives



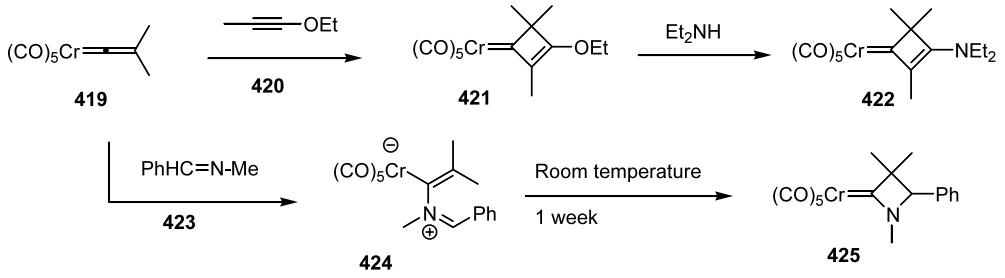
Scheme 60.



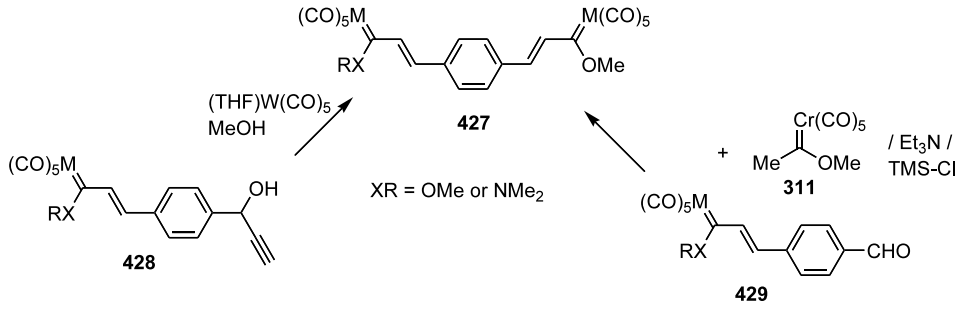
Scheme 61.

(e.g. **399**) in high yield [432]. The key step in this transformation is coupling of the terminal alkyne with the coordinatively unsaturated tungsten source to provide tungsten–vinylidene intermediate **398**. The combined thermal/photochemical conditions led to the products in considerably higher yield than room temperature photolysis. A repetitive version of this reaction was employed for the synthesis of the oligosaccharide portion of digitalis [433].

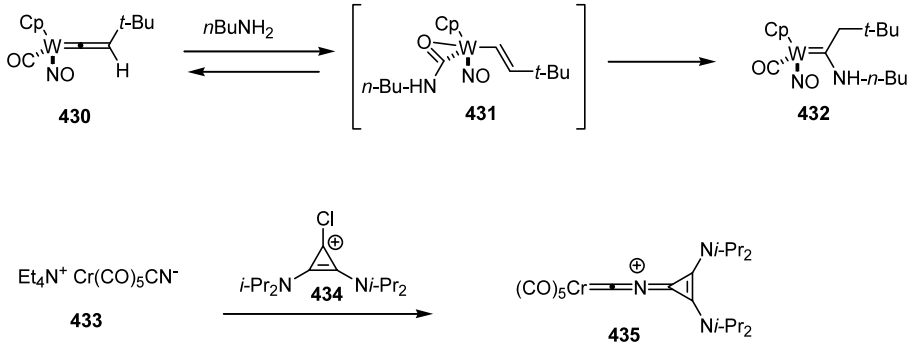
The coupling of 2-ethynylphenylketone derivative **400** (Scheme 60) with ketene acetals in the presence of $(THF)W(CO)_5$ was reported [434]. This usual coupling, resulting in ketal **408**, was proposed to proceed through formation of a vinylidene (**403**) and rearrangement to pyrylium cation derivative **405**. The conversion of **400** to **405** is reminiscent of additions of nucleophiles to η^2-alkyne complexes (e.g. **404**). Cycloaddition of the ketene acetal then affords the cyclic carbene complex intermediate **407**, which undergoes an intramolecular C–H insertion to afford the product. The analogous reaction employing 2-ethynylacetophenone (isopropyl group of **400** replaced by methyl) afforded only an alkyne hydration product. Capture of similar vinylidene intermediates through intramolecular reaction with a silyl



Scheme 62.



Scheme 63.

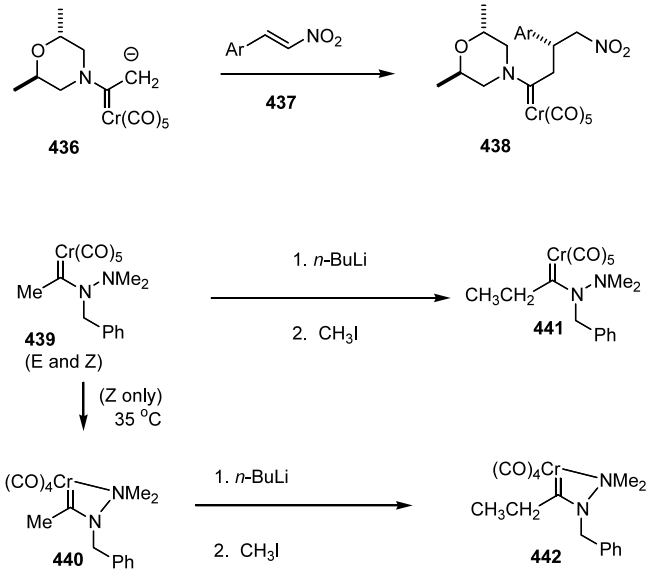


Scheme 64.

enol ether was also reported [435]. Products derived from vinylidene or η^2-alkyne–tungsten complex intermediates were also obtained in these reactions.

The intramolecular coupling of alkynyltungsten complexes (e.g. **409**, Scheme 61) with epoxides was reported [436]. Reaction of tungsten complex **409** with boron trifluoride etherate led to the lactone derivative **412**. Reaction of the alkynyltungsten species with the activated epoxide affords a vinylidene intermediate **410**, which then is attacked by the alkoxide to afford a cyclic carbene complex **411**. Oxidation then provides the lactone derivative. Similar tungsten–vinylidene complexes could also be generated from the coupling of alkynyltungsten complexes with aldehydes in the presence of Lewis acids. Reaction of complex **413** with acetylenic aldehydes led after oxidation to alkylidenefuranones (e.g. **418**) [437]. Formation of the vinylidene, followed by intramolecular attack of an alkoxide on the vinylidene, followed by loss of water affords the alkenylcarbene complex **417**. Treatment with water and acetone leads to the corresponding lactone. A mechanistically similar process was utilized in the intramolecular coupling of alkynyltungsten complexes with acyliminium salts [438].

Cyclobutenylidene complexes (e.g. **421**, Scheme 62) were produced in the coupling of chromium vinylidene complex **419** (generated in situ from reaction of chromium acylates with triflic anhydride) with ethoxypropyne (**420**) [439]. The resultant β-alkoxycarbene complexes react with secondary amines to afford the corresponding β-aminocarbene complexes (e.g. **422**). Coupling of this complex with imines (e.g. **423**) led to vinylchromium ylide complex **424**, which slowly cyclized to the aminocarbene complex **425** [440]. More hindered imines failed to undergo the transformation to the cyclic aminocarbene complex.

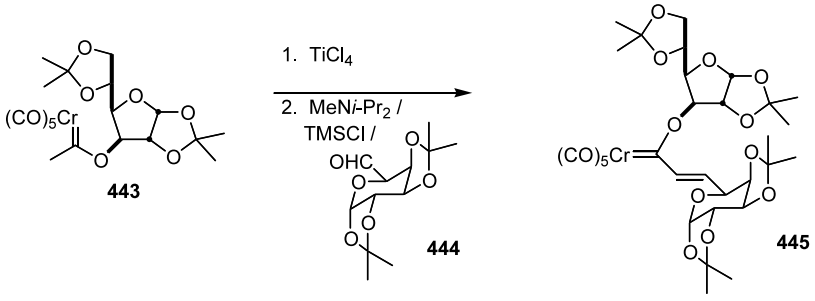


Scheme 65.

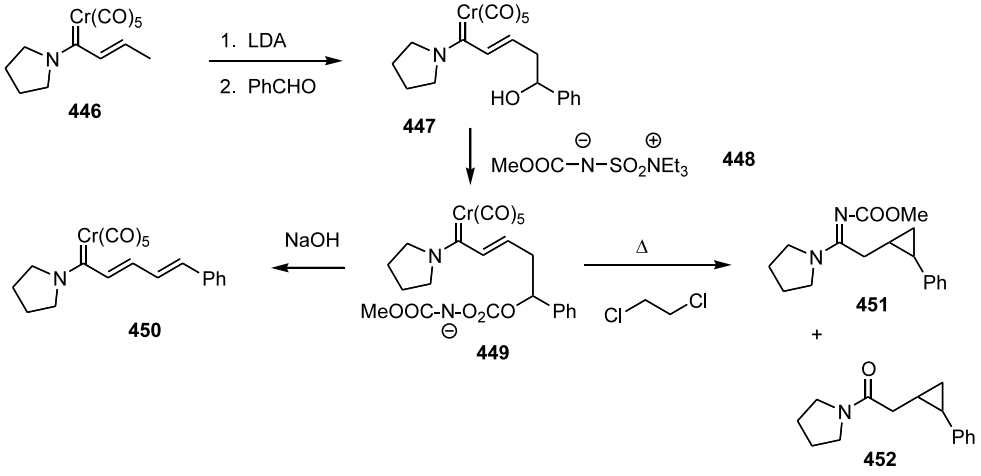
A series of bis(carbene) complexes of general structure **427** (Scheme 63) were prepared [441]. Reaction of propargyl alcohol–carbene complex **428** with metal pentacarbonyl sources in methanol led to the bis(carbene) complexes. Alternatively these carbene complexes could be prepared through reaction of carbene complex stabilized anions with aldehyde derivative **429**.

Other reaction processes were also reported for Group VI metal–vinylidene complexes. The reaction of tungsten vinylidene complex **430** (Scheme 64) with amines was studied [442]. The reaction initially affords a carbamoyl(alkenyl)tungsten complex **431** in equilibrium with the staring complex. The aminocarbene complex **432** was obtained when longer reaction times were employed. Photolysis of propyne in the presence of tungsten hexacarbonyl led to a mixture of the η^2-alkyne complex, the vinylidene complex, and the bimetallic complex $(CH_3)_2C{=}C[W(CO)_5]_2$ [443]. Chromium–azaallenylidene complex **435** was prepared through the coupling of chromium–cyanide complex **433** with cyclopropenyl cation **434** [444].

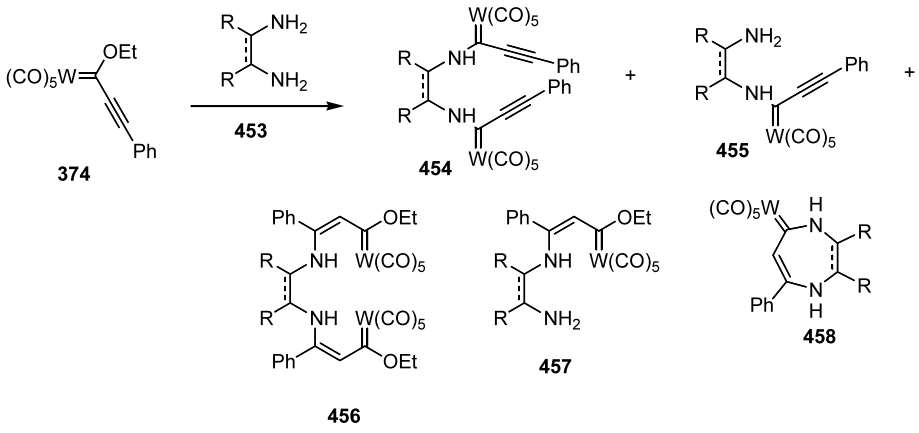
2.3.3.10. Reactions involving carbanions derived from Group VI metal–carbene complexes. Several examples of reactions that involve deprotonation of a Group VI Fischer carbene complex at the α-position, followed by reaction with an electrophile were reported in 2001. Reaction of chiral carbene complex-derived carbanions (e.g. **436**, Scheme 65) with nitroalkenes led to Michael addition products (e.g. **438**) [445]. The addition proceeded with a moderate degree of diastereoselectivity,



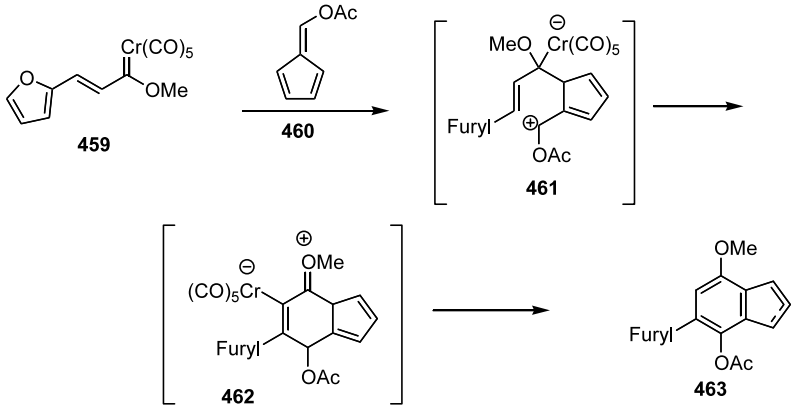
Scheme 66.



Scheme 67.



Scheme 68.

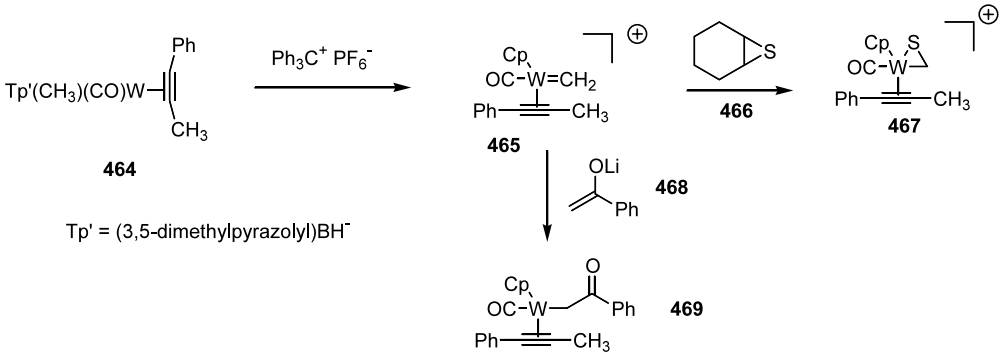


Scheme 69.

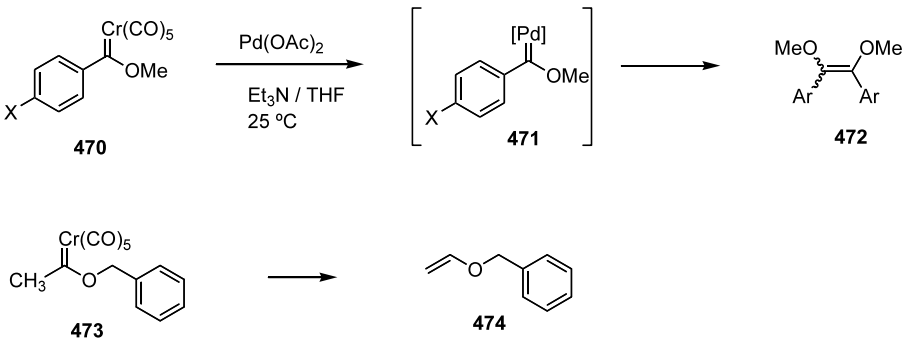
and was higher for nitrostyrene derivatives featuring an electron-withdrawing group and for Z nitrostyrenes. The alkylation reactions of hydrazinocarbene complexes (e.g. **439** and **440**) were explored [446]. Mild thermolysis of carbene complex **439** led to the corresponding chelated carbene complex **440**. Both complexes were readily protonated by *n*-butyllithium and subsequent reactions with alkyl halides, epoxides, aldehydes and enones (Michael addition) were reported for the carbanions. Derivatives of both complexes were air-oxidized to afford the corresponding amides.

Carbene complex derived carbanions were utilized in aldol-like processes. Carbene complex-linked carbohydrate derivatives (e.g. **445**, Scheme 66) were prepared through the coupling of carbanions derived from carbohydrate-containing carbene complexes (e.g. **443**) with carbohydrate–aldehydes (e.g. **444**) [447]. Related couplings using pyran-containing aldehydes and simple methylcarbene complexes led to aldol-like products (i.e. α,β-unsaturated carbene complexes) [448].

The base-induced coupling of aldehydes with α,β-unsaturated aminocarbene complexes (e.g. **446**, Scheme



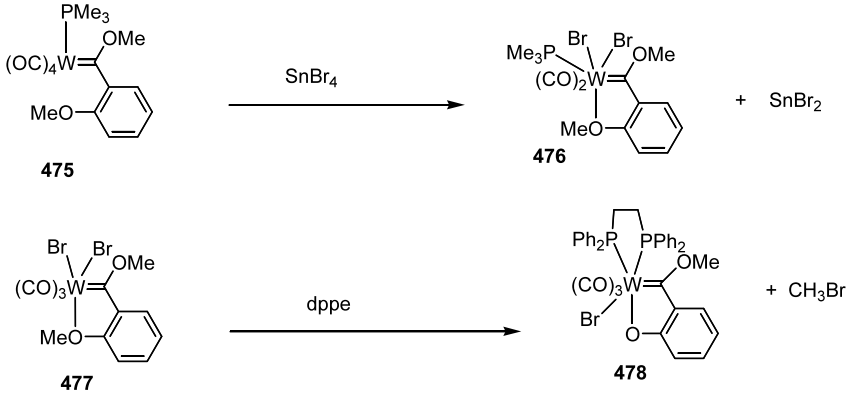
Scheme 70.



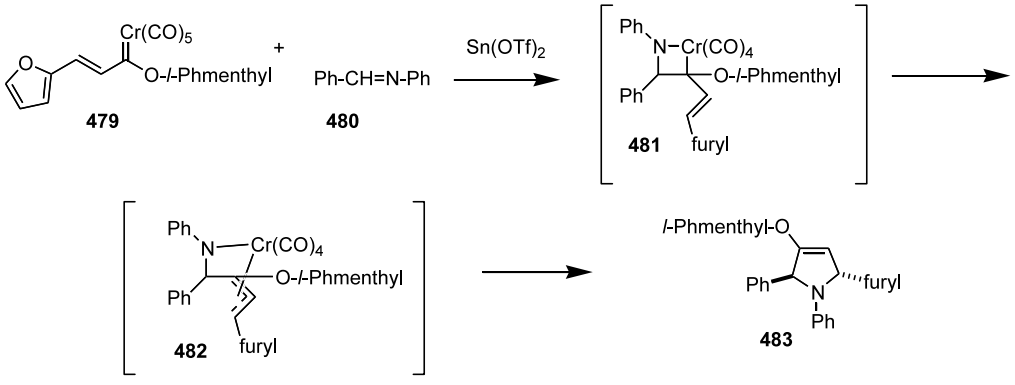
Scheme 71.

67) was reported [449]. The reaction affords δ-alkoxy-α,β-unsaturated carbene complexes (e.g. **447**) through deprotonation at the γ-position followed by coupling with the aldehyde at the γ-position. Attempted dehydration using Burgess reagent (**448**) was also reported. Coupling of δ-hydroxycarbene complexes with the reagent afforded the sulfonate ester (e.g. **449**), which underwent conversion to the α,β,γ,δ-unsaturated carbene complex (e.g. **450**) upon treatment with sodium hydroxide. An unusual cyclopropanation reaction was observed upon thermolysis of the sulfonate ester. Addition of the sulfonate nitrogen to the carbene carbon followed by simultaneous 1,2-shift of chromium and intramolecular displacement of the sulfonate ester led to a mixture of the imine (e.g. **451**) and the corresponding hydrolysis product (e.g. **452**).

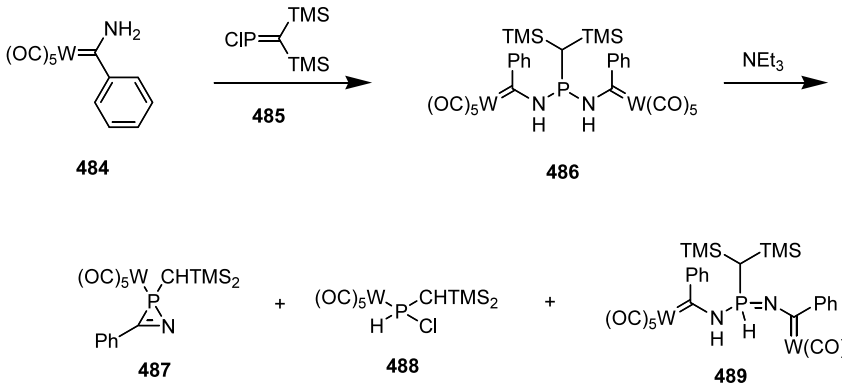
2.3.3.11. Reactions involving the addition of nucleophiles to the carbene carbon. The reaction of various primary diamines of general structure **453** (Scheme 68) with alkynylcarbene tungsten and chromium complexes was reported [450]. At −78 °C, mostly the 1,2-addition products (e.g. **454** and **455**) were observed, however Michael addition products (e.g. **456** and **457**) were predominant when the reaction was conducted at room temperature. The reaction with 1,2-diaminoben-



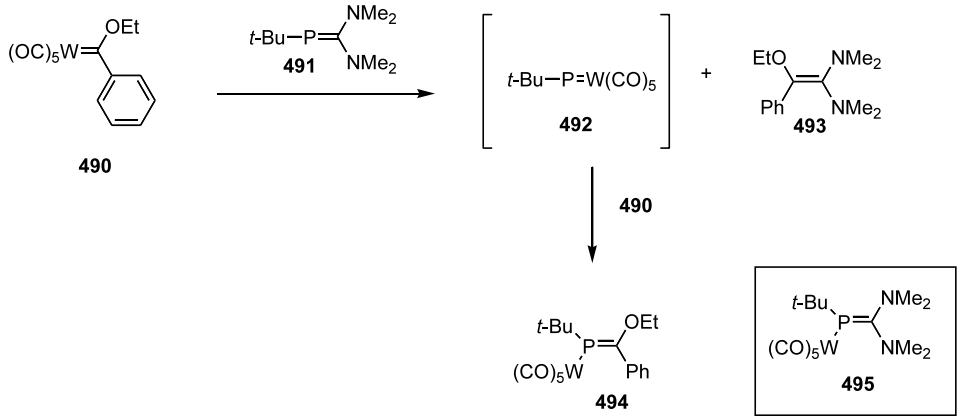
Scheme 72.



Scheme 73.



Scheme 74.



Scheme 75.

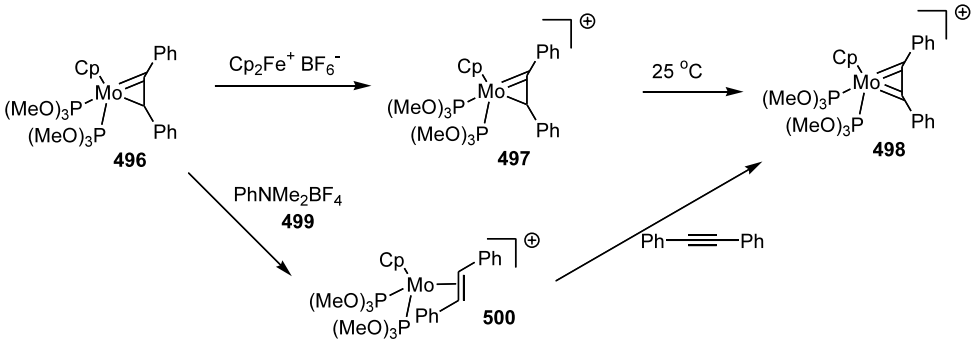
zene led to a mixture of the di-Michael product (**456**) and the monoaddition product **457**. The reaction of alkoxycarbene–tungsten complexes with various amino acid derivatives was reported [451], which resulted in aminocarbene complexes. Reaction of carbene complexes with bovine serum albumin resulted predominantly in carbene complex derivatives of the lysine residues.

A net [6+3]-cycloaddition process was observed in the coupling of α,β-unsaturated chromium carbene complexes (e.g. **459**, Scheme 69) with fulvenes (e.g. **460**) [452]. In this reaction, a mechanism involving electrophilic attack by the carbene complex at the 2-carbon of the fulvene, affording intermediate **461**, followed by simultaneous 1,3-shift of chromium and nucleophilic attack at the exocyclic carbon of the delocalized cation, followed by aromatization leads to the cycloaddition product **463**. Compound **463** was obtained as a mixture of alkene regioisomers.

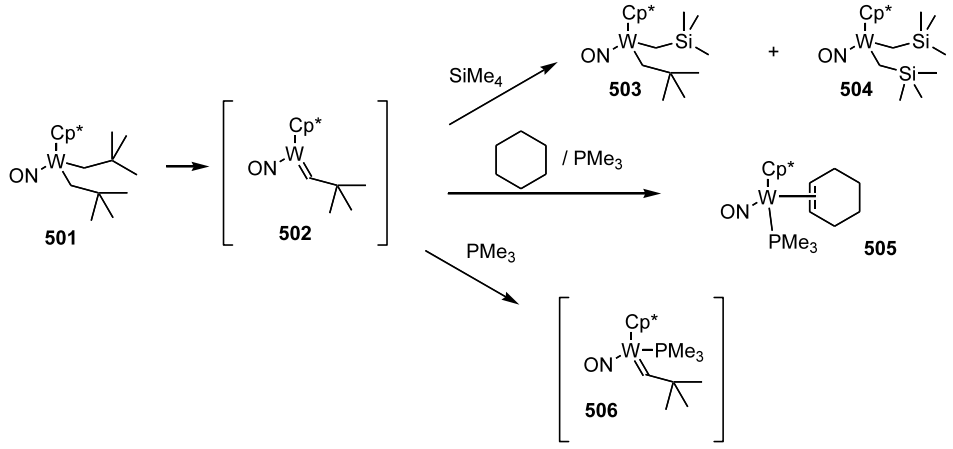
Cationic tungsten–carbene complexes **465** (Scheme 70) were generated by hydride abstraction from neutral methyltungsten complex **464** [453]. Reaction with various nucleophiles (e.g. enolate **468**) led to the neutral alkyltungsten complex (e.g. **469**). Reaction with cyclohexene sulfide (**466**) led to the η^2-thioformaldehyde complex **467**.

2.3.3.12. Other reactions of Group VI metal–carbene complexes. The reaction of Fischer carbene–chromium complexes with palladium (II) acetate was investigated (Scheme 71) [454]. Carbene dimerization (**470**→**472**) was the major reaction pathway for (alkoxy)arylcarbene complexes; both inter- and intramolecular versions of this reaction were demonstrated. Alkylcarbene complexes (e.g. **473**) were transformed to enol ethers (e.g. **474**). (Amino)arylcarbene complexes coupled with electron-deficient alkenes to provide carbonyl anion addition products. In all of these processes, a mechanism involving conversion of the chromium carbene complex to a palladium–carbene complex (e.g. **471**) was proposed.

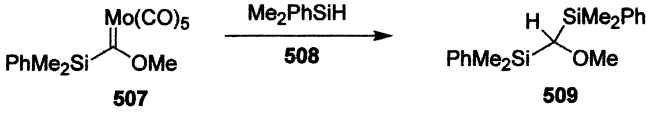
Reaction of tungsten complex **475** with tin(IV) halides led to the heptacoordinate tungsten(II) carbene complexes (e.g. **476**, Scheme 72) [455]. The analogous pentacarbonyl derivative did not undergo this reaction. The authors suggest that a high lying HOMO is required for the halogen addition process. Reaction of related tricarbonyl analog **477** with diphosphines led to the



Scheme 76.



Scheme 77.



Scheme 78.

corresponding chelate diphosphine complexes (e.g. **478**) accompanied by a methyl halide [456].

The nonphotochemical reaction of imines with α,β-unsaturated carbene complexes (e.g. **479**, Scheme 73) in the presence of stannous triflate led to dihydropyrrole derivatives (e.g. **483**) [457]. A mechanism involving [2+2]-cycloaddition, followed by rearrangement of the σ-allyl complex (e.g. **481**) to the π-allyl complex (e.g. **482**), followed by reductive elimination was proposed. The reaction using the phenylmenthylcarbene complexes proceeded with a high degree of relative asymmetric induction.

The reactions of aminocarbene–tungsten complexes (e.g. **484**, Scheme 74) with phosphorus electrophiles were reported [458]. The reaction of complex **484** with chlorophosphane **485** led initially to diaminophosphine–dicarbene derivative **486**, which could be isolated, accompanied by tungsten–azaphosphine complex **487**. Further treatment of **486** with triethylamine led to azaphosphirene complex **487**, phosphine complex **488**, and phosphimine carbene complex **489**. A phosphine-substituted analog of carbene complex **484** led only to analogs of complexes **487**.

The reaction of Fischer carbene complexes with phosphaalkenes (e.g. **491**, Scheme 75) was reported [459]. Coupling at −40 °C led to a mixture of phosphine complexes (e.g. **494** and **495**) and alkene **493**. A mechanism involving [2+2]-cycloaddition followed by

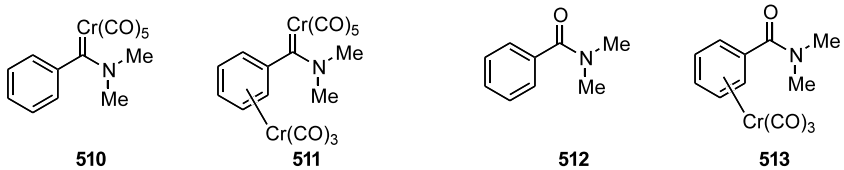
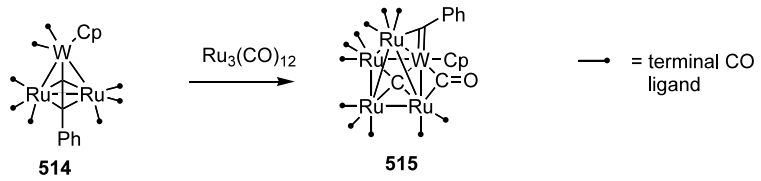


Fig. 12. Examination of methyl group chemical shift differences aminocarbene complexes and the corresponding amines.



Scheme 79.

retro-[2+2]-cycloaddition was proposed. Subsequent reaction of the resulting phosphanediyl complex **492** with the starting carbene complex leads to the other phosphaalkene complex **494**. These reaction processes were fairly general, however in one case a carbene dimerization product was the major product.

The oxidation of various η^2-alkenylmolybdenum complexes (e.g. **496**, Scheme 76) was examined [460]. Treatment with ferrocenium ion initially produced the simple one-electron oxidation product **497**, which then loses a hydrogen atom to afford the alkyne complex **498**. Reaction with dimethylaniline radical cation (**499**) led to stilbene complex **500**, which affords alkyne complex **498** upon treatment with diphenylacetylene. The simple one-electron oxidation product **497** was formed upon reaction with tris(pentafluorophenyl)borane at low temperature. Treatment of molybdenum–acetylene complexes that feature bridging phosphine ligands with ferrocenium cation led to the cationic η^2-alkenyl complexes [461].

Tungsten–carbene complexes (e.g. **502**, Scheme 77) were implicated as intermediates in alkyl group exchange reactions of dineopentyltungsten complex **501** [462] and in various C–H activation reactions of cyclohexane derivatives [463]. The reaction proceeds through α-elimination and reductive elimination to generate the carbene complex intermediate, followed by C–H oxidative addition. The mechanism was supported through deuterium labeling studies and isolation of carbene complex **506** when complex **501** is heated in the presence of trimethylphosphine. Efforts to form a stable carbene complex through deprotonation of the molybdenum analog of dialkyl complex **501** were unsuccessful [464].

The coupling of silylcarbene complexes (e.g. **507**, Scheme 78) with silicon hydrides was reported [465]. The reaction afforded disilylmethane derivatives (e.g. **509**) in moderate to excellent yield, depending upon the metal.

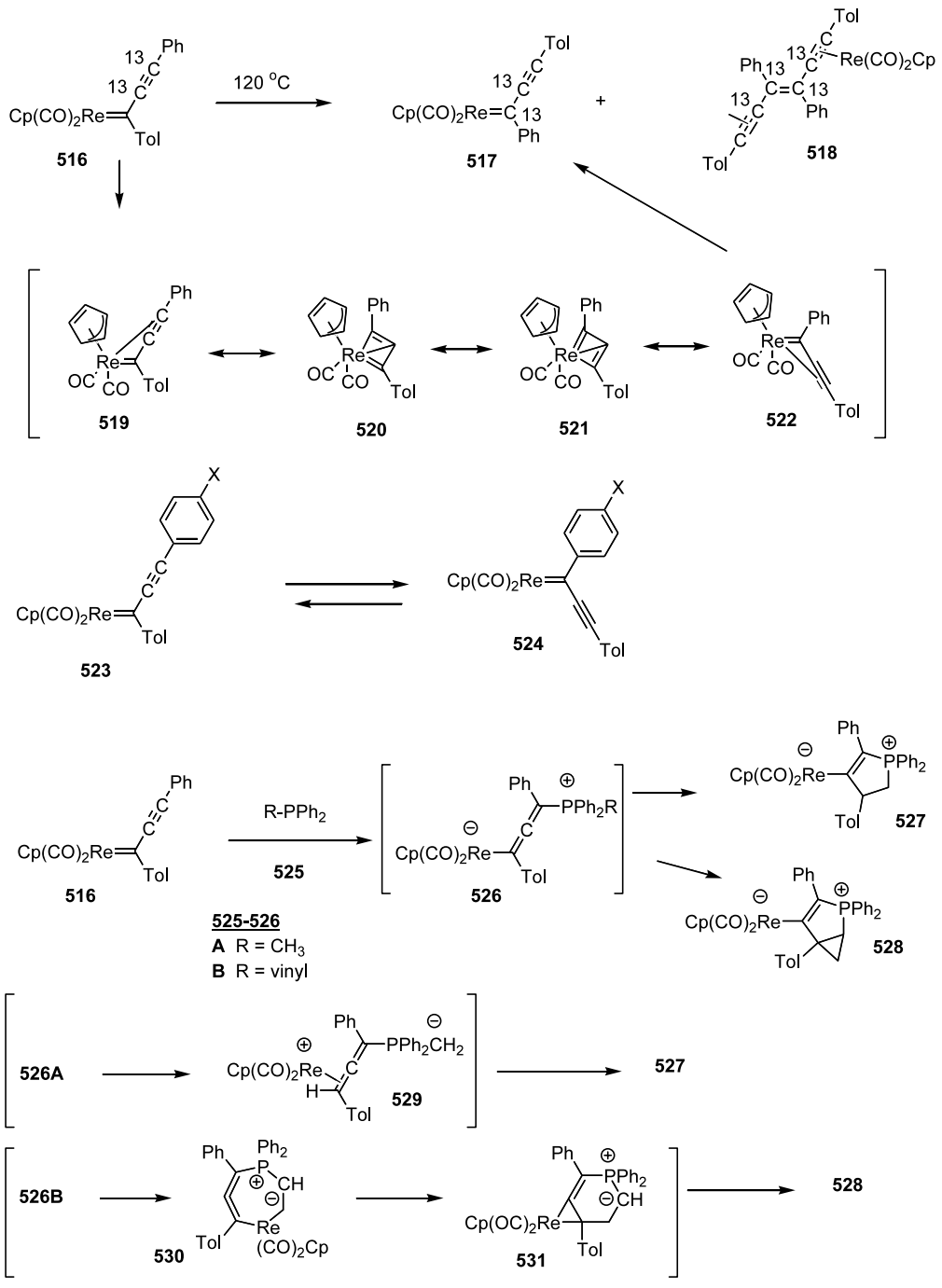
An NMR comparison of aryl aminocarbene–chromium complexes (e.g. **510**, Fig. 12), the analogous complexes where the aromatic ring is complexed to chromium (e.g. **511**), and the analogous amides was reported [466]. The difference in the chemical shift of the methyl groups was largest (about 1 ppm) for the uncomplexed carbene complex (**510**). The chemical shift differences were much lower for the corresponding amide (0.3 ppm) (**512**) and for the carbene complex featuring a coordinated aromatic ring (about 0.05 ppm) (**511**). The differences were attributed to a substantial decrease in electron density upon complexation. The same trend was observed for complexed and uncomplexed benzamide derivatives.

A polynuclear complex featuring a carbyne ligand bridged through tungsten and ruthenium (**515**, Scheme 79) was reported [467]. The complex is formed through thermolysis of the trinuclear complex **514** in the presence of $Ru_3(CO)_{12}$; a small amount of a higher nuclearity bridging carbyne complex was also reported. Treatment of the cluster with hydrogen and thiophenol was reported, however these reaction processes did not affect the carbyne ligand.

Additional processes invoking Group VI metal–carbene complexes were also reported. A thiocarbene–chromium complex was produced in low yield through the coupling of a dimeric chromium complex with a disulfide [468]. An attempt to isolate a chromium carbene complex through thermal decomposition of $Cp^*Cr(CH_2TMS)_2$ in the presence of various chelating ligands failed [469].

2.3.4. Group VII metal–carbene complexes

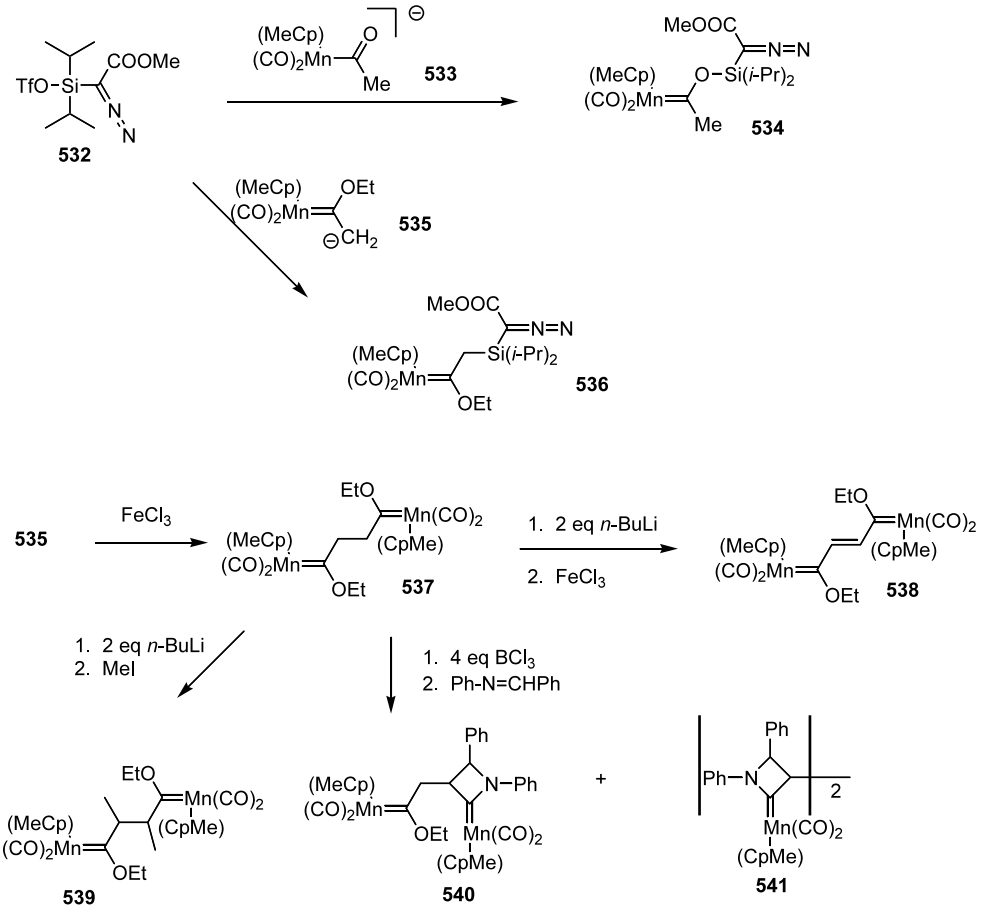
Thermolysis of alkynylcarbene–rhenium complex **516** (Scheme 80) led to dimeric enediyne complex **518** [470]. A slower thermal process involving a 1,3-shift of the carbene system was also observed, resulting in complex **517**. The electronic effect of this process was assessed by examining the equilibrium constant in a series of complexes of general structure **523/524**. Electron-withdrawing X groups lead to an increase in the proportion of **524** at equilibrium. A mechanism involving ring slippage and no CO-dissociation was proposed based on the powerful indenyl effect. Several resonance forms (**520**–**522**) can be written for initial ring slippage intermediate **519**. Cp* analogs of complex **516** were also investigated and found to undergo a similar reversible rearrangement [471]. Prolonged thermolysis led to the product from oxidative addition into one of the methyl C–H bonds. Reaction of carbene complex **516** with phosphines led to cyclic phosphorus ylide derivatives (e.g. **527**, **528**) [472]. Formation of these complexes occurs through Michael addition of phosphorus. In the case of the methylphosphine, proton transfer from intermediate **526A**, followed by intramolecular nucleophilic addition to rhenium–allene functionality in complex **529** leads to the cyclic product **527**.



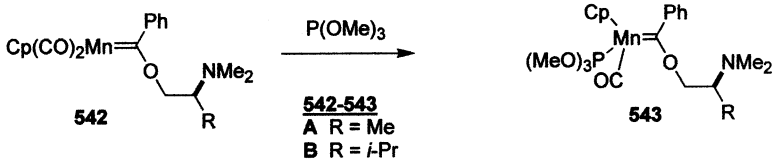
Scheme 80.

In the case of the vinylphosphine, nucleophilic addition of the rhenium anion functionality to the vinylphosphine of intermediate **526B**, followed by reductive elimination of rhenium, and intramolecular nucleophilic addition to the allene–rhenium functionality of complex **531** leads to the cyclopropane derivative. Deuterium labeling studies support this mechanism. Reaction of a manganese analog with $Co_2(CO)_8$ was also reported [473]. A related study is featured in the carbyne complex section (Scheme 136).

A variety of manganese– and tungsten–carbene complexes that feature α-silyl α-diazoester groups (e.g. **534**, **536**, Scheme 81) were prepared [474]. The manganese complexes were considerably more stable than the tungsten complexes. Both O-silyl (**534**) and C-silyl (**536**) manganese complex derivatives were prepared. Oxidative dimerization of manganese carbene-derived carbanions **535** was reported [475]. A variety of reaction processes were reported for the resulting dicarbene complex **537**. Double deprotonation followed by oxida-



Scheme 81.

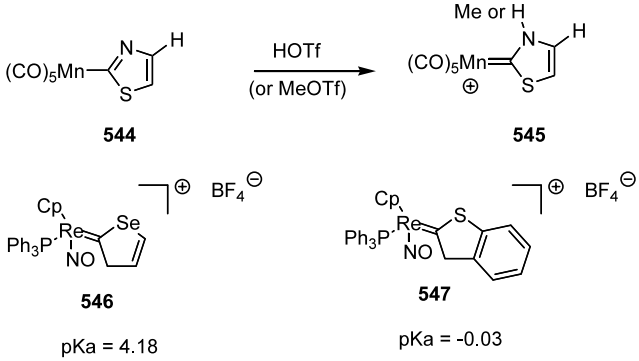


Scheme 82.

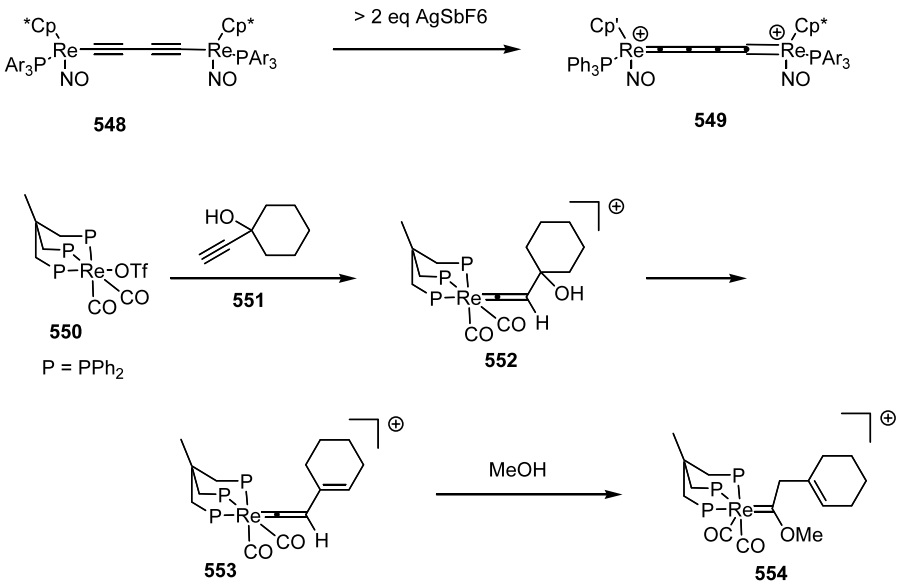
tion or alkylation led to dicarbene complexes **538** or **539**, respectively. Reaction with Lewis acids followed by imines led to cyclic aminocarbene–manganese complexes (e.g. **540**, **541**), presumably via the vinylidene intermediate. Reaction with Lewis acids led to compounds spectroscopically consistent with carbyne complexes, which afforded complexes **540** or **541** upon treatment with imines.

Ligand exchange studies for chiral manganese carbene complexes (e.g. **542**, Scheme 82) were reported [476]. The ligand exchange process was moderately diastereoselective for the formation of compound **543A**, however only one stereoisomer was observed with the isopropyl analog **543B**.

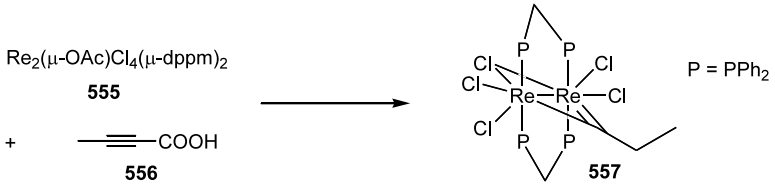
Several studies concerning the reversible protonation/deprotonation of cyclic Group VII carbene complexes were reported in 2001. Protonation or methylation of 2-thiazolylmanganese complexes (e.g. **544**, Scheme 83)



Scheme 83.



Scheme 84.



Scheme 85.

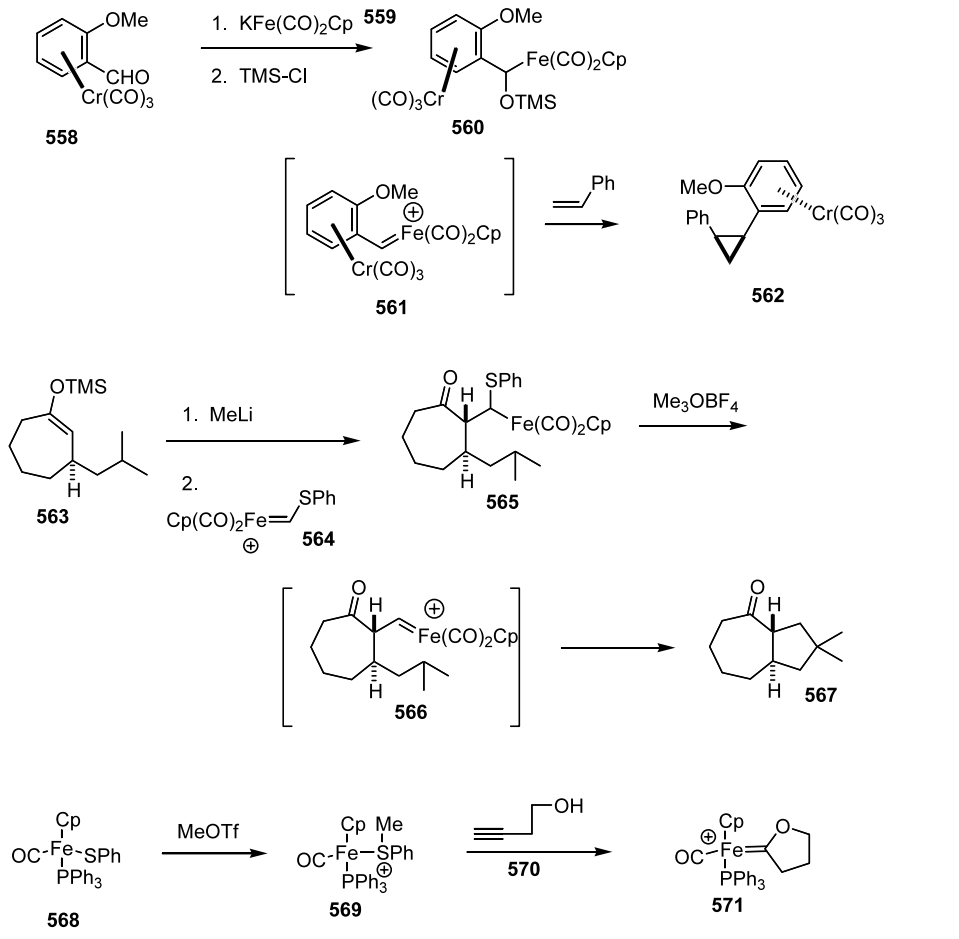
resulted in the synthesis of 2-thiazolyildene–manganese complexes (e.g. **545**) [477]. The acidity of several 546 and **547**) was determined [478]. The pK_a of these complexes was determined in 1:1 acetonitrile:-water.

Several examples of Group VII metal–cumulene complexes were reported in 2001 (Scheme 84). Oxidation of all carbon-bridged dirhenium complex **548** led to the dicationic cumulenylidene-bridged dirhenium complex **549** [479]. Rhenium vinylidene complexes (e.g. **552**, **553**) were generated from the reaction of rhenium triflate **550** with propargyl alcohol **551**, which eventually loses water to form alkenylvinylidene complex **553** [480]. The alkoxycarbene complex (**554**) was obtained if the reaction was performed in methanol, or if methanol was added to vinylidene complex **553**. An allenylidene complex was obtained when phenyl propargyl alcohol was employed.

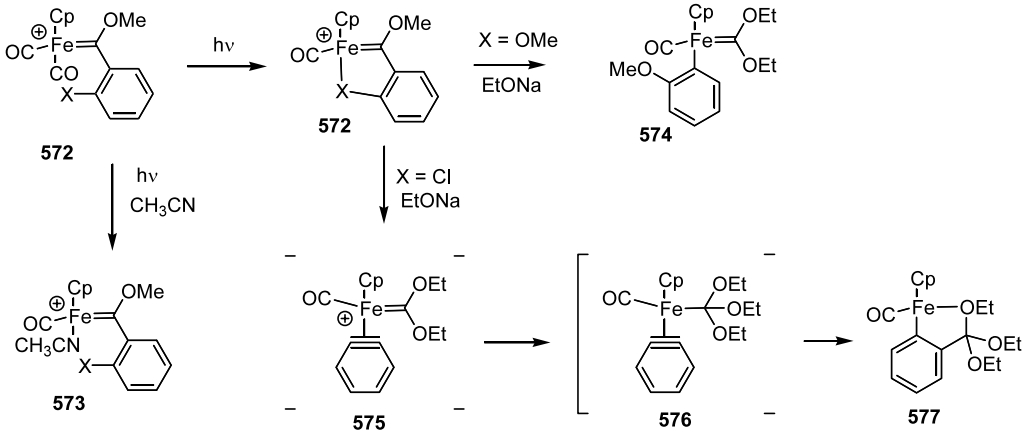
Other examples of Group VII metal carbene complexes were also reported. The formation of dirhenium-bridged carbyne complex (**557**, Scheme 85) from butynecarboxylate anion (**556**) and dirhenium complex **555** was reported [481]. A rhenium carbene complex was generated from low-temperature photolysis of methyltrioxorhenium [482].

2.3.5. Group VIII metal–carbene complexes

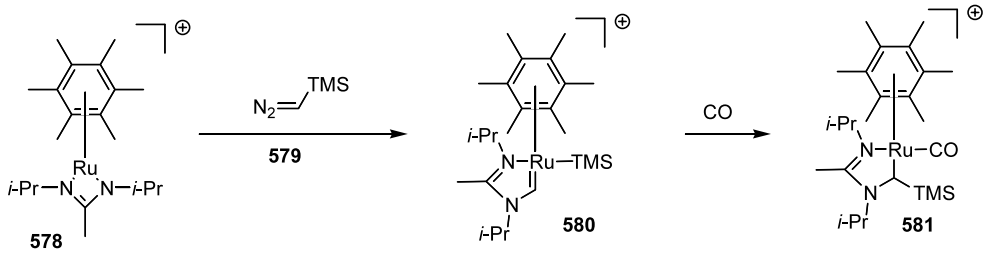
2.3.5.1. Cationic metal–carbene complexes that are not cumulenes. A homochiral iron–carbene complex (**561**, Scheme 86), generated in situ from a homochiral siloxyiron complex **560**, afforded chiral cyclopropane **562** with a high degree of diastereoselectivity [483]. The *cis* selectivity that is unique for styrene derivatives was attributed to π-stacking interaction. A variety of thiophenylalkyliron complexes of (e.g. **565**, Scheme 86) were prepared through the coupling of silyl enol ethers with iron carbene complex **564** [484]. Treatment of the thiophenylalkyliron complexes with a methylating agent leads to in situ generation of a cationic carbene complex (e.g. **566**), which subsequently undergoes intramolecular C–H insertion to afford bicyclic ketones (e.g. **567**). Synthesis of a variety of cationic cyclic carbene complexes (e.g. **571**) was reported using the reaction of thiophenyl–iron complex **568** with methyl triflate followed by reaction with an alkynol [485].



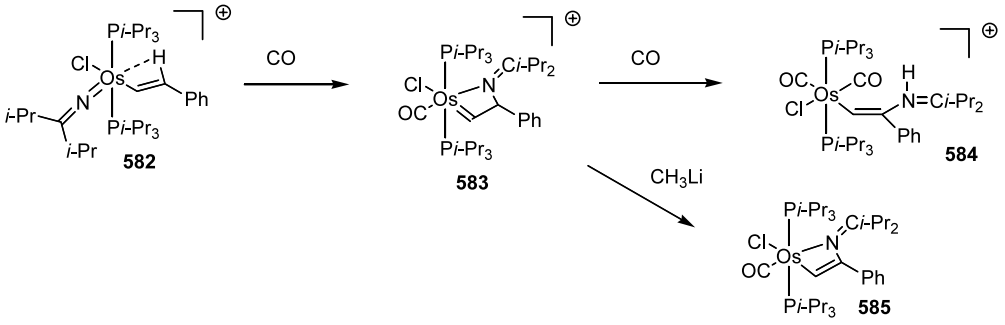
Scheme 86.



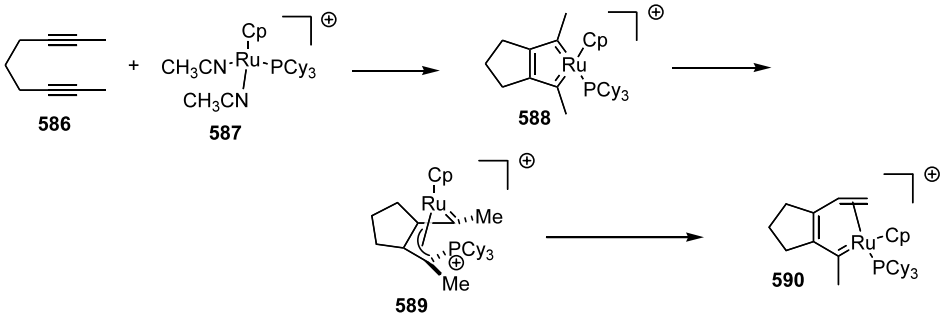
Scheme 87.



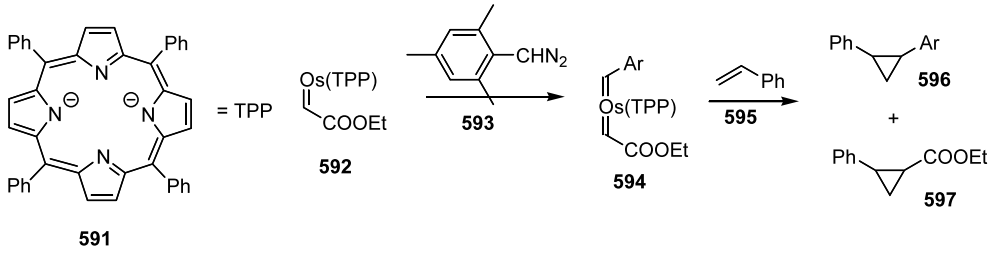
Scheme 88.



Scheme 89.



Scheme 90.



Scheme 91.

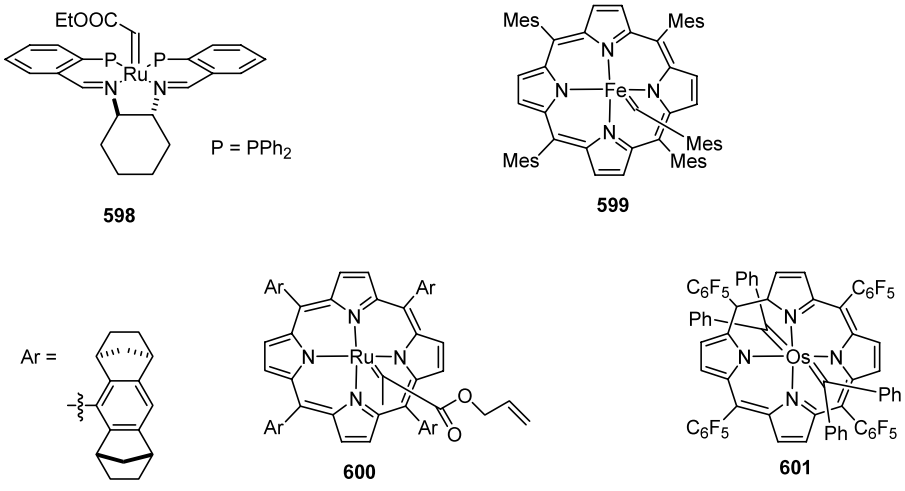
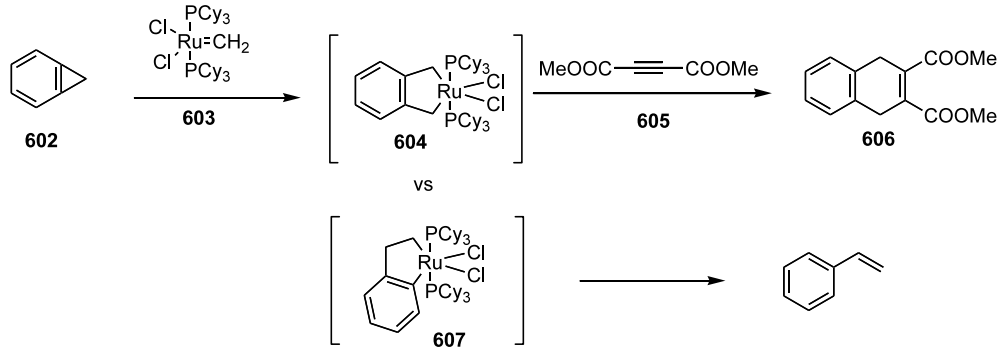


Fig. 13. Representative examples of Group VIII–metal carbene complexes prepared through coupling with diazo compounds.

Manganese nitrosyl analogs of complex **571** were also prepared using this reaction sequence. The reaction of cationic bridging carbyne–diiron complexes with a variety of sulfur nucleophiles led to the corresponding neutral bridging thiocarbene complexes [486].



Scheme 92.

A variety of cationic *o*-substituted arylcarbene–iron complexes (e.g. **572**, Scheme 87) were prepared and their photolysis reactions examined [487]. Photolysis led either to a chelate complex (e.g. **572**) or ligand substitution product (e.g. **573**), depending upon the X-substituent and the solvent. Reaction of anisylcarbene complexes (**572**, X = OMe) with alkoxides led to complexes featuring dialkoxycarbene and aryl ligands (e.g. **574**). Nucleophilic addition of alkoxide to the carbene carbon followed by aryl migration was proposed to account for formation of these products. A similar reaction using complex **572** (X = Cl) led to the *o*-(trialkoxymethylphenyl)iron complex **577**, possibly via benzyne complex intermediates (e.g. **575**, **576**).

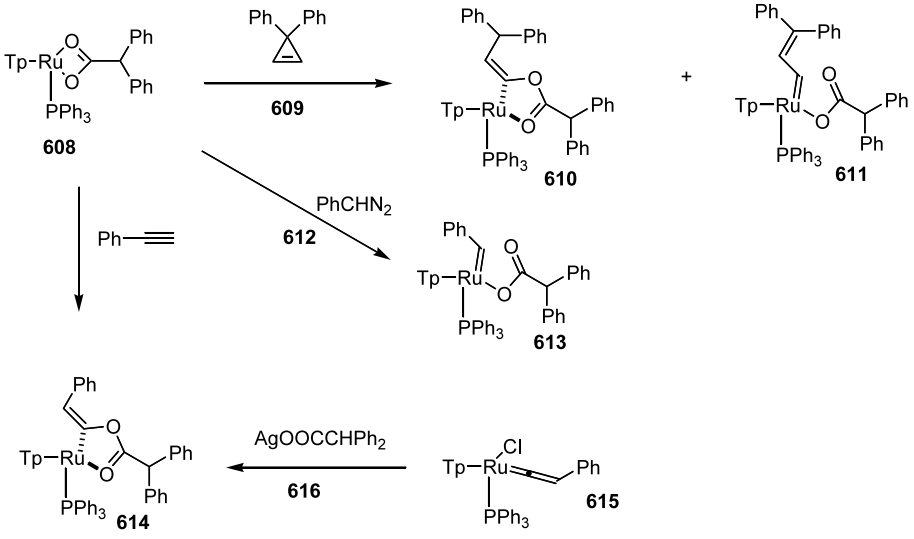
Cationic ruthenium–carbene complexes (e.g. **580**, Scheme 88) were prepared from the reaction of ruthenium complex **578** with trimethylsilyldiazomethane (**579**) [488]. Reaction with CO or isonitriles led to a corresponding trimethylsilylalkyl complex (e.g. **581**), which was retransformed back into complex **580** upon photolysis.

Reaction of cationic alkenyl azavinylidene osmium complex **582** (Scheme 89) with CO led to the corresponding azametallacyclic carbene complex **583** [489]. Reaction with additional CO led to alkenyl complex **584**. Deprotonation with methyllithium led to azametallacycle **585**.

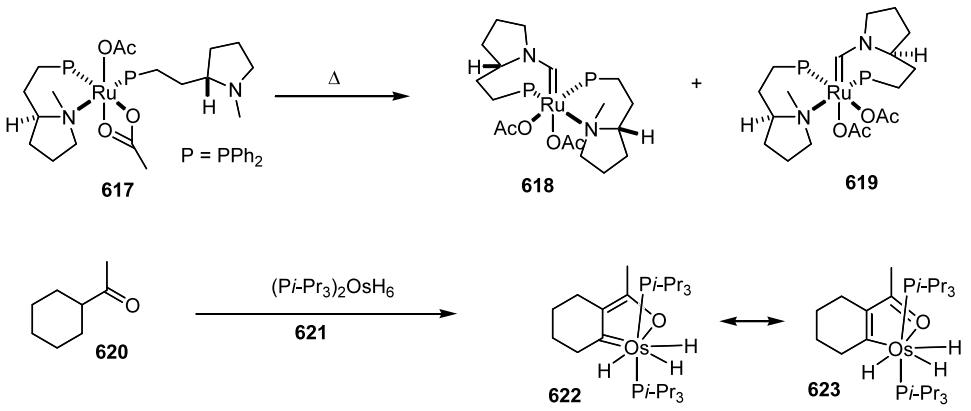
A dicarbene–ruthenium complex (e.g. **588**, Scheme 90) was generated from the coupling of ruthenium complex **587** with diynes spaced by 2–4 carbons (e.g. **586**) [490,491]. The unstable dicarbene complex transformed to the π-allyl–carbene complex (e.g. **589**), which rearranged to the α,β,γ,δ-unsaturated carbene complex **590** at room temperature. A similar process was observed in the coupling of Cp*(COD)RuCl with two equivalents of an alkyne [492]. Reaction with phosphines or phosphites led also to the π-allyl carbene complexes analogous to **589**. A related process involving ethynylferrocene was also reported [493].

Dicationic ruthenium carbene complexes were proposed as intermediates in the ruthenium-catalyzed dimerization of propargylic alcohols [494].

2.3.5.2. Neutral nonheteroatom-substituted metal–carbene complexes that are not cumulenes. Numerous additional examples of the synthesis and reactivity of



Scheme 93.



Scheme 94.

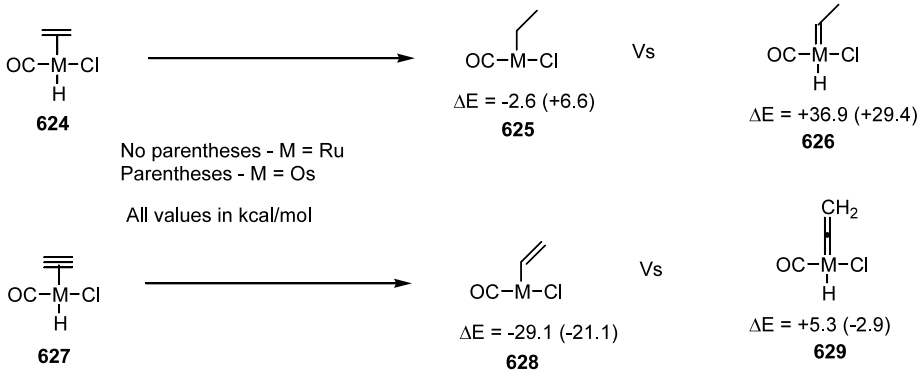
this class of compounds have been presented in the alkene metathesis section. The Grubbs and Nolan catalysts fall into this classification.

Reaction of osmium–porphyrin carbene complex **592** (Scheme 91) with aryldiazomethanes (e.g. **593**) led to a bis(carbene) complex (e.g. **594**) [495]. Carbene complex **592** also serves as a catalyst for the cyclopropanation of alkenes by diazo compounds. The reaction of complex **592** with styrene in the presence of one mole of aryldiazo compound led to a mixture of cyclopropanes (**596** and **597**) resulting from ethoxycarbonylcarbene and arylcarbene transfer.

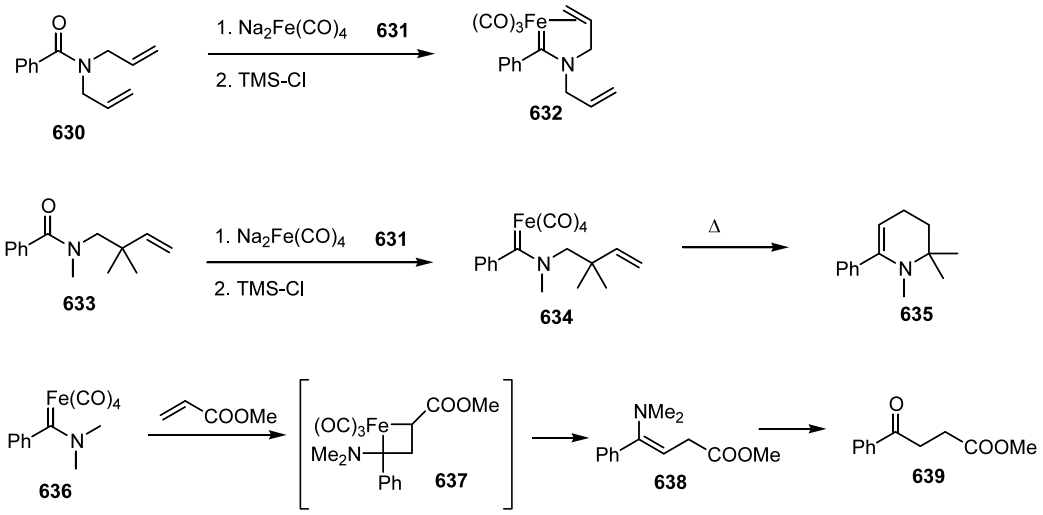
Several other papers appearing in 2001 reported on the preparation of Group VIII metal–carbene complexes directly from diazo compounds (Fig. 13). All the complexes in Fig. 13 were prepared as part of a study of metal-catalyzed cyclopropanation reactions using diazo compounds and alkenes. Examples include: (1) solution characterization of a ruthenium carbene complex derived from ethyl diazoacetate (**598**) [496]; (2) formation of an iron–porphyrin carbene complex (**599**) from mesityldiazomethane [497]; (3) formation of ruthenium–porphyrin carbene complexes (e.g. **600**) [498]; and (4) analogous studies using osmium porphyrin bis(carbene) complexes (e.g. **601**) [499].

Reaction of methylene–ruthenium complex **603** (Scheme 92) with benzocyclopropene (**602**) in the presence of dimethyl acetylenedicarboxylate (**605**) led to dihydronaphthalene derivative **606** [500]. A mechanism involving formation of ruthenaacyclopentane derivative **604**, followed by decomplexation to form *o*-xylylene, followed by Diels–Alder reaction was proposed. Formation of a trace amount of styrene was attributed to regioisomeric ruthenacyclopentane derivative **607**. The analogous reaction with the Tebbe reagent led to stable titanacyclopentane derivative analogous to **607**.

A variety of ruthenium–carbene complexes were formed from the reaction of ruthenium–carboxylate complex **608** (Scheme 93) with various organic substrates [501]. Reaction with 3,3-diphenylcyclopropene (**609**) led to a mixture of vinylcarbene complex **611** and enol ester complex **610**; the enol ester complex was transformed to the carbene complex upon photolysis or thermolysis. The phenylcarbene complex **613** was prepared from reaction of complex **608** with phenyldiazomethane (**612**). Enol ester complex **614** was prepared from reaction of complex **608** with phenylacetylene; the same compound was also prepared by reaction of the vinylidene–chloride complex **615** with the silver carboxylate.



Scheme 95.

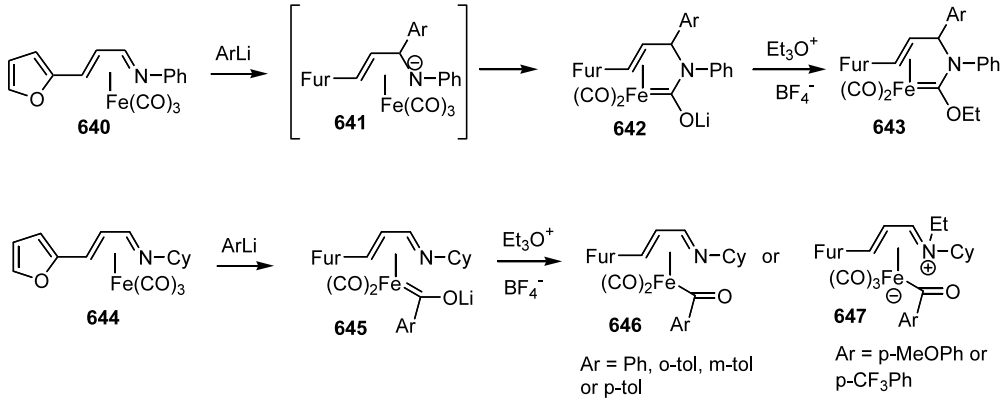


Scheme 96.

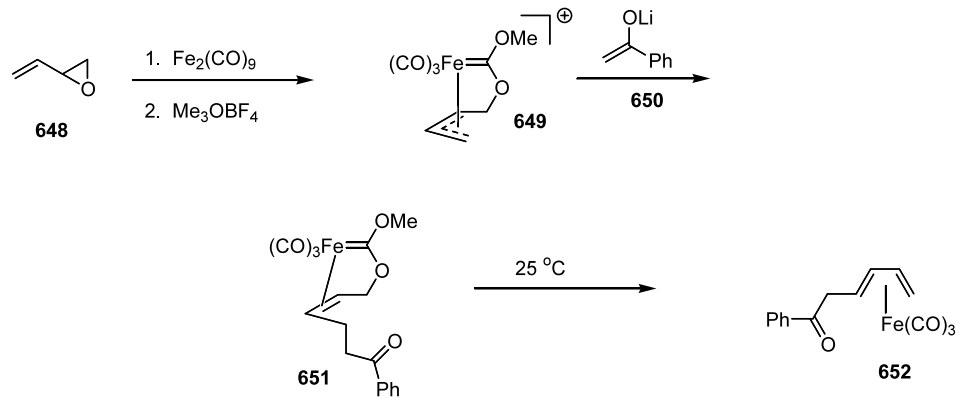
Formation of Group VIII metal–carbene complexes through C–H oxidative addition processes was reported in 2001. Enantiomeric ruthenium carbene complexes **618** and **619** (Scheme 94) were formed from complex **617** through intramolecular C–H oxidative addition followed by α-hydride elimination and dehydrogenation [502]. An osmium carbene complex (**622**) in resonance with a β-osma-enone structure (**623**) was formed in the unusual double C–H activation reaction of osmium–dihydride complex **621** with acetylcyclohexane (**620**) [503].

Other experimental studies of carbene complexes in this category include: (1) demonstration of various ligand substitution processes for ruthenium(II)–carbene complexes [504]; (2) formation of a cyclopropenylidene–iron complex from an iron–zirconate and diphenylcyclopropenone [505]; (3) formation of a triruthenium complex featuring a ruthenacyclopentadienyl ligand from a ruthenium cluster complex and various alkynes and diynes [506]; and (4) involvement of a bridging carbyne–diruthenium complex intermediate in the photochemical H–D exchanges between silicon hydrides and bridging dicarbene–diruthenium complexes [507].

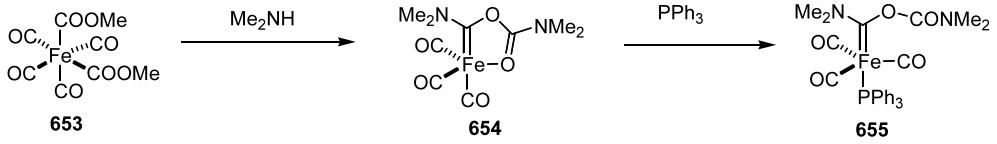
A density functional theory study of the formation of carbene complexes (e.g. **626**, Scheme 95) or vinylidene complexes (e.g. **629**) from coupling of ruthenium and osmium hydrides with ethylene or acetylene was reported [508]. Conversion of the ethylene complex **624** to the ethyl complex **625** was the most favorable pathway regardless of the metal, however conversion to the carbene complex **626** was less unfavorable if the metal was osmium. A similar trend was observed for analogous acetylene complex **627**. Formation of vinyl complex **628** was the more favored pathway for both metals. Formation of vinylidene complex **629** was exothermic for the osmium complex and endothermic for the ruthenium complex. A theoretical study of the formation of a ruthenium carbene complex [CH_3CH=$Ru(PH_3)_2Cl_2$] from coupling of a ruthenium dihydride complex [$RuH_2Cl_2(PH_3)_2$] with acetylene was conducted [509]. Two energetically reasonable pathways were identified for formation of the carbene complex. One



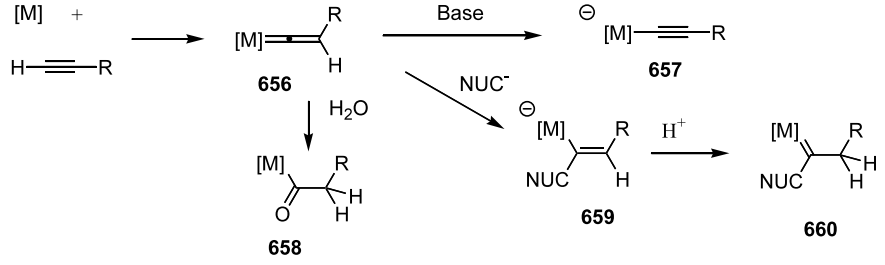
Scheme 97.



Scheme 98.



Scheme 99.



Scheme 100.

pathway involves complexation, alkyne insertion to form the η^2-vinyl complex, followed by reductive elimination of H and $-CH_2R$ to form the carbene complex. Another reasonable pathway involves reductive elimination of HCl, then alkyne insertion and protonation of the resulting vinylruthenium species.

A theoretical study of iron carbene complexes of general structure $X_2C{=}Fe(CO)_4$ (and species featuring other two-electron donor ligands in addition to carbenes) was reported [510]. The carbene complexes studied include the vinylidene ($=C{=}CH_2$), methylene ($=CH_2$) and difluoromethylene ($=CF_2$) complexes. In all cases the carbene ligand prefers the equatorial position. Studies focus on the bond lengths, bond dissociation energies, and donor–acceptor properties of the carbene ligand.

2.3.5.3. Heteroatom-substituted Group VIII–metal carbene complexes. Iron–aminocarbene complexes (i.e. **632**, **634**, **636**, Scheme 96) were produced in the reaction of tertiary amides with Collman's reagent (**631**) in the presence of trimethylsilyl chloride [511]. Formation of a chelate is critical to the success of this reaction. Carbene complex **634** was formed from amide **633** only in low yield; thermolysis of **634** led to the dihydropiperidene derivative **635**. Coupling of simple iron–aminocarbene complexes (e.g. **636**) with α,β-unsaturated esters led to γ-ketoesters (e.g. **639**) [512]. A mechanism involving formation of a metallacyclobutane (e.g. **637**), followed by β-hydride elimination and reductive elimination to form an enamine (e.g. **638**), followed by hydrolysis to form ketone **639** was proposed.

Iron–carbene complexes (e.g. **643**, Scheme 97) were generated from the coupling of azadiene iron complex **640** with aryllithium reagents followed by alkylation [513]. The proposed mechanism involves initial attack of the aryllithium at the imine carbon followed by attack of the nitrogen anion at a CO ligand, followed by alkylation at oxygen to form the carbene complex. Use of the corresponding alkyimine **644** led to the 17e metal acyl complexes **646**. In two cases the iminium salt complexes **647** were obtained.

The coupling of vinyl epoxides (e.g. **648**, Scheme 98) with diiron nonacarbonyl followed by alkylation led to

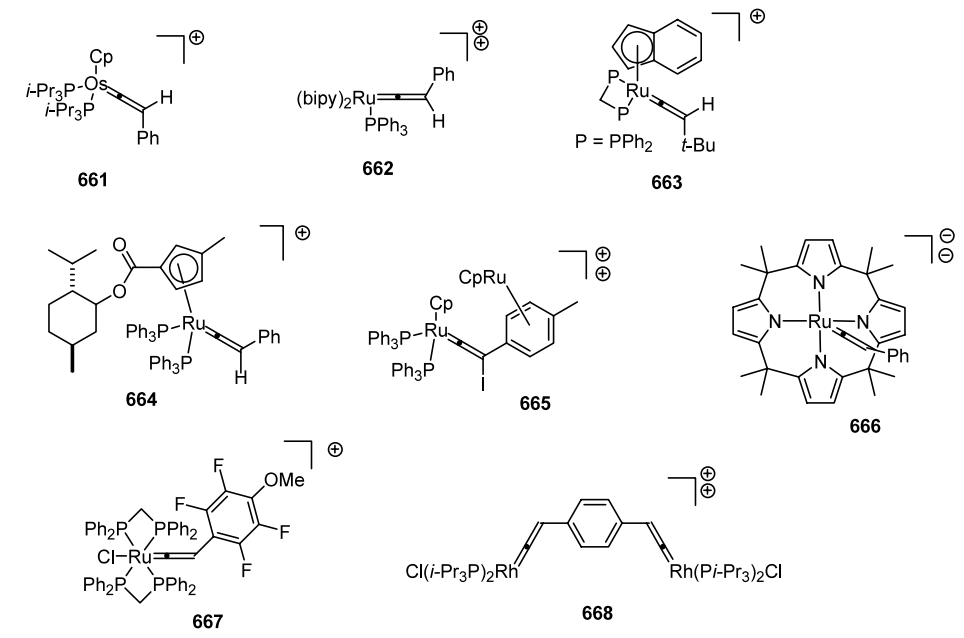
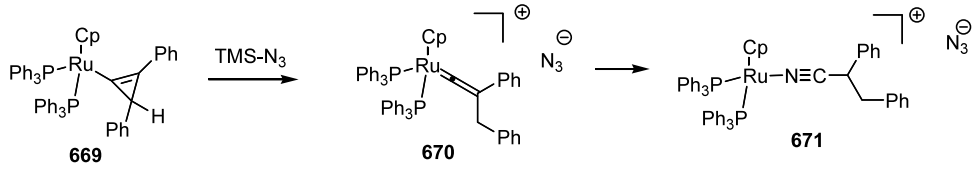


Fig. 14. Representative Group VIII metal–vinylidene complexes reported in 2001.

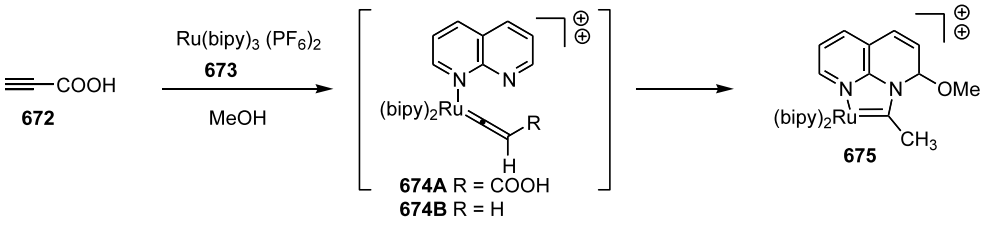


Scheme 101.

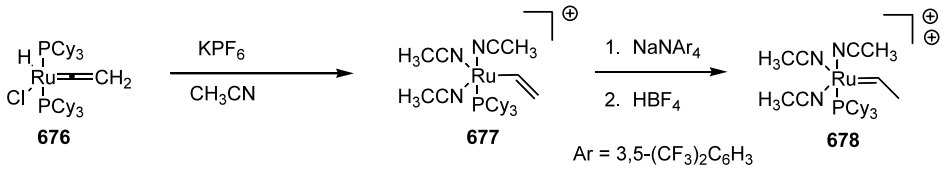
iron carbene π-allyl chelates (e.g. **649**) [514]. The complexes reacted with nucleophiles at the π-allyl ligand to afford the alkene carbene chelates (e.g. **651**), which eventually transform to the corresponding η^4-diene iron complexes (e.g. **652**) at room temperature. Similar transformations were demonstrated for dienyl epoxides and for vinylaziridines. Cobalt carbene complexes were prepared from vinyl epoxides and $CpCo(CO)_2$ followed by alkylation.

Other preparations of carbene complexes in this class were also reported. Acyloxy aminocarbene–iron complexes (e.g. **654**, Scheme 99) were prepared from iron complex **653** and dimethylamine followed by CO loss [515]. Coupling of carbene complex **654** with phosphines led to the η^1-carbene complexes (e.g. **655**). Bridging alkoxycarbyne–diiron complexes were prepared via alkylation of bridging carbonyl complexes [516].

2.3.5.4. Group VIII metal–vinylidene complexes. Many examples of the formation of metal vinylidene complexes (**656**, Scheme 100) via coupling of coordinatively unsaturated Group VIII metal complexes with terminal or silylated alkynes were reported in 2001. Representative examples are depicted in Fig. 14. Common reaction pathways for these complexes include reaction with alcohols to form Fischer carbene complexes (**660**, NUC=OR), analogous reaction with amines to form aminocarbene complexes (**660**, $NUC=NR_2$), or water to form metal acyls (**658**), and deprotonation at the β-position to form alkynylmetal complexes (**657**). Other



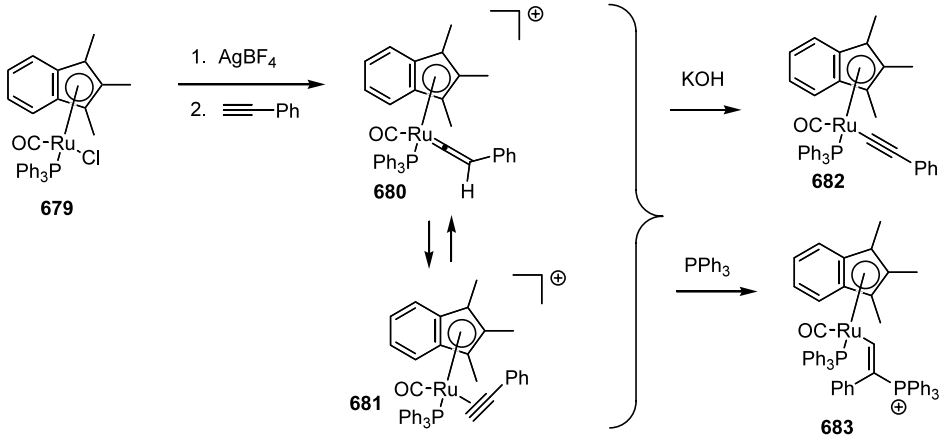
Scheme 102.



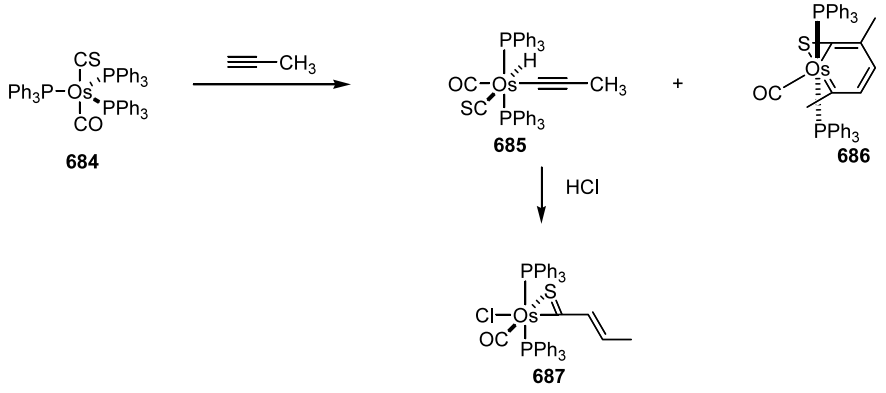
Scheme 103.

common synthetic routes to metal vinylidenes included addition of electrophiles to metal acetylide complexes (e.g. the reverse of the reaction synthesizing **657**), and treatment of acylmetal complexes with dehydrating agents (i.e. the reverse of the reaction synthesizing **658**).

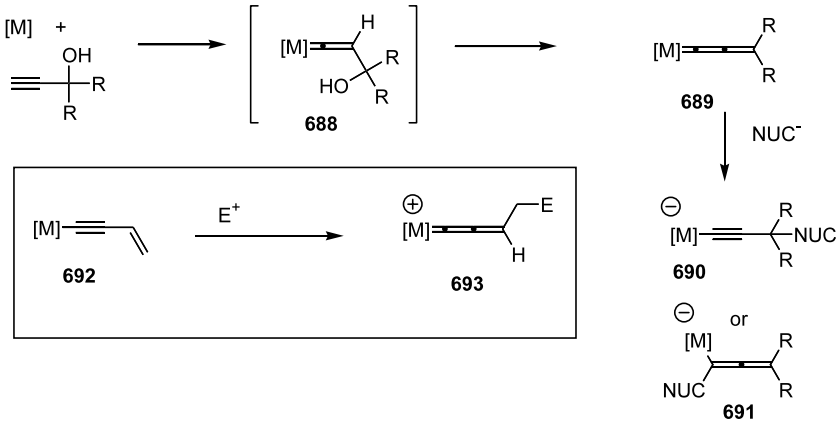
Specific reports which highlight the reaction pathways in Scheme 100 are depicted in Fig. 14, and include: (1) formation of cationic osmium–vinylidene complexes (e.g. **661**) through protonation of a neutral alknylosmium complexes [517], (2) formation and nonlinear optical/electrochemical studies of cationic ruthenium carbene complexes [518], (3) formation of dicationic ruthenium–vinylidene complex **662** and subsequent formation of aminocarbene complexes through addition of aniline derivatives [519], (4) formation of ruthenium–vinylidene complexes that feature indenyl and dppm ligands (e.g. **663**) and subsequent coupling of the acidic methylene group of the dppm ligand with the vinylidene ligand [520]; (5) formation and deprotonation of chelating phosphine–ether vinylidene complexes [521]; (6) formation of vinylidene–ruthenium complexes from ruthenium–Cp complexes and terminal alkynes, and subsequent formation of aminocarbene complexes (the same paper also reports formation of ruthenium carbene complexes from diazo compounds) [522]; (7) formation of optically active cationic ruthenium vinylidene complexes (e.g. **664**) from an optically active ruthenium complex [523]; (8) formation of cationic ruthenium–vinylidene complexes from protonation of alkynylruthenium complexes [524]; (9) formation of bimetallic ruthenium–vinylidene complexes (e.g. **665**) by protonation or iodination of the corresponding alkynylruthe-



Scheme 104.



Scheme 105.



Scheme 106.

nium complex [525]; (10) formation and electrochemical/NLO studies of ruthenium vinylidene complexes that contain chelating phosphine ligands [526]; (11) formation of dianionic ruthenium tetrapyrrole vinylidene complexes (e.g. **666**) and subsequent conversion to the alkoxycarbene or acyl complexes; dimerization of these complexes was effected by treatment of the vinylidene complex with phenyl azide [527]; (12) formation of fluoroarylvinylidene ruthenium complexes (e.g. **667**) and in situ deprotonation to form the alkynylruthenium complexes [528]; (13) formation of bis(vinylidene) ruthenium complexes (e.g. **668**) and heterobimetallic analogs from *p*-diethynylbenzene [529]; (14) formation and deprotonation of ruthenium vinylidene complexes derived from diethynylbiphenyl derivatives [530]; and (15) synthesis and electrochemistry of vinylidene complexes conjugated to the barbituric acid ring system [531].

Numerous processes suggest Group VIII metal vinylidene complexes as intermediates (Scheme 101), including: (1) hydration of alkynylruthenium complexes [532]; (2) formation of cationic nitrile complexes (e.g. **671**) from cyclopropenylruthenium complex **669** and trimethylsilyl azide; intermediate vinylidene complex **670** can be isolated [533]; and (3) formation of cyclic enol esters from ruthenium-catalyzed cyclization of alkyne–carboxylic acids [534].

The synthesis of dicationic ruthenium carbene complex **675** (Scheme 102) from ruthenium complex **673** and propiolic acid (**672**) was reported [535]. The formation of this complex was proposed to occur through forma-

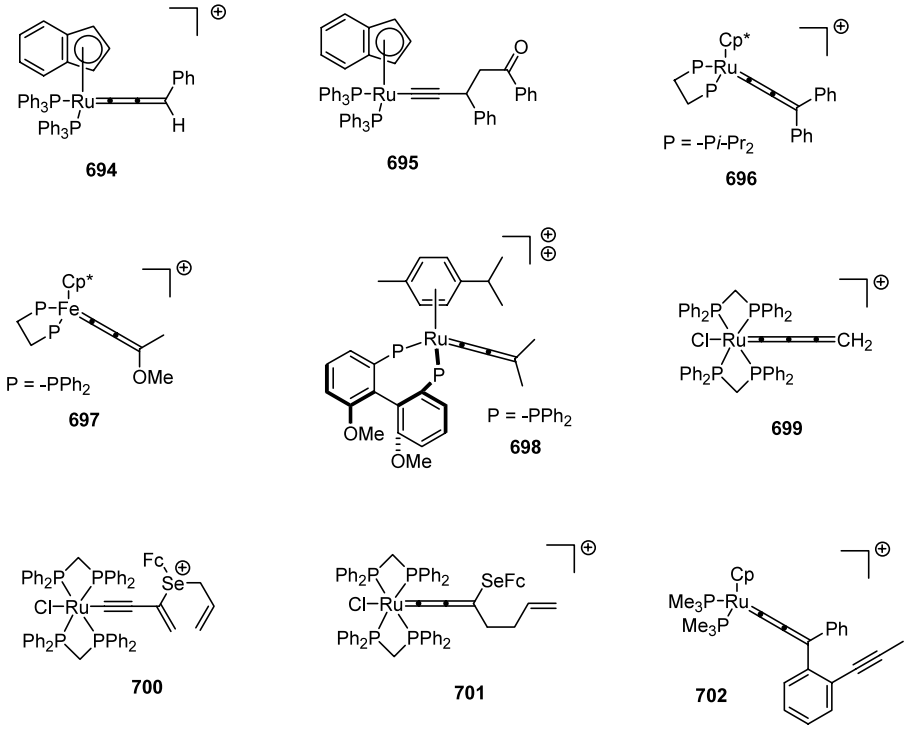
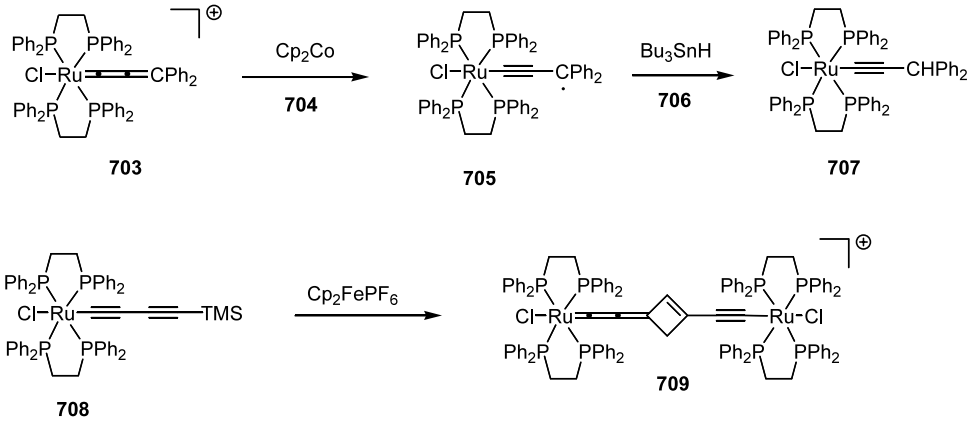


Fig. 15. Representative Group VIII metal cumulenylidene complexes reported in 2001.



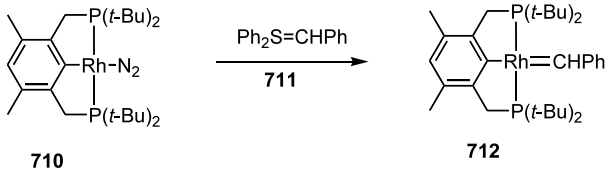
Scheme 107.

tion of vinylidene complex **674A**, followed by decarboxylation to form vinylidene complex **674B**, followed by net addition of methanol; the timing of carbene complex formation and decarboxylation was not definitive. Deprotonation using potassium hydroxide afforded a cationic vinylruthenium complex.

Neutral vinylidene–ruthenium complexes featuring a hydride ligand (e.g. **676**, Scheme 103) were transformed to cationic vinylruthenium complexes (e.g. **677**) upon treatment with potassium hexafluorophosphate in acetonitrile [536]. Protonation of **677** afforded dicationic ruthenium–carbene complex **678**. Reaction of complexes analogous to **676** that contain a chelating phosphine led to analogous complexes [537].

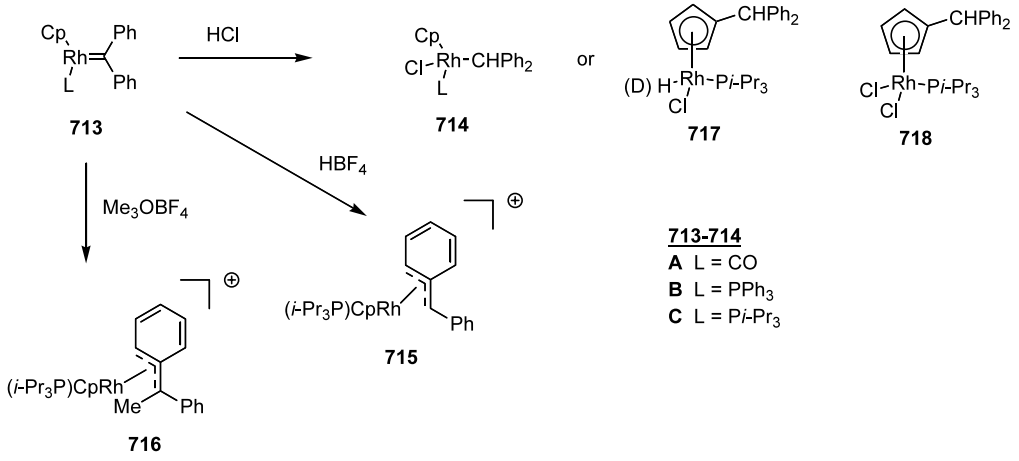
Fluxional ruthenium vinylidene/alkyne complexes (e.g. **680/681**, Scheme 104) were obtained by treatment of indenylruthenium halide complex (e.g. **679**) with silver hexafluorophosphate followed by a terminal alkyne [538]. The proportion of η^2-alkyne complex was less for the more sterically bulky triisopropylphosphine analogs of complexes **680/681**. Deprotonation afforded an alkynyl complex (e.g. **682**), while reaction with triphenylphosphine afforded a vinylphosphonium salt complex (e.g. **683**).

Coupling of osmium complex **684** (Scheme 105) with propyne led to acetylide complex **685** and the osmabenzene–sulfide complex **686** [539]. Protonation of the alkynylosmium complex led to the η^2-thioacyl complex **687**, by way of the vinylidene complex.

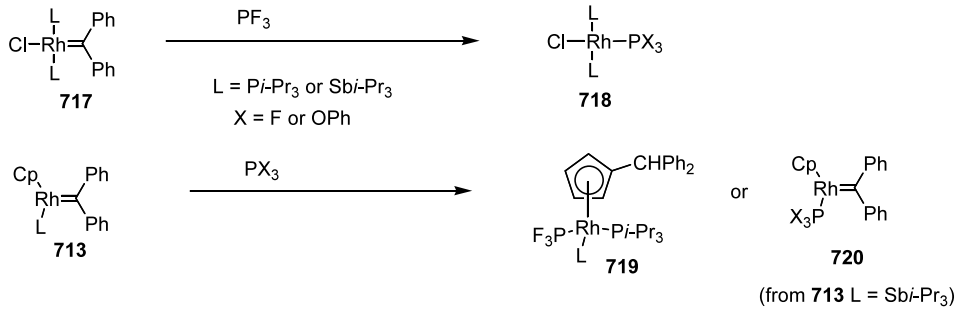


Scheme 108.

2.3.5.5. Group VIII metal complexes of higher cumulenes. Metal–higher cumulene complexes (**689**, **693**, Scheme 106) are produced from the coupling of coordinatively unsaturated Group VIII metal complexes with propargyl alcohols (usually those that contain no hydrogens β- to the OH group), or by addition of electrophiles to the δ-carbon of alkenylethynyl–metal



Scheme 109.

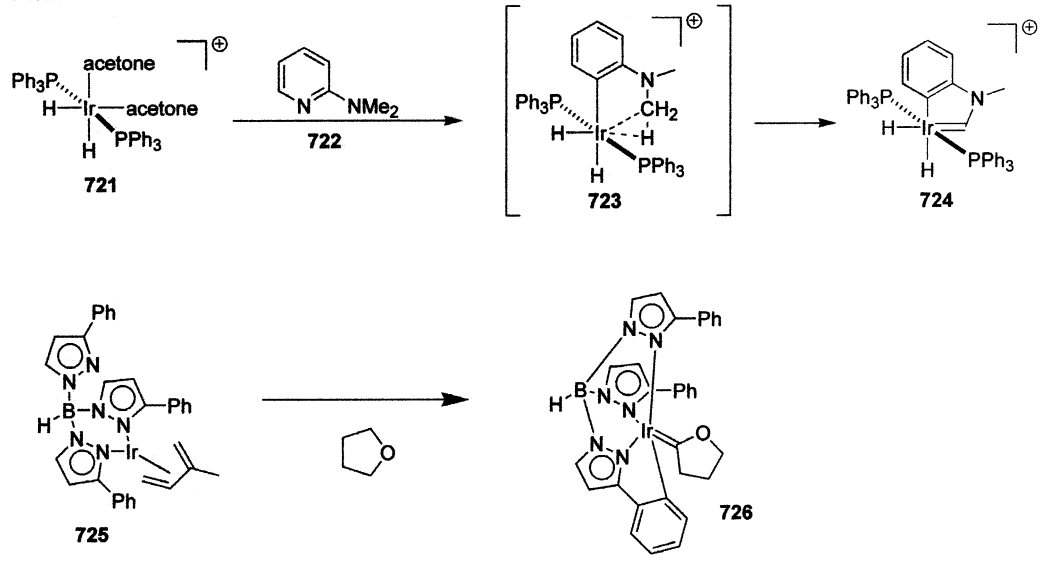


Scheme 110.

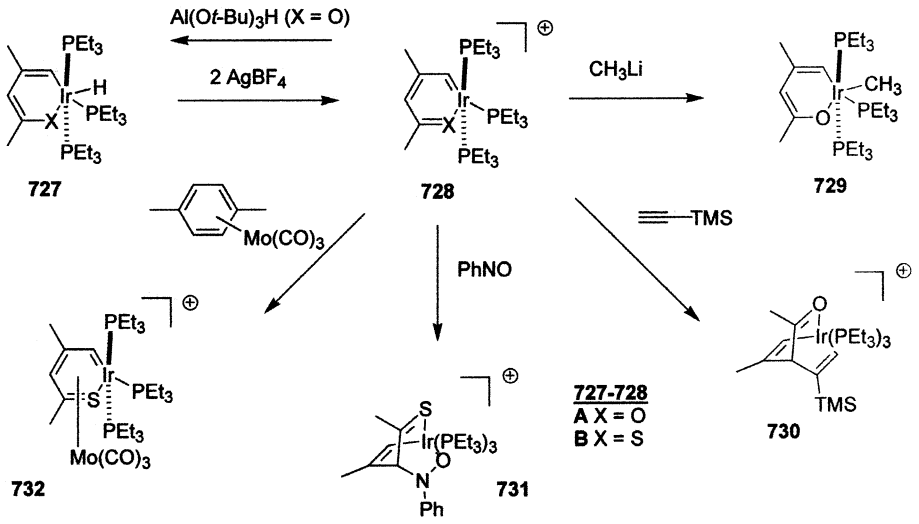
complexes (**692**). A variety of reaction processes of Group VIII metal–cumulene complexes were reported in 2001. Common reaction pathways for these complexes include reaction with nucleophiles at the γ-position, resulting in alkynylmetal complexes (**690**), or attack at the γ-position, resulting in allenylmetal complexes (**691**). Representative examples of this class of compounds are depicted in Fig. 15.

Specific reports which highlight the reaction pathways in Scheme 106 are depicted in Fig. 15, and include: (1) reaction of various cationic ruthenium–allenylidene complexes (e.g. **694**) with enolates, which affords alkyne–ketone derivatives (e.g. **695**) through attack at the γ-position [540]; (2) addition of phosphine nucleophiles to γ-carbon of allenylidene–triosmium complexes [541]; (3) stepwise formation of cationic ruthenium allenylidene complex **696**; in this case the intermediate alkynylruthenium complex and the α-hydroxyvinylidene complex were observable in solution [542]; (4) formation of iron–allenylidene complex **697** from the reaction of 1-trimethylsilyl-1,3-butadiyne with an iron chloride in methanol (this paper also discusses formation of simple vinylidenes) [543]; (6) formation of a dicationic ruthenium allenylidene complex (**698**) through reaction of a ruthenium arene complex with 2-methyl-3-butyn-2-ol [544]; (7) formation of cationic ruthenium allenylidene complex **701** through coupling of 1,3-butadiyne with a ruthenium halide (affording unstable butatrienylidene–ruthenium complex intermediate **699**) followed by coupling with ferrocenyl allyl selenide at the γ-position (affording selenonium salt **700**) followed by Cope rearrangement [545]; (8) related studies using allylic amines in place of the allylic selenide [546]; and (9) cationic γ-alkynylarylallenylidene–ruthenium complexes (e.g. **702**), which catalyze the conversion of tributyltin hydride to hexabutylditin [547].

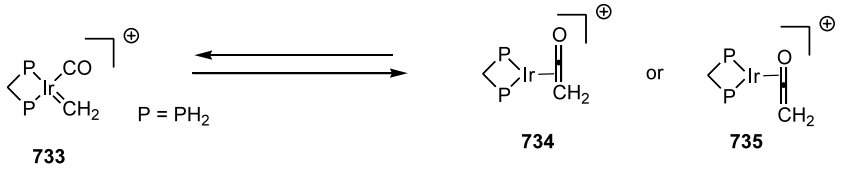
Reduction of cationic allenylidene–ruthenium complexes (e.g. **703**, Scheme 107) and higher homologues with cobaltocene (**704**) electrochemically led to observable free radicals (e.g. **705**) [548]. These species reacted rapidly with tributyltin hydride to afford the corresponding alkynylruthenium complexes (e.g. **707**), which were also obtained through direct reaction of allenylidene complexes with sodium borohydride. Bimetallic



Scheme 111.



Scheme 112.



Scheme 113.

allenylidene complex **709** was obtained through oxidation-induced dimerization of dialkynylruthenium complex **708** [549].

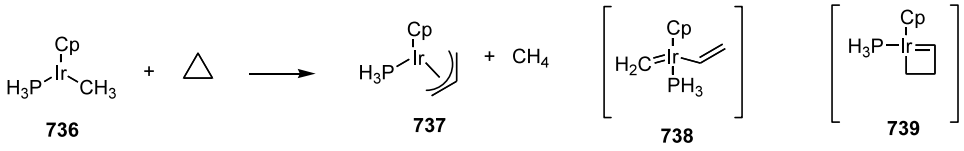
2.3.6. Group IX metal–carbene complexes

2.3.6.1. Simple carbene complexes. Direct formation of carbene complexes from sulfur ylides (e.g. **711**, Scheme 108) was reported [550]. Reaction of rhodium–dinitrogen complex **710** with sulfur ylide **711** led to rhodium–carbene complex **712**. Other carbene complexes were also prepared from directly from sulfur ylides, including Grubbs catalyst I and osmium carbene complexes.

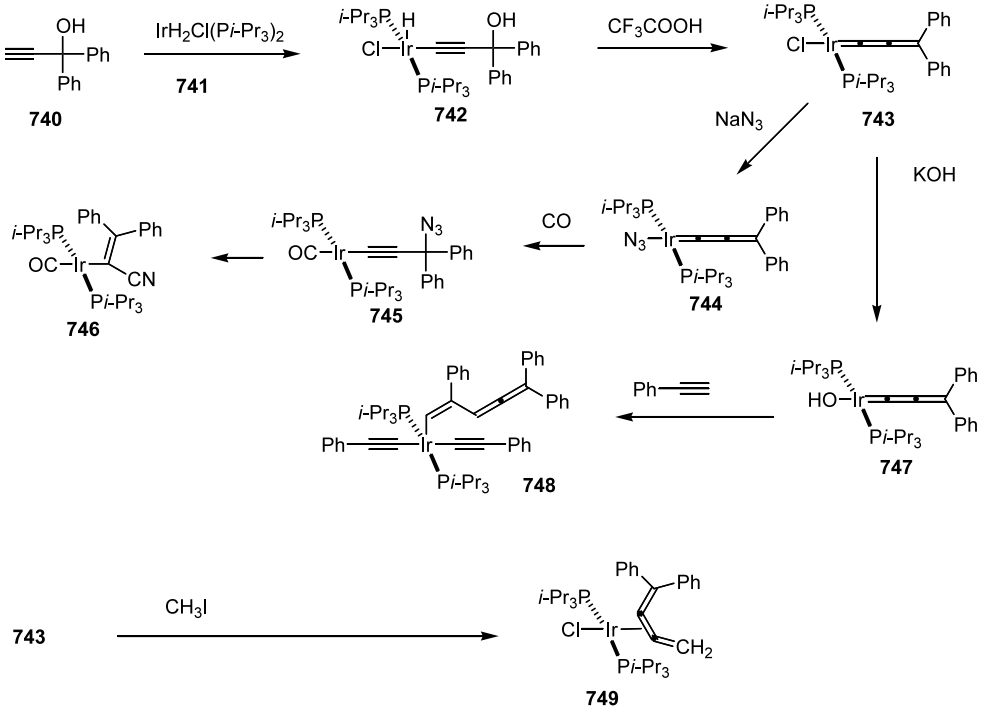
Protonation of carbene complexes of general structure **713** (Scheme 109) (L = CO or phosphines) was studied [551]. Protonation at the metal followed by hydrogen migration was the preferred mechanism for the formation of complex **714** from complexes **713A** and **713B**. Protonation of the trisopropylphosphine complex **713C** led to the Cp-substituted complex **717** or **718** if excess HCl was employed. The analogous d^5-Cp complex **713C** led to the complex **717** with deuterium at the indicated position. Protonation of triisopropylphosphine complex **713C** with HBF_4 led to the η^3-benzyl complex **715**; analogous product **716** was formed through methylation.

A series of ligand exchange and coupling reactions were reported for diarylcarbene–rhodium derivatives (e.g. **713**, **717**, Scheme 110) [552]. Reaction of carbene complexes of general structure **717** with PX_3 derivatives resulted in replacement of the carbene ligand. Reaction of Cp complexes **713** with PX_3 derivatives led to the Cp-substituted product **719** or the simple ligand exchange products **720**. A mechanism involving ligand substitution followed by coupling of the Cp and carbene ligands was proposed and supported through deuterium labeling studies.

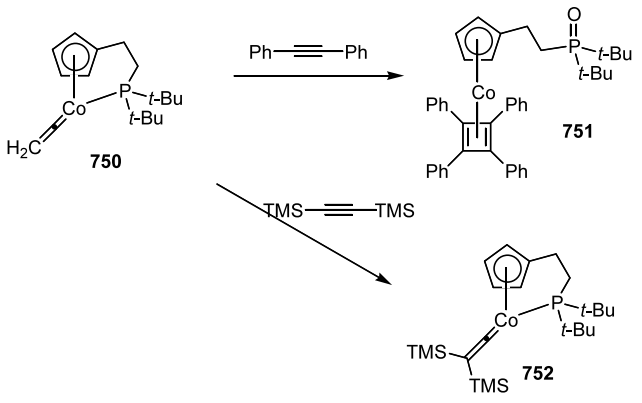
Several papers in 2001 discussed the synthesis of Group IX metal carbene complexes through C–H oxidative addition processes (Scheme 111). Synthesis of Fischer carbene–iridium complexes (e.g. **724**, Scheme 111) from tertiary amine **722** and iridium complex **721** was reported [553]. Intramolecular C–H oxidative addition after formation of the pyridyl complex was



Scheme 114.



Scheme 115.

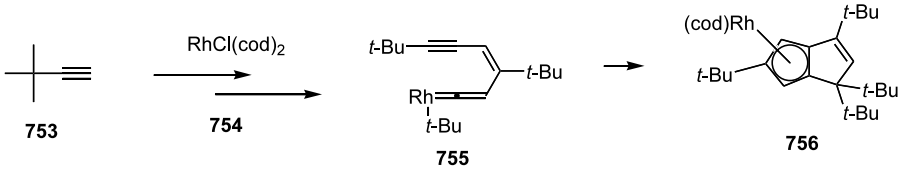


Scheme 116.

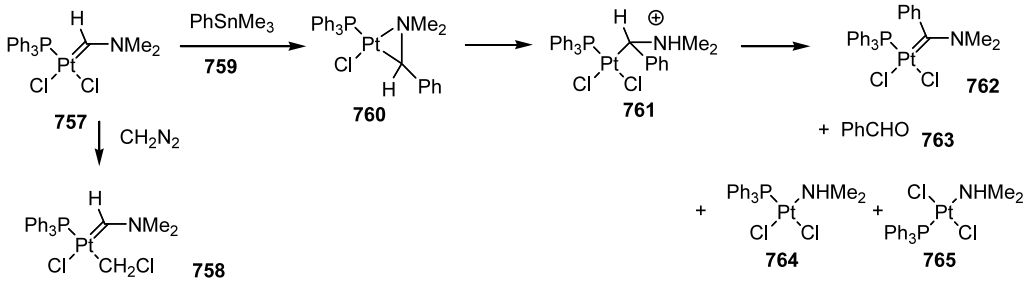
the key step in this reaction. An intermediate complex featuring an agostic C–H interaction (**723**) could be observed at low temperature. A C–H activation-based carbene complex synthesis was also observed in the reaction of iridium diene complexes (i.e. **725**) with THF [554]. In this case C–H oxidative addition at the phenyl substituent of the substituted Tp ligand was also noted. A more conventional synthesis of cyclic alkoxycarbene–iridium complexes using 3-butyn-1-ol was also reported [555].

The synthesis of iridapyrone systems (e.g. **728A**, Scheme 112) [556] and the sulfur analogs (e.g. **728B**) [557] were reported. Oxidation of neutral chelated β-iridaenone complexes (e.g. **727**) with silver tetrafluoroborate led to cationic complex **728**. The reaction of cationic complex **728A** with a variety of nucleophiles led to neutral complexes (e.g. **727A**, **729**). Complex **728A** undergoes an apparent Diels–Alder reaction, affording metallabicycles (e.g. **730**) upon treatment with trimethylsilylacetylene or methyl acrylate. A Diels–Alder adduct (**731**) was formed upon reaction of complex **728B** with nitrosobenzene. An arene exchange process, resulting in bimetallic complex **732**, was observed upon treatment of complex **728B** with (*p*-xylene)$Mo(CO)_3$. An (η^6-iridathiabenzene)–RuCp* was also prepared from complex **728B**.

Several papers report on processes that propose Group IX metal carbene complexes as intermediates. Only processes that do not involve diazo compounds as the carbene precursor are included unless there is some effort to isolate or analyze the carbene complex. Iridium



Scheme 117.



Scheme 118.

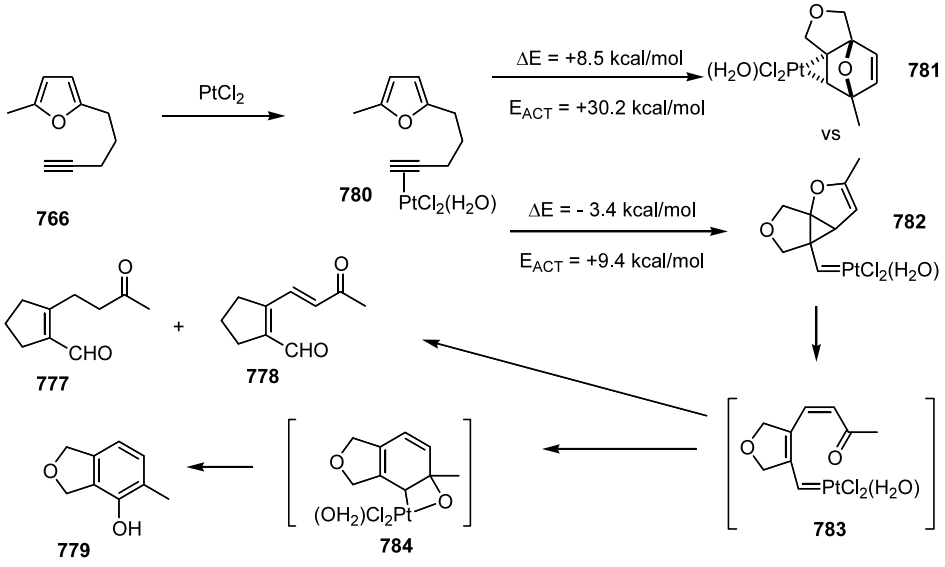
carbene complexes were proposed as intermediates in the iridium-catalyzed conversion of cyclohexane and hydrogen to hexane and smaller alkanes [558]. Cobalt-catalyzed cyclopropanation of alkenes by diazo compounds was studied by the PM3 method [559]. These studies focus on understanding the origins of stereoselectivity in the reaction of the cobalt carbene complex with the alkene.

A theoretical analysis of the interconversion of iridium carbene carbonyl complex **733** (Scheme 113) and iridium ketene complexes (**734** and **735**) was reported [560]. Conversion of complex **733** to ketene complex **734** is endothermic by 7.8 kcal mol^{-1}. Coordination to the alkene π-bond (e.g. as in **734**) is favored over coordination to the C–O π-bond (e.g. as in **735**). A comment about experimental work on this research topic also appeared [561].

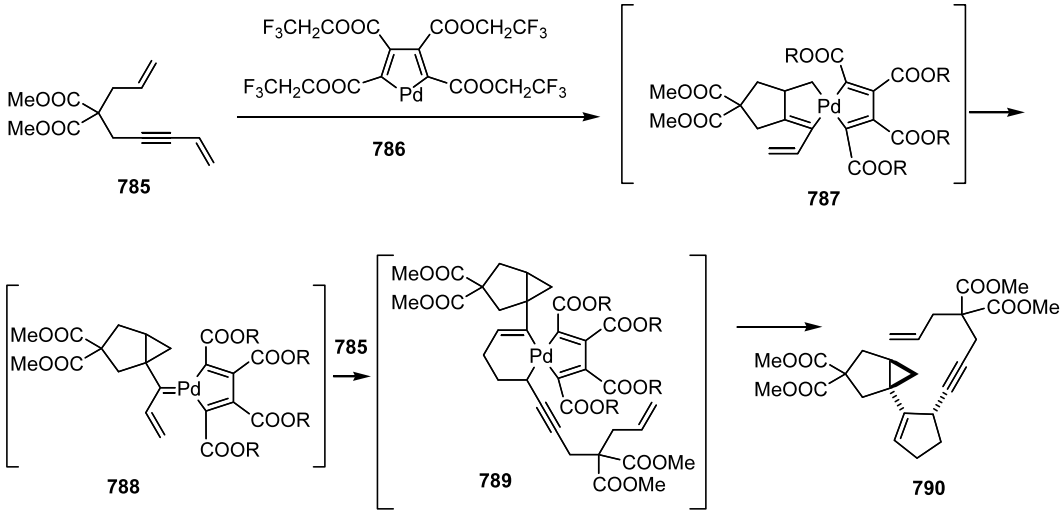
The reaction of iridium complex **736** (Scheme 114) with cyclopropane to form π-allyl complex **737** was analyzed by density functional theory [562]. Carbene complexes **738** and **739** were considered as likely intermediates in the complex reaction pathway leading to π-allyl complex **737**.

2.3.6.2. Cumulene complexes. Similar synthetic procedures and reactivity patterns were generally observed for Group IX and Group VIII (Schemes 100 and 106) metal–cumulene complexes.

Coupling of iridium–dihydride complex **741** (Scheme 115) with alkynols (e.g. **740**) led to an alkynyliridium complex (e.g. **742**), which afforded an allenylidene complex (e.g. **743**) upon treatment with trifluoroacetic acid [563]. Reaction with sodium azide initially afforded an iridium–azide complex (e.g. **744**), which afforded the corresponding propargyl azide **745** upon reaction with CO. Further reaction resulted in cyanoalkene complex **746**. A hydroxide–iridium complex (e.g. **747**) was formed upon treatment of complex **743** with hydroxide ion. Further reaction with excess phenylacetylene led to alkenyliridium complex **748**. Reaction of complex **743** with sodium iodide led to the simple halogen exchange product, while reaction with iodomethane led to the η^2-butatriene complex **749** [564]. A mechanism involving alkylation at iridium, methyl migration, C–H oxidative addition, and reductive elimination of HI was proposed. Related studies involving rhodium–allenylidene complexes and nucleophiles were also reported [565]. A



Scheme 119.



Scheme 120.

series of rhodium–vinylidene complexes were prepared and their IR/Raman spectra examined [566].

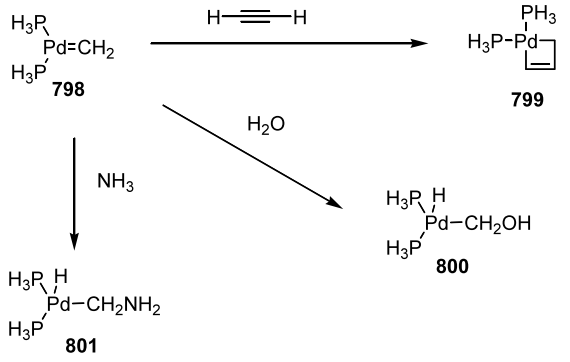
Coupling of cobalt–vinylidene complex **750** (Scheme 116) with alkynes was reported [567]. Reaction with diphenylacetylene led to the cyclobutadiene complex **751**. A vinylidene exchange process occurred upon treatment with bis(trimethylsilyl)acetylene, leading to first to an η^2-alkyne complex, which rearranged to disilylvinylidene complex **752**.

Rhodium vinylidene complexes (e.g. **755**, Scheme 117) were suggested as intermediates in a mechanistically complex process involving the conversion of terminal alkynes (e.g. **753**) to hydropentalenylrhodium complexes (e.g. **756**) [568]. Several regioisomeric analogs of **756** were obtained, depending upon the starting alkyne.

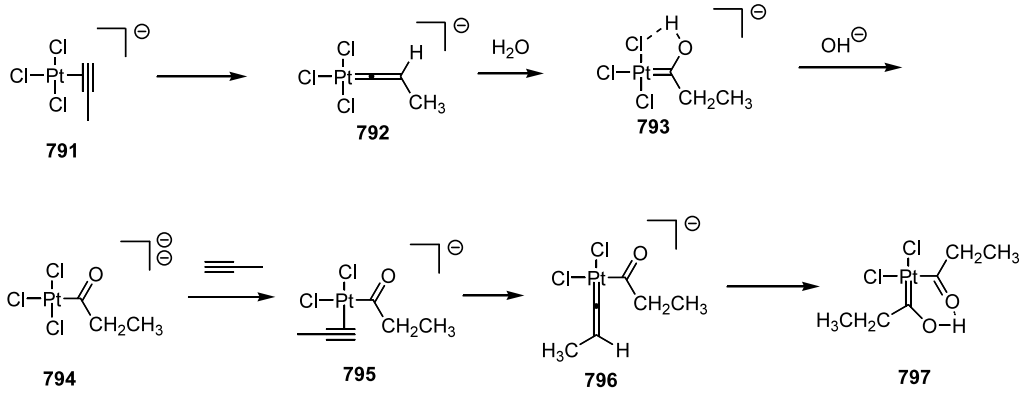
2.3.7. Group X metal–carbene complexes

The reactions of aminocarbene–platinum complex **757** (Scheme 118) were investigated [569]. The chloromethyl complex **758** was obtained from reaction with diazomethane. Reaction with phenyl trimethylstannane (**759**) led to a mixture of phenylcarbene complex **762**, benzaldehyde (**763**) and platinum complexes **764** and **765**. The reaction proceeded through formation of a phenylplatinum complex, followed by formation of the chelate complex **760**, followed by conversion to ylide complex **761**. Complexes **760** and **761** could be isolated.

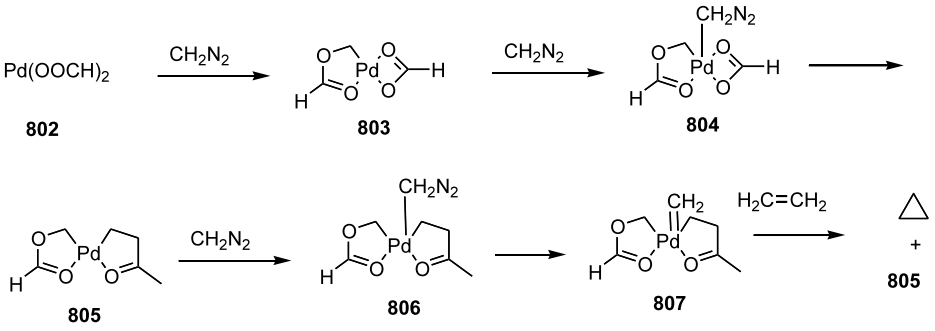
Platinum carbene complexes (e.g. **782**, **783**, Scheme 119) were proposed as intermediates in the conversion of furan–alkyne derivatives (e.g. **776**) to compounds **777**–



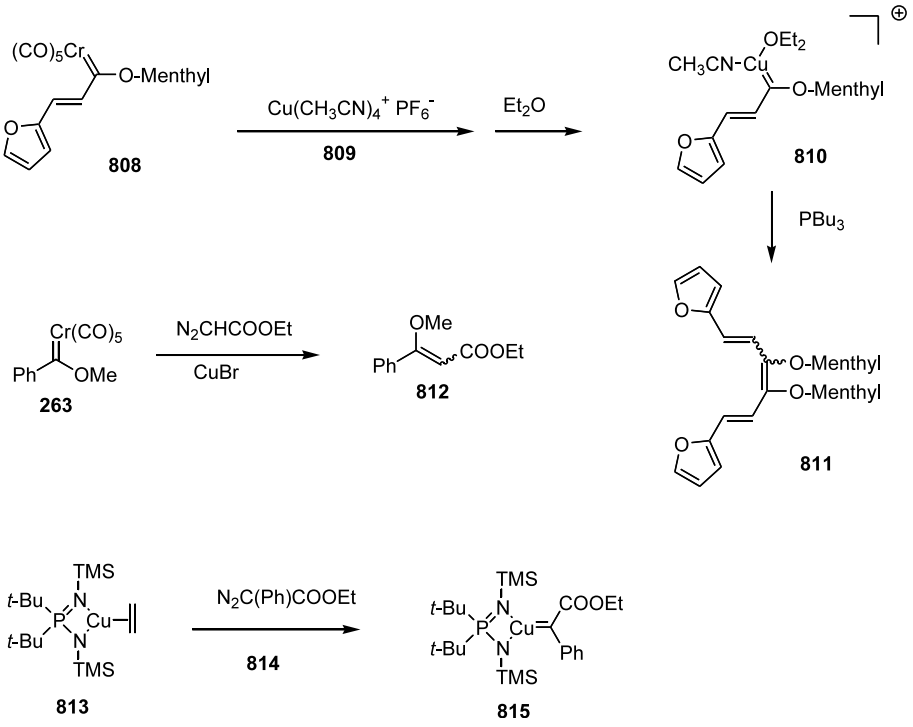
Scheme 122.



Scheme 121.



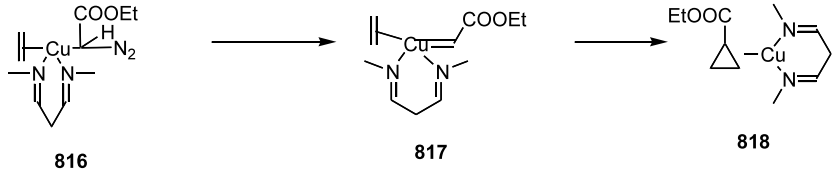
Scheme 123.



Scheme 124.

779 [570]. The key step in the mechanism involves formation of carbene complex **782** from platinum alkyne complex **780**. Rearrangement of carbene complex **782** affords intermediate ketone–carbene complex **783**, which either undergoes hydrolysis to afford compounds **777** and **778** or [2+2]-cycloaddition to afford metallacycle **784**, which leads to compound **779** after reductive elimination to form the epoxide followed by ring opening to generate the aromatic species. The cyclopropanation step (conversion of **780** to **782**) was modeled by density functional theory, and determined to be exothermic ($\Delta E = -3.4$ kcal mol^{-1}) while the intramolecular Diels–Alder reaction (conversion of **780** to **781**) was determined to be endothermic ($\Delta E = +8.5$ kcal mol^{-1}).

Group X metal–carbene complexes were suggested as intermediates in various metal-catalyzed reactions of



Scheme 125.

enynes. A palladium carbene complex (e.g. **788**, Scheme 120) was proposed for the conversion of dienyne derivative **785** to the cyclized dimeric compound **790** [571]. Platinum carbene complexes were considered as possible intermediates in platinum-catalyzed enyne metathesis [572].

The formation of internally hydrogen bonded alkoxycarbene–platinum complexes (e.g. **797**, Scheme 121) from platinum halides and terminal alkynes in the presence of water was analyzed by density functional theory [573]. The preferred mechanistic pathway involves formation of the vinylidene complex (e.g. **792**), followed by addition of water, conversion to the acylplatinum complex (e.g. **794**), followed by the same sequence of reactions on acylplatinum complex **794**.

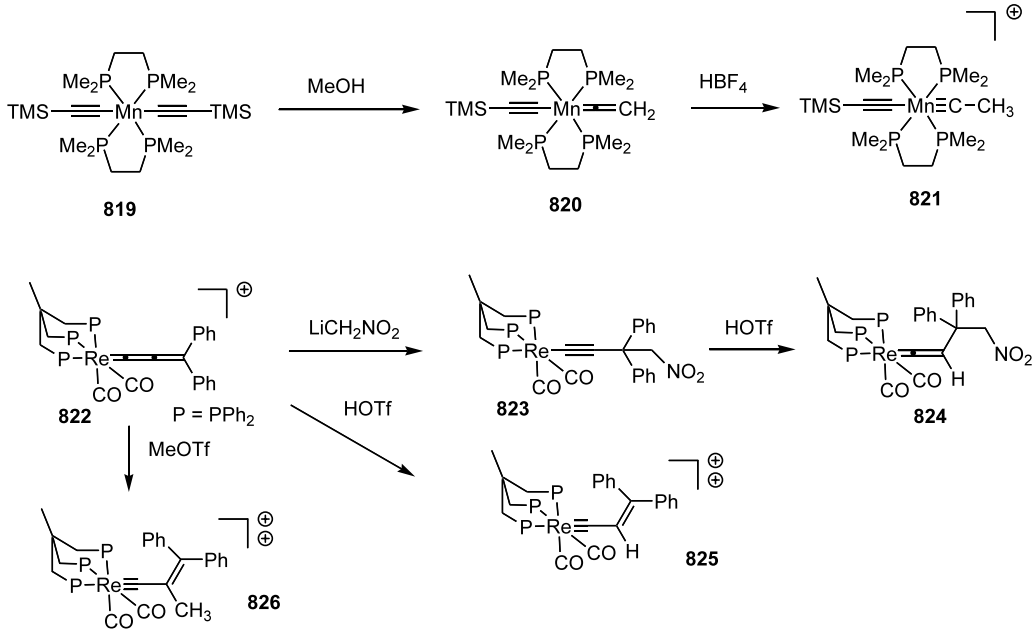
Addition reactions of palladium–carbene (e.g. **798**, Scheme 122) (and silylene and stanylene analogs) complexes were investigated using density functional theory [574]. In the carbene complex, reaction with the alkyne occurs through initial complexation at palladium, while initial interaction is with the tin or silicon in silylene/stannylene analogs. The reaction proceeds with a higher energy barrier for the carbene complexes. The preferred reaction pathways for water and ammonia are as depicted in Scheme 122.

A density functional theory study of palladium(II) chloride catalyzed cyclopropanation was reported [575]. The most reasonable pathway identified involves a chloromethylpalladium complex and not a palladium carbene complex. A similar study was also reported using palladium(II) formate (Scheme 123) [576]. The favored mechanism involves the insertion or two equivalents of methylene into the C–O bond to give intermediate **805**, which then reacts with a third equivalent of diazo compound to give after nitrogen loss carbene complex **807**, which couples with ethylene to provide cyclopropane and complex **805** in a step with no energy barrier.

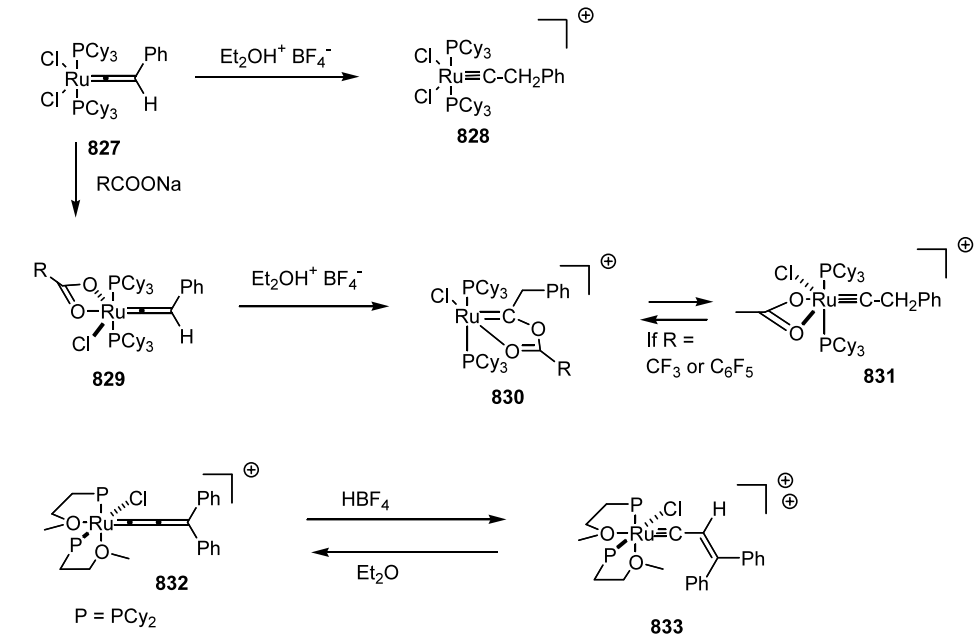
2.3.8. Group XI carbene complexes

Successful transfer of a carbene ligand from chromium to copper was reported (Scheme 124) [577]. Treatment of chromium carbene complex **808** with copper(I) species **809** led to copper–carbene complex **810**, which afforded the carbene dimer (**811**) upon treatment with tributylphosphine. Other copper-induced reactions of chromium–carbene complexes were also reported. Reaction of methoxycarbene complex analogs (e.g. complex **263**) with copper salt **809** led to the carbene dimer. Coupling of a variety of carbene complexes with ethyl diazoacetate in the presence of cuprous bromide led to the β-alkoxy enoates (e.g. **812**). A copper carbene complex (**815**) was isolated from the coupling of copper ethylene complex **813** with ethyl diazophenylacetate (**814**) [578].

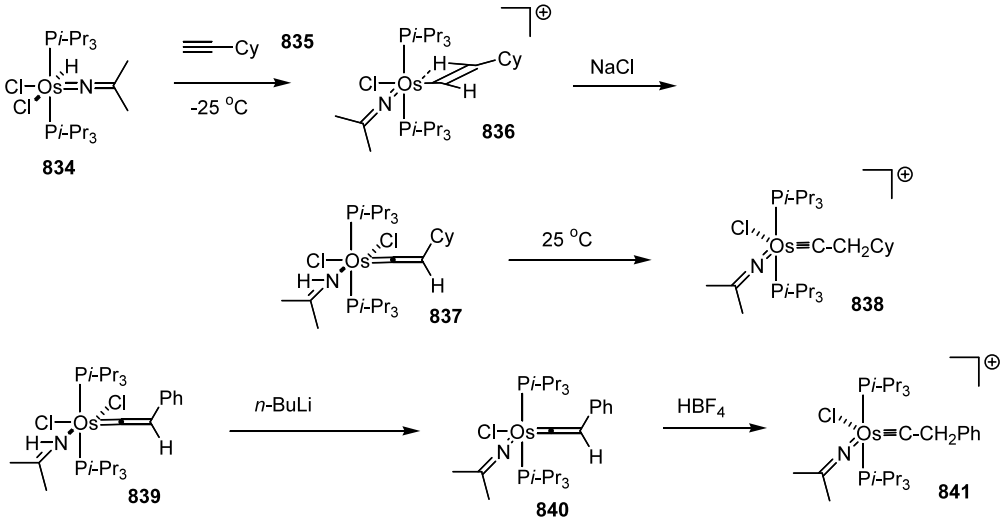
Copper-catalyzed cyclopropanation was studied by density functional theory [579]. The copper carbene alkene complex was determined to be a reasonable intermediate in cyclopropanation reactions using copper phenanthroline complexes. A similar study was reported for copper malonaldiimine complexes [580]. The rate-determining step in these reactions is loss of nitrogen from the copper complex of the diazo compound (e.g. conversion of **816** to **817**, Scheme 125). The cyclopro-



Scheme 126.



Scheme 127.



Scheme 128.

panation step takes place through direct carbene insertion of the metal–carbene species to yield a catalyst–product complex (**818**). Stereochemical predictions of a bis(oxazoline)–copper(I) catalyst) have been rationalized based on analysis of the preferred reaction pathway.

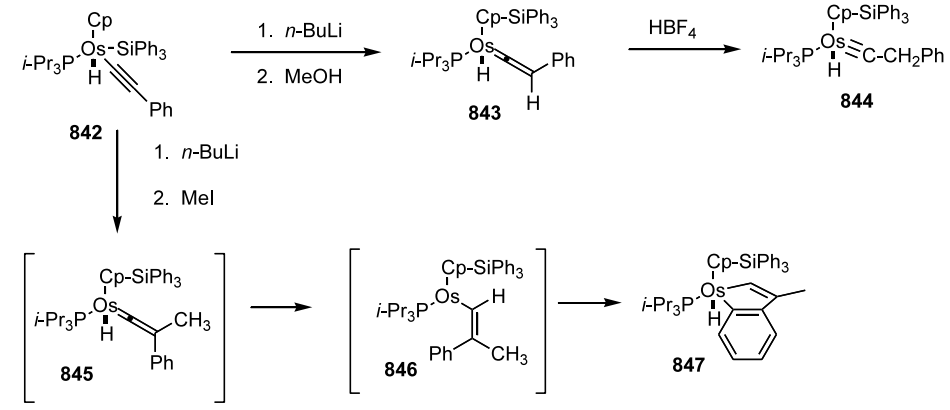
2.3.9. Lanthanide and actinide carbene complexes

A carbene–metal species was formed in the reaction of thorium atoms with carbon monoxide [581]. This species was characterized by infrared spectroscopy and extensive theoretical studies were undertaken for this species. The species CThO was suggested to have a triplet ground state and a bent structure.

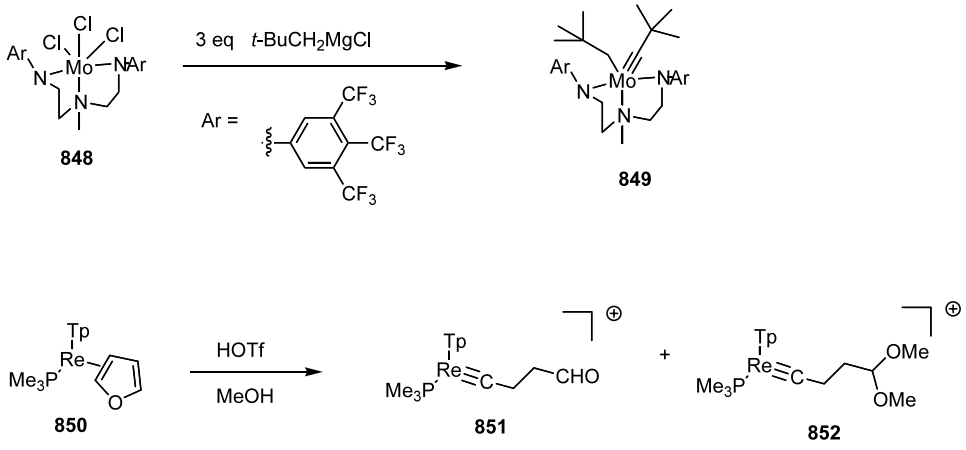
3. Metal–carbyne or metal–alkylidyne complexes

3.1. Review articles

Review articles featuring metal carbyne complexes that appeared in 2001 highlight the following topics: (1) the historical development of compounds containing metal–carbon multiple bonds [582]; (2) synthesis of



Scheme 129.



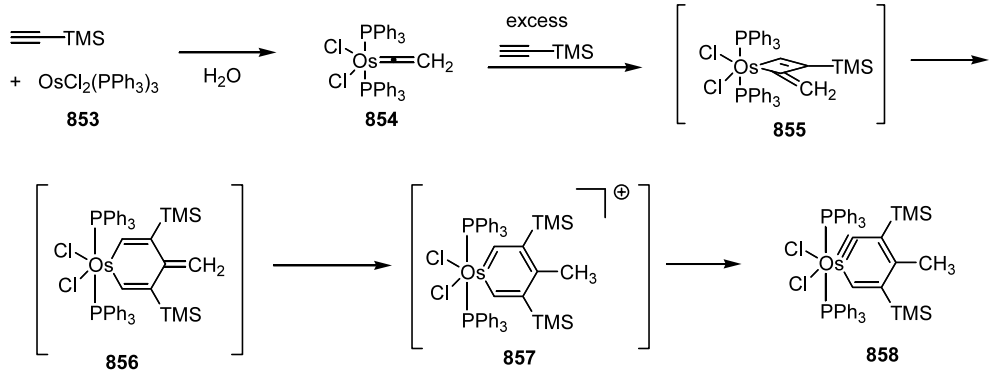
Scheme 130.

osmium and ruthenium carbene and carbyne complexes through coupling of enol ethers with metal hydrides [583]; and (3) aminocarbyne complexes [584]. Although not directly focusing on metal–carbyne complexes, other review articles feature a substantial section on metal–carbyne complexes. Topics covered include: (1) the coordination chemistry on CNH, the simplest isocyanide [585]; and (2) transition metal-catalyzed alkyne metathesis [586].

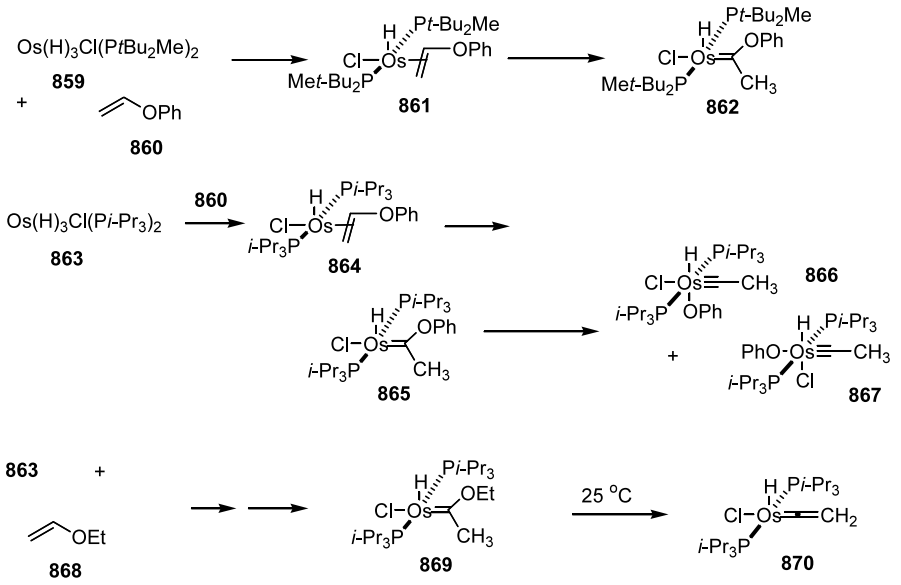
3.2. Synthesis and/or generation

3.2.1. Generation through protonation of metal–vinylidene or metal–alkynyl complexes

Reaction of dialkynylmanganese complex **819** (Scheme 126) with methanol led to neutral vinylidene complex **820** [587]. Reaction of complex **819** with excess HF led to carbyne complex **821**, which can also be formed through protonation of vinylidene complex **820**.



Scheme 131.

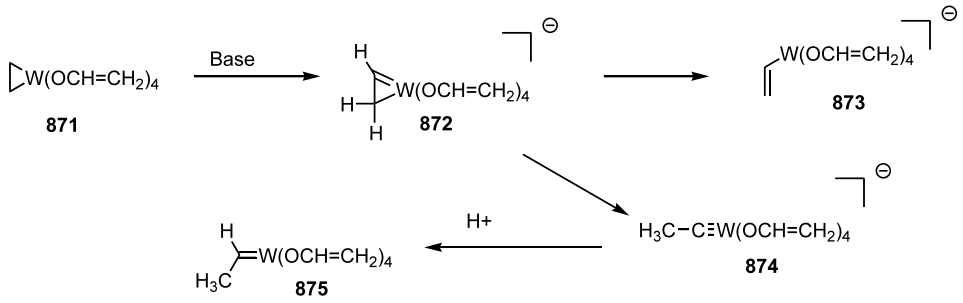


Scheme 132.

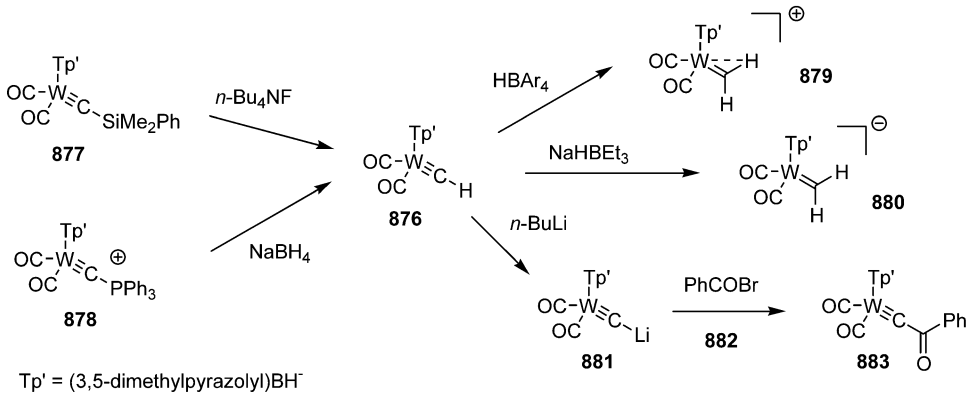
The reaction profile for cationic rhenium allenylidene complex **822** was evaluated [588]. Reaction with nucleophiles occurs at the γ-carbon to afford an alkynylrhenium complex (e.g. **823**), which can be protonated to form the cationic vinylidene complex (e.g. **824**). Direct protonation or methylation of allenylidene complex **822** led to dicationic carbyne complexes (**825** or **826**).

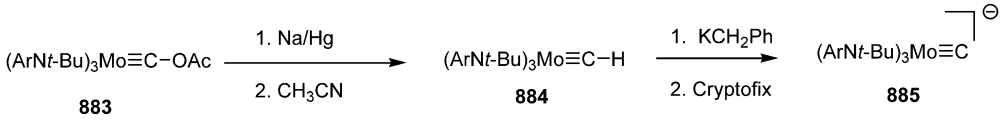
Ruthenium carbyne complexes (e.g. **828**, Scheme 127) were generated through protonation of ruthenium vinylidene complex **827** [589]. Various ligand exchange processes were also reported for this vinylidene complex. The reaction of carboxylate derivatives of **827** (**829**) with acid led to the chelated acyloxycarbene complex **830**. The corresponding trifluoroacetate complex was in equilibrium with the carbyne complex (e.g. **831**). Carbyne complex **828** served as a catalyst for the ROMP of cyclooctene. A dicationic ruthenium carbyne complex (**833**) was generated through protonation of cationic ruthenium allenylidene complex **832** [590]. This process could be reversed by the addition of diethyl ether.

Synthesis of carbyne complexes featuring azavinylidene ligands (e.g. **838**, Scheme 128) was achieved through reaction of azavinylidene–hydride complex **834** with terminal alkynes in the presence of silver salts [591]. Reaction at low temperature afforded alkenylosmium complex **836**, which transforms to vinylidene complex **837** upon treatment with sodium chloride. Upon warming to room temperature complex **837** transforms to the carbyne complex **838**. Alternatively, reaction of imine–osmium vinylidene complexes (e.g. **839**) with *n*-butyllithium followed by reaction with fluoroboric acid also led to cationic carbyne complexes (e.g. **841**) [592]. Related studies were reported for Cp analogs (Scheme 129) [593]. Reaction of osmium complex **842** with *n*-butyllithium followed by methanol led to vinylidene complex **843**, which afforded the cationic carbyne complex (**844**) upon protonation. Reaction of osmium alkynyl complex **842** with *n*-butyllithium followed by methyl iodide led to osmacycle **847**. In both reactions, initial deprotonation at the Cp ring followed by silyl migration was proposed. In the synthesis of **847**, a mechanism involving formation of a β-methylvinylidene intermediate **845**, which then undergoes hydride migration to form alkenylosmium complex **846**, followed by intramolecular oxidative addition to form **847** was proposed.

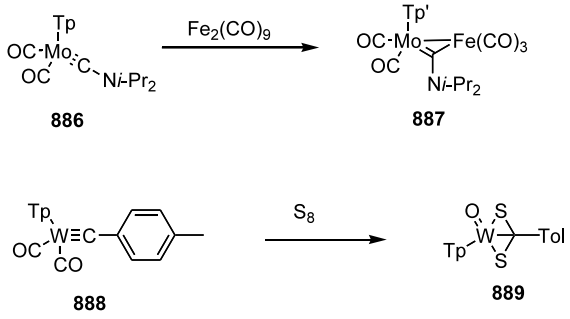


Scheme 133.





Scheme 134.

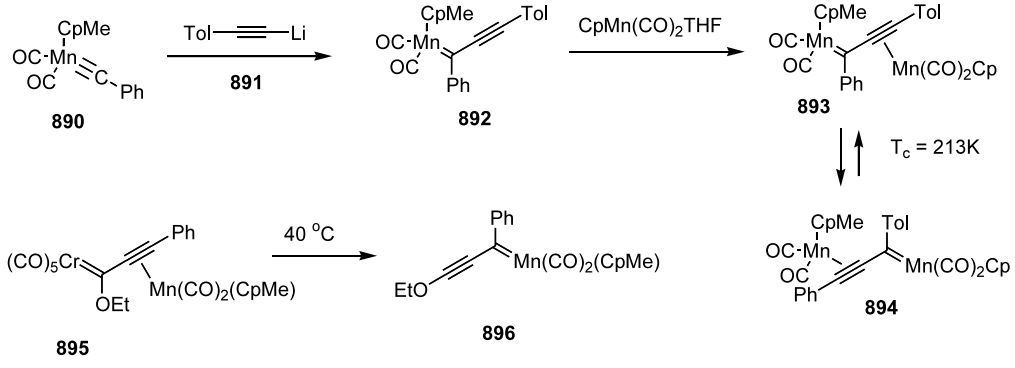


Scheme 135.

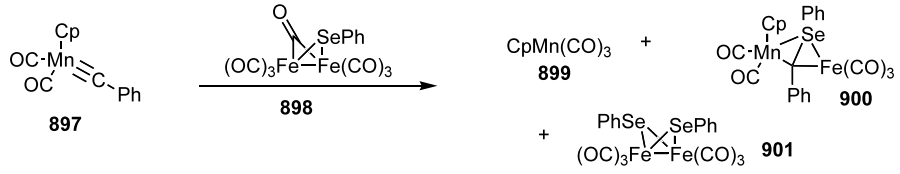
3.2.2. Synthesis of metal–carbyne complexes through other routes

The coupling of molybdenum complex **848** (Scheme 130) with excess neopentylmagnesium chloride led to the carbyne complex **849** [594]. Similar reactions were observed for analogous tungsten complexes. Rhenium–carbyne complexes (e.g. **851**, **852**, Scheme 131) were produced by protonation of η^2-furan rhenium complex **850** [595].

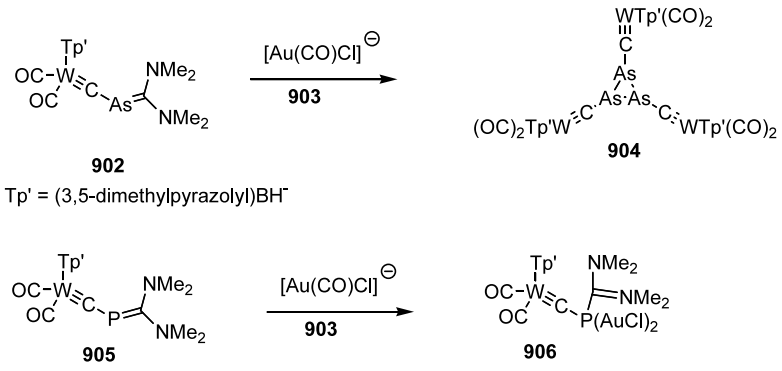
An osmabenzyne complex (**858**, Scheme 131) was observed in the coupling of osmium complex **853** with excess trimethylsilylacetylene [596]. Reaction with one



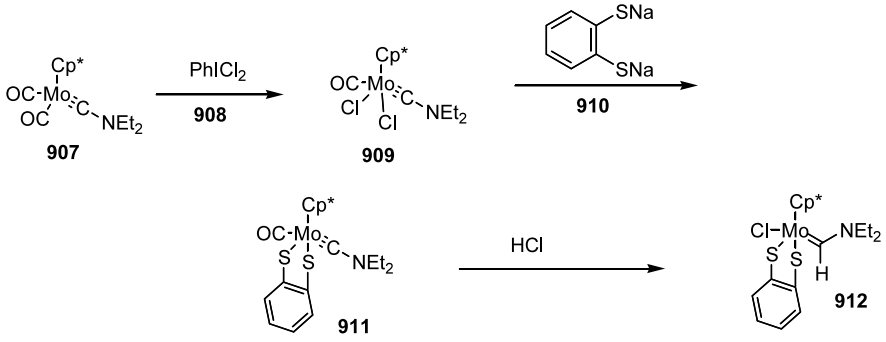
Scheme 136.



Scheme 137.



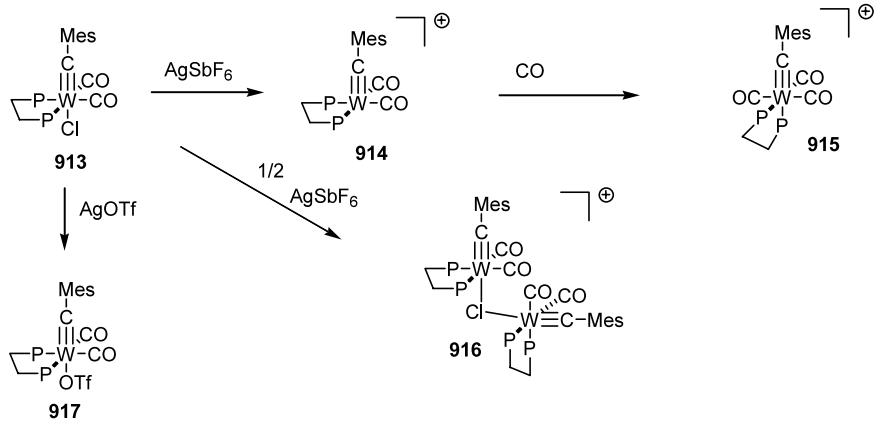
Scheme 138.



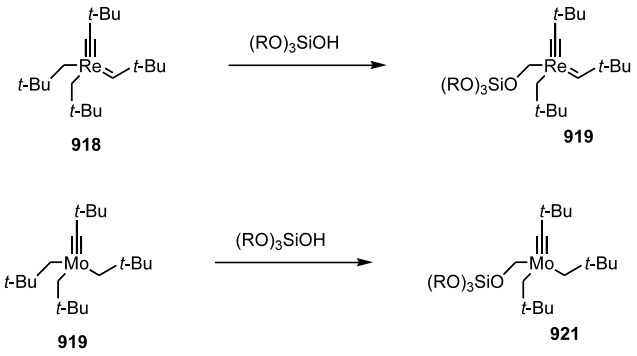
Scheme 139.

equivalent of alkyne led to osmium vinylidene complex **854**. A mechanism involving [2+2]-cycloaddition of trimethylsilylacetylene with the vinylidene complex, followed by an alkyne insertion, followed by protonation at the exocyclic alkene leads to cationic osmabenzene complex **857**, which affords osmabenzyne complex **858** upon proton loss. This paper was commented upon [597].

A series of osmium carbene and carbyne complexes were prepared from the reaction of osmium hydride species with various unsaturated organic species (Scheme 132) [598]. Reaction of osmium complex **859** with phenyl vinyl ether (**860**) led to the carbene complex **862**. Carbene complex **862** exists as a pair of rotamers. The analogous reaction using the triisopropylphosphine analog (**863**) led to carbyne complexes **866** and **867**, however a carbene complex (**865**) could be observed as an intermediate. The conversion of the carbene complex to the carbyne complex was an acid-catalyzed process. A stable carbene complex was also produced using dihydrofuran as the enol ether component. A stable carbene complex (**869**) was produced from ethyl vinyl ether



Scheme 140.



Scheme 141.

(**868**), which transformed to vinylidene complex **870** within 48 h at room temperature. These reaction processes were also evaluated computationally.

Base-induced rearrangements of calixarenetungsten–ethylene complexes were studied by density functional theory using simple tungsten complex **871** (Scheme 133) as a model for the parent ethylene–calixarene tungsten complex [599]. Deprotonation affords the anionic η^2-alkenyl complex **872**, which can rearrange to the corresponding carbyne complex **874** ($\Delta E = -84$ kJ mol^{-1}) or the vinyltungsten complex **873** ($\Delta E = +43$ kJ mol^{-1}). Protonation of the carbyne complex leads to the carbene complex.

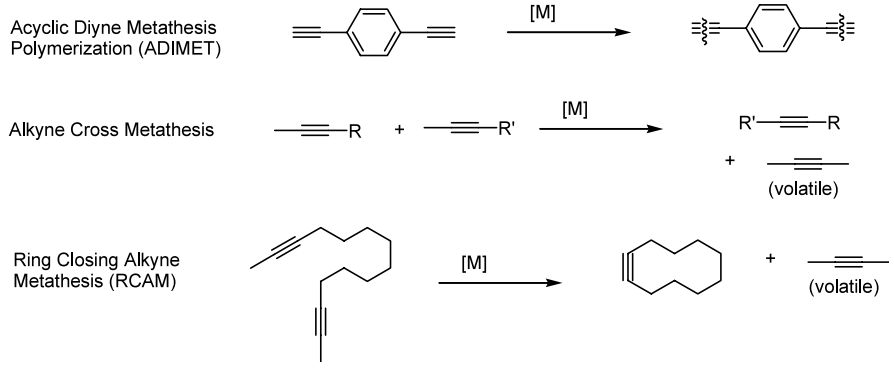
3.3. Reactivity

3.3.1. Addition reactions of metal–carbyne complexes

The reactivity profile for carbyne complex **876** (Scheme 134) was examined [600]. The complex was prepared from either carbyne complex **877** or **878**. The pK_a of carbyne complex **876** was determined to be 28.7 in THF. Protonation of **876** afforded cationic carbene complex **879**, which features an agostic interaction. Hydride addition afforded the corresponding anionic complex **880**. Deprotonation with *n*-butyllithium followed by the addition of various electrophiles (e.g. benzoyl bromide, **882**) led to substituted analogs of carbyne complex (e.g. **883**). Deprotonation reactions were also reported for carbyne complex **884**, obtained through reduction of acyloxycarbyne complex **883** [601]. Deprotonation followed by Cryptofix led to the carbide derivative **885**. Substituted carbyne complex derivatives of **883** were obtained upon treatment of complex **885** with various electrophiles.

Reaction of aminocarbyne–molybdenum complex **886** (Scheme 135) with diiron nonacarbonyl led to the addition product, heterobimetallic complex **887** [602]. Reaction of carbyne complex **888** with elemental sulfur led to the dithiocarboxylato complex **889** [603].

The reaction of cationic manganese–carbyne complex **890** (Scheme 136) with alkynyllithium reagents led to alkynylcarbene–manganese complex (e.g. **892**) [604]. Complexation of the alkyne afforded complex **893**, which exhibits dynamic equilibrium with complex **894**, similar to that observed for the analogous rhenium carbene complexes in Scheme 80. Related carbene complexes (e.g. **896**) could also be generated through thermolysis of alkynylcarbene–chromium manganese complex **895**. The reaction of manganese– and rhenium–carbyne complexes (e.g. **897**, Scheme 137) with diiron carbonyls led to heterobimetallic complexes



Scheme 142.

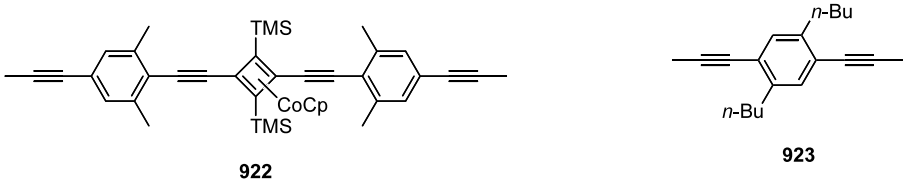
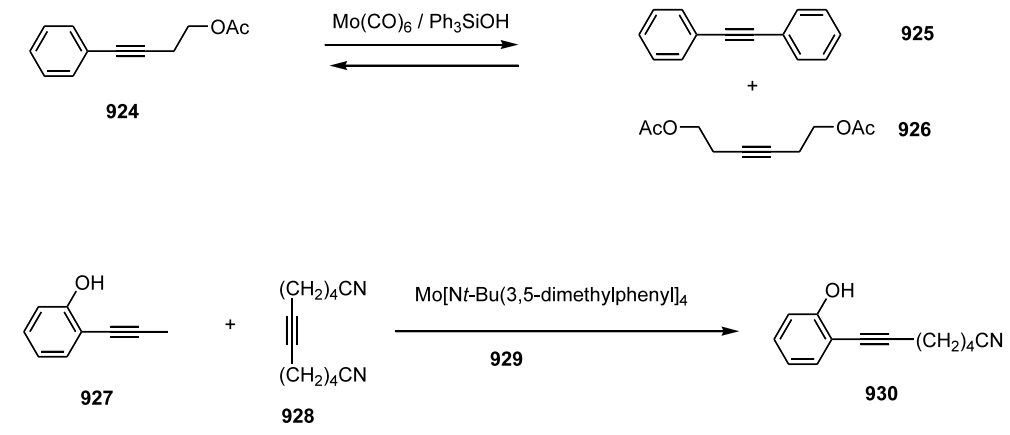
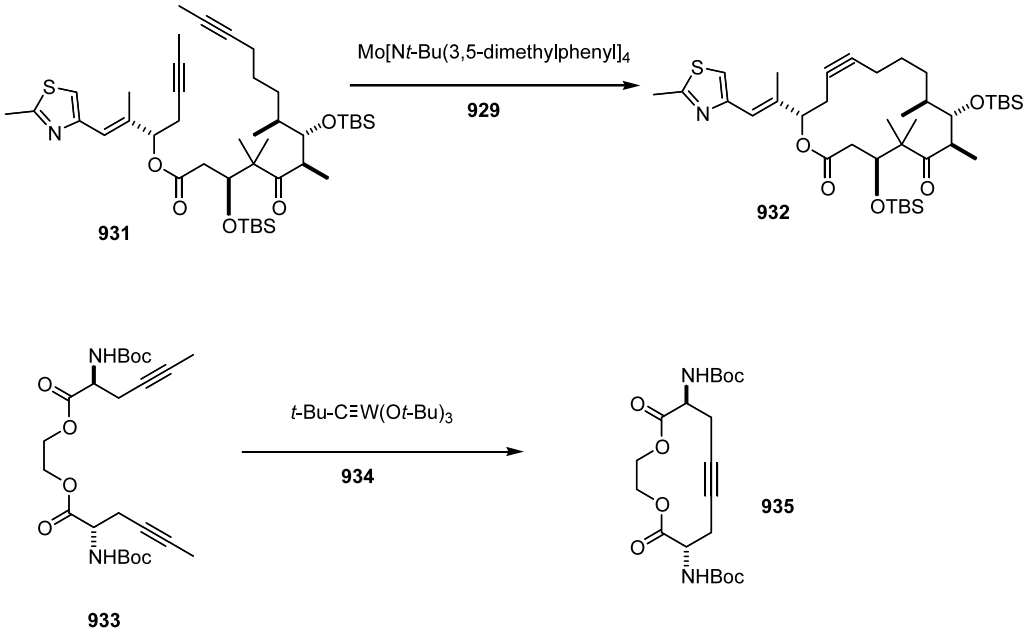


Fig. 16. Representative monomers polymerized through alkyne metathesis.



Scheme 143.



Scheme 144.

(e.g. **900**), accompanied by minor amounts of carbonyl compounds **899** and **901** [605].

A patent was awarded for the use of carbyne complexes to effect ROMP of norbornene [606].

3.3.2. Ligand exchange and other processes that do not involve the carbyne ligand

The reaction of arsenocarbyne–molybdenum and tungsten complexes (e.g. **902**, Scheme 138) with gold–carbonyl complex **903** led to the triarsenic complex **904** [607]. Phosphorus analogs (e.g. **905**) led to gold–phosphine complex **906**.

Oxidation of tungsten– and molybdenum carbyne complexes (e.g. **907**, Scheme 139) with phenyliodinium dichloride (**908**) led to the corresponding dichloro carbyne complexes (e.g. **909**) [608]. Ligand substitution reactions were demonstrated for carbyne complex **909**. Protonation of the dithio carbyne complex **911** with HCl led to the aminocarbene complex **912**. Various ligand substitution reactions were reported for carbyne complex **913** (Scheme 140) [609]. Treatment with silver triflate led to the corresponding carbyne triflate **917**. Treatment with silver hexafluoroantimonate led to the coordinatively unsaturated cationic carbyne complex **914**, which was unstable but readily coupled with CO or THF to afford the coordinatively saturated complexes (e.g. **915**). Reaction with half an equivalent of silver hexafluoroantimonate led to the chloride-bridged dimeric complex **916**. Isocyanide–alkenylcarbyne tungsten complexes were prepared by reaction of alkenylcarbyne analogs of complex **913** with isocyanide ligands, and were studied by electrochemistry [610].

The coupling of carbene(carbyne)rhenium complex **918** (Scheme 141) with various silyloxy species was

reported [611]. Solid-supported (silica-bond) and structurally similar monomeric derivatives of general structure **919** were prepared for comparison purposes. The silica-supported complex was characterized through 2D solid state NMR. A similar technique was applied for the preparation of molybdenum carbyne complexes bound to silica (e.g. **921**) [612].

3.3.3. Alkyne metathesis

Alkyne metathesis, which involves metal carbyne complexes as intermediates, has been covered comprehensively regardless of whether the initiator is a carbyne complex. Several reports using alkyne metathesis for natural product synthesis and for polymer synthesis appeared in 2001. The general classes of alkyne metathesis reactions are depicted in Scheme 142.

Several examples of polymer synthesis using alkyne metathesis were reported in 2001; representative substrates are depicted in Fig. 16. High molecular weight alkyne-containing polymers were prepared from monomers featuring multiple alkyne groups (e.g. **922** [613] and **923** [614]). In both cases polymerization was effected using a catalyst consisting of $Mo(CO)_6$ in the presence of a phenolic compound.

Several examples utilizing alkyne metathesis for the synthesis of nonpolymeric compounds were also reported. Metathesis equilibration of phenyl alkyl acetylene derivative **924** (Scheme 143) was achieved through reaction with $Mo(CO)_6$ in the presence of triphenylsilanol [615]. Cross metathesis of *o*-propynylphenol (**927**) and a variety of symmetrical alkynes (e.g. **928**) in the presence of molybdenum amide complex **929** was reported [616]. Ring closing alkyne metathesis was used to close the macrocyclic ring of epothilone (e.g. conversion of **931** to **932**, Scheme 144) [617,618]. Synthesis of macrocyclic α-aminoester derivatives (e.g. **935**) from dialkynes (e.g. **933**) was demonstrated using tungsten carbyne complex **934** as a catalyst [619].

Acknowledgements

We thank the National Science Foundation, the National Institutes of Health, and the Petroleum Research Fund, Administered by the American Chemical Society, for financial support of the portion of research herein emanating from our laboratories.

References

[1] J.W. Herndon, Coord. Chem. Rev. 227 (2002) 1.
[2] M.P. Doyle, T. Ren, Prog. Inorg. Chem. 49 (2001) 113.
[3] S. Kitagaki, S. Hashimoto, J. Synth. Org. Chem. Jpn. 59 (2001) 1157.
[4] D.C. Forbes, M.C. McMills, Curr. Org. Chem. 5 (2001) 1091.
[5] M.P. Doyle, W. Hu, Synlett (2001) 1364.
[6] D.J. Timmons, M.P. Doyle, J. Organomet. Chem. 617–618 (2001) 98.
[7] H.M.L. Davies, E.G. Antoulinakis, J. Organomet. Chem. 617–618 (2001) 47.
[8] A. Padwa, J. Organomet. Chem. 617–618 (2001) 3.
[9] J.C. Green, R.G. Scurr, P.R. Arnold, F.G.N. Cloke, J. Chem. Soc. Chem. Commun. (1997) 1963.
[10] A.A. Danopoulos, D.M. Hankin, G. Wilkinson, S.M. Cafferkey, T.K.N. Sweet, M.B. Hursthouse, Polyhedron 16 (1997) 3879.
[11] W.A. Herrmann, T. Weskamp, V.P.W. Bohm, Adv. Organomet. Chem. 48 (2001) 1.
[12] A.H. Cowley, J. Organomet. Chem. 617–618 (2001) 105.
[13] D. Enders, H. Gielen, J. Organomet. Chem. 617–618 (2001) 70.
[14] L.T. Li, S.M. Ma, Chin. J. Org. Chem. 21 (2001) 75.
[15] See: R.H. Crabtree, The Organometallic Chemistry of the Transition Metals, 2nd ed., Wiley-Interscience, New York, 1994, pp. 25–31See: .
[16] T.K. Firman, C.R. Landis, J. Am. Chem. Soc. 123 (2001) 11728.
[17] J. Org. Chem. 66 (2001) (1) preface.
[18] L. Jafarpour, S.P. Nolan, J. Organomet. Chem. 617–618 (2001) 17.
[19] A.H. Hoveyda, R.R. Schrock, Chem. Eur. J. 7 (2001) 945.
[20] J. Ruwwe, J.M. Martín-Alvarez, C.R. Horn, E.B. Bauer, S. Szafert, T. Lis, F. Hampel, P.C. Cagle, J.A. Gladysz, Chem. Eur. J. 7 (2001) 3931.
[21] B.X. Zhao, Chin. J. Org. Chem. 21 (2001) 83.
[22] S. Kotha, N. Sreenivasachary, Indian J. Chem. Sect. B 40 (2001) 763.
[23] H. Katayama, F. Ozawa, J. Synth. Org. Chem. Jpn. 59 (2001) 40.
[24] T.M. Trnka, R.H. Grubbs, Acc. Chem. Res. 34 (2001) 16.
[25] B. Clapham, T.S. Reger, K.D. Janda, Tetrahedron 57 (2001) 4637.
[26] A.K. Ghosh, E.S. Koltum, G. Bilcer, Synthesis (2001) 1281.
[27] S. Dahmen, S. Bräse, Synthesis (2001) 1431.
[28] A.C. Comely, S.C. Gibson, Angew. Chem. Int. Ed. 40 (2001) 1012.
[29] Y.R. de Miguel, E. Brulé, R.G. Margue, J. Chem. Soc. Perkin Trans. 1 (2001) 3085.
[30] M.G. Elliott, G. Williams, J. Chem. Soc. Perkin Trans. 1 (2001) 2303.
[31] A.J. Souers, J.A. Ellmann, Tetrahedron 57 (2001) 7431.
[32] L.T. Li, S.M. Ma, Chin. J. Org. Chem. 21 (2001) 398.
[33] R. Madsen, D. Tanner, M. Johansnsen, Dansk Kemi 82 (2001) 19.
[34] V. Cadierno, M.P. Gamasa, J. Gimeno, Eur. J. Inorg. Chem. (2001) 571.
[35] R. Beckhaus, C. Santamaria, J. Organomet. Chem. 617–618 (2001) 81.
[36] K.H. Dötz, C. Jäkel, W.C. Haase, J. Organomet. Chem. 617–618 (2001) 119.
[37] R.G. Cavell, R.P. Kamalesch Babu, K. Apurna, J. Organomet. Chem. 617–618 (2001) 158.
[38] H.G. Raubenheimer, S. Cronje, J. Organomet. Chem. 617–618 (2001) 170.
[39] T.S. Powers, W.D. Wulff, J. Quinn, Y. Shi, W. Jiang, R. Hsung, M. Parisi, A. Rahm, X.W. Jiang, G.P.A. Yap, A.L. Rheingold, J. Organomet. Chem. 617–618 (2001) 182.
[40] J. Barluenga, J. Flórez, F.J. Fañanás, J. Organomet. Chem. 624 (2001) 5.
[41] Y.C. Lin, J. Organomet. Chem. 617–618 (2001) 141.
[42] S.W. Lai, M.C.W. Chan, Y. Wang, H.W. Lam, S.M. Peng, C.M. Che, J. Organomet. Chem. 617–618 (2001) 133.
[43] R.A. Michelin, A.J.L. Pombeiro, M.F.C. Guedes de Silva, Coord. Chem. Rev. 218 (2001) 75.
[44] J.B. Diminnie, X. Liu, H. Cai, Z. Wu, J.R. Blanton, T. Chen, A.A. Tuinman, K.T. Quisenberry, C.E. Vallet, R.A. Zuhr, D.B.

Beach, Z. Peng, Y.D. Wu, T.E. Concolino, A.L. Rheingold, Z. Xue, Pure Appl. Chem. 73 (2001) 331.
[45] A.J. Fletcher, S.D.R. Christie, J. Chem. Soc. Perkin Trans. 1 (2001) 1.
[46] A. Kirschning, M. Jesberger, K.U. Schöning, Synthesis (2001) 507.
[47] M.T. Liang, D.X. Wang, Chin. J. Org. Chem. 21 (2001) 97.
[48] M.K. Whittlesey, Organomet. Chem. 29 (2001) 350.
[49] C. Florianai, R. Floriani-Moro, Adv. Organomet. Chem. 47 (2001) 167.
[50] M.A. Esteruelas, L.A. Oro, Adv. Organomet. Chem. 47 (2001) 1.
[51] M.S. Sanford, M. Ulman, R.H. Grubbs, J. Am. Chem. Soc. 123 (2001) 749.
[52] M.S. Sanford, J.A. Love, R.H. Grubbs, J. Am. Chem. Soc. 123 (2001) 6543.
[53] T.M. Trnka, M.W. Day, R.H. Grubbs, Angew. Chem. Int. Ed. 40 (2001) 3441.
[54] M.A.O. Volland, C. Adlhart, C.A. Kiener, P. Chen, P. Hofmann, Chem. Eur. J. 7 (2001) 4621.
[55] M.A.O. Volland, B.F. Straub, I. Gruber, F. Rominger, P. Hofmann, J. Organomet. Chem. 617–618 (2001) 288.
[56] P. Nieczper, P.W.N.M. van Leeuwen, J.C. Mol, M. Lutz, A.L. Spek, J. Organomet. Chem. 625 (2001) 58.
[57] D. Sémeril, J. Le Nôtre, C. Bruneau, P.H. Dixneuf, A.F. Kolomiets, S.N. Osipev, New J. Chem. 25 (2001) 16.
[58] B. Çetinkaya, S. Demir, I. Özdemir, L. Toupet, D. Sémeril, C. Bruneau, P.H. Dixneuf, New J. Chem. 25 (2001) 519.
[59] J.N. Coalter, III, K.G. Caulton, New J. Chem. 25 (2001) 679.
[60] T.L. Choi, C.W. Lee, A.K. Chatterjee, R.H. Grubbs, J. Am. Chem. Soc. 123 (2001) 10417.
[61] J. Louie, R.H. Grubbs, Angew. Chem. Int. Ed. 40 (2001) 247.
[62] J.S. Kingsbury, S.B. Garber, J.M. Giftos, B.L. Gray, M.M. Okamoto, R.A. Farrer, J.T. Fourkas, A.H. Hoveyda, Angew. Chem. Int. Ed. 40 (2001) 4251.
[63] S. Randl, N. Buschmann, S.J. Connon, S. Blechert, Synlett (2001) 1547.
[64] J. Dowden, J. Savović, Chem. Commun. (2001) 37.
[65] A. Fürstner, H. Krause, L. Ackermann, C.W. Lehmann, Chem. Commun. (2001) 2240.
[66] A. Fürstner, O. Goth, A. Düffels, G. Seidl, M. Liebl, B. Gabor, R. Mynott, Chem. Eur. J. 7 (2001) 4811.
[67] W. Buchowicz, F. Ingold, J.C. Mol, M. Lutz, A.L. Spek, Chem. Eur. J. 7 (2001) 2842.
[68] L. Delaude, A. Demonceau, A.F. Noels, Chem. Commun. (2001) 986.
[69] K. Nomura, A. Sagara, Y. Imanishi, Chem. Lett. (2001) 36.
[70] Y. Takashima, Y. Nakayama, A. Harada, Chem. Lett. (2001) 48.
[71] K. Melis, D. De Vos, P. Jacobs, F. Verpoort, J. Mol. Catal. A 169 (2001) 47.
[72] M. Mayr, B. Mayr, M.R. Bucheiser, Angew. Chem. Int. Ed. 40 (2001) 3839.
[73] P. Nieczpor, W. Buchowicz, W.J.N. Meester, F.P.J.T. Rutjes, J.C. Mol, Tetrahedron Lett. 42 (2001) 7103.
[74] U. Siemeling, R.R. Schrock, A. Stammler, H.G. Stammler, O. Kuhnert, Z. Anorg. Allg. Chem. 627 (2001) 925.
[75] K. Kodama, Chem. Abstr. 134 (2001) 340823.
[76] H. Hiraike, T. Morita, Chem. Abstr. 135 (2001) 273399.
[77] H. Yamazaki, A. Sasaki, Y. Inoue, A. Aihara, H. Kawai, Chem. Abstr. 134 (2001) 353682.
[78] T. Sugawara, Chem. Abstr. 134 (2001) 353702.
[79] J.M. Botha, J.P.K. Reynhardt, C. Schalkwyk, H.C. Vosloo, Chem. Abstr. 135 (2001) 79275.
[80] K.C. Hultzsch, P.J. Bonitatebus, Jr., J. Jernelius, R.R. Schrock, A.H. Hoveyda, Organometallics 20 (2001) 4705.
[81] W.C.P. Tsang, R.R. Schrock, A.H. Hoveyda, Organometallics 20 (2001) 5658.
[82] D.R. Cefalo, A.F. Kiely, M. Wuchrer, J.Y. Jamieson, R.R. Schrock, A.H. Hoveyda, J. Am. Chem. Soc. 123 (2001) 3139.
[83] S.L. Aeilts, D.R. Cefalo, P.J. Bonitatebus, Jr., J.H. Hauser, A.H. Hoveyda, R.R. Schrock, Angew. Chem. Int. Ed. 40 (2001) 1452.
[84] T.J. Seiders, W. Ward, R.H. Grubbs, Org. Lett. 3 (2001) 3225.
[85] A. Fürstner, L. ackermann, K. Beck, H. Hori, K. Langermann, M. Liebl, C. Six, W. Leitner, J. Am. Chem. Soc. 123 (2001) 9000.
[86] R.C. Buijsman, E. van Vuuren, J.G. Sterrenburg, Org. Lett. 3 (2001) 3785.
[87] A. Fürstner, L. Ackermann, B. Gabor, R. Goddard, C.W. Lehmann, R. Mynott, F. Steltzer, O.R. Thiel, Chem. Eur. J. 7 (2001) 3236.
[88] Y.M. Alam, K. Yang, G.I. Georg, Org. Lett. 3 (2001) 1411.
[89] W. Buchowicz, M.N. Holerca, V. Percec, Macromolecules 34 (2001) 3842.
[90] M. Tlenkopatchev, S. Fomine, J. Organomet. Chem. 630 (2001) 157.
[91] J. Handzlik, J. Ogonowski, J. Mol. Catal. A 175 (2001) 215.
[92] J. Silberg, T. Schareina, R. Kempe, K. Wurst, M.R. Buchmeiser, J. Organomet. Chem. 622 (2001) 6.
[93] H.D. Maynard, S.Y. Okada, R.H. Grubbs, J. Am. Chem. Soc. 123 (2001) 1275.
[94] C. Detrembleur, C. Jérôme, M. Claes, P. Louette, R. Jérôme, Angew. Chem. Int. Ed. 40 (2001) 1268.
[95] A. Grenz, S. Ceccarelli, C. Bohm, Chem. Commun. (2001) 1726.
[96] T. Arnaud, A.G.M. Barrett, R. Seigfried, Tetrahedron Lett. 42 (2001) 7899.
[97] T. Arnaud, A.G.M. Barrett, B.T. Hopkins, F.J. Zécril, Tetrahedron Lett. 42 (2001) 8215.
[98] A.G.M. Barrett, S.M. Cramp, A.J. Hennessey, P.A. Procopiou, R.S. Roberts, Org. Lett. 3 (2001) 271.
[99] E.J. Enholm, M.E. Gallagher, Org. Lett. 3 (2001) 3397.
[100] E.J. Enholm, J.S. Cottone, Org. Lett. 3 (2001) 3959.
[101] C. Bohn, C.L. Dinter, I. Schiffers, L. Defrére, Synlett (2001) 1875.
[102] J.P. Claverie, S. Viala, V. Maurel, C. Novat, Macromolecules 34 (2001) 382.
[103] H.W. Allcock, W.R. Laredo, E.C. Kellam, III, R.V. Morford, Macromolecules 34 (2001) 787.
[104] H.R. Allcock, E.C. Kellam, III, M.A. Hofmann, Macromolecules 34 (2001) 5140.
[105] H.R. Allcock, C.R. de Denus, R. Prange, W.R. Laredo, Macromolecules 34 (2001) 2757.
[106] B.L. Langsdorf, X. Zhou, M. Lonergan, Macromolecules 34 (2001) 2450.
[107] K.J. Watson, D.R. Anderson, S.T. Nguyen, Macromolecules 34 (2001) 3507.
[108] J.M. Kim, H.T. Shin, K.H. Park, T.H. Kim, S.Y. Ju, D.K. Han, K.D. Ahn, Macromolecules 34 (2001) 4291.
[109] K. Nomura, S. Takahashi, Y. Iminishi, Macromolecules 34 (2001) 4712.
[110] A. Mariana, S. Fiori, Y. Chekanov, J.A. Pojman, Macromolecules 34 (2001) 6539.
[111] R. Charvet, B.M. Novak, Macromolecules 34 (2001) 7680.
[112] L. Noirez, M. Ungerank, F. Steltze, Macromolecules 34 (2001) 7885.
[113] C.W. Bielawski, D. Benitez, T. Morita, R.H. Grubbs, Macromolecules 34 (2001) 8610.
[114] C.W. Bielawski, R.H. Grubbs, Macromolecules 34 (2001) 8838.
[115] D. Amoroso, G.P.A. Yap, D.E. Fogg, Can. J. Chem. 79 (2001) 958.
[116] S. Meier, H. Reisinger, R. Haag, S. Mecking, R. Mülhaupt, F. Stelzer, Chem. Commun. (2001) 855.
[117] R.G. Davies, V.C. Gibson, M.B. Hursthouse, M.E. Light, E.L. Marshall, M. North, D.A. Robson, I. Thompson, A.J.P. White, D.J. Williams, P.J. Williams, J. Chem. Soc. Perkin Trans. 1 (2001) 3365.

[118] D. Gao, Y. Roh, N.L. Bauld, Adv. Synth. Catal. 343 (2001) 269.
[119] K. Eder, E. Reichel, H. Schottenberger, C.G. Huber, M.R. Buchmeister, Macromolecules 34 (2001) 4334.
[120] K.R. Brzezinska, T.J. Deming, Macromolecules 34 (2001) 4348.
[121] M. Kimura, K. Wada, K. Ohta, K. Hanabusa, H. Shirai, N. Kobayashi, Macromolecules 34 (2001) 4706.
[122] P.M. O'Donnell, K. Brzezinska, D. Powell, K.B. Wagener, Macromolecules 34 (2001) 6845.
[123] T.E. Hopkins, J.H. Pawlow, D.L. Koren, K.S. Deters, S.M. Solivan, J.A. Davis, F.J. Gómez, K.B. Wagener, Macromolecules 34 (2001) 7920.
[124] S.W. Craig, J.A. Manzer, E.B. Coughlin, Macromolecules 34 (2001) 7929.
[125] S. Aimee, A.J. Arce, O. Chiantore, R. Gobetto, A. Russo, Y. De Sanctis, J. Organomet. Chem. 622 (2001) 43.
[126] O. Arjona, A.G. Csáky, M.C. Murcia, J. Plumet, M.B. Mula, J. Organomet. Chem. 627 (2001) 105.
[127] M.J. Bassindale, P. Hamley, J.P.A. Harrity, Tetrahedron Lett. 42 (2001) 9055.
[128] D.L. Wright, L.C. Usher, M. Estrella-Jimenez, Org. Lett. 3 (2001) 4275.
[129] S. Randl, S.J. Connor, S. Blechert, Chem. Commun. (2001) 1796.
[130] D.S. La, E.S. Sattely, J.G. Ford, R.R. Schrock, A.H. Hoveyda, J. Am. Chem. Soc. 123 (2001) 7767.
[131] S.N. Osipov, N.M. Kobelíkova, G.T. Shchetnikov, A.F. Kolomiets, C. Bruneau, P.H. Dixneuf, Synlett (2001) 621.
[132] K.C. Nicolaou, J.A. Vega, G. Vassilikogiannako, Angew. Chem. Int. Ed. 40 (2001) 4441.
[133] L. Zhang, C.W. Borgsenko, T.A. Albright, E.R. Bittner, T.R. Lee, J. Org. Chem. 66 (2001) 5275.
[134] L. Zhang, C.W. Borgsenko, T.R. Lee, J. Org. Chem. 66 (2001) 5284.
[135] S. BouzBouz, J. Cossy, Org. Lett. 3 (2001) 1451.
[136] J. Cossy, S. BouzBouz, A.H. Hoveyda, J. Organomet. Chem. 624 (2001) 327.
[137] J. Cossy, S. BouzBouz, A.H. Hoveyda, J. Organomet. Chem. 634 (2001) 216.
[138] T.L. Choi, A.K. Chatterjee, R.H. Grubbs, Angew. Chem. Int. Ed. 40 (2001) 1277.
[139] S. Imhof, S. Randl, S. Blechert, Chem. Commun. (2001) 1692.
[140] A. Dondoni, P.P. Giovanninni, A. Mara, J. Chem. Soc. Perkin Trans. 1 (2001) 2380.
[141] U. Eichelberger, M. Mansourova, L. Hennig, M. Findeisen, S. Giesa, D. Müller, P. Welzel, Tetrahedron 57 (2001) 9737.
[142] C. Pietraszuk, H. Fischer, M. Kujawa, B. Marciniec, Tetrahedron Lett. 42 (2001) 1175.
[143] K. Grela, M. Bienick, Tetrahedon Lett. 42 (2001) 6425.
[144] D. Forget-Champagne, M. Mondon, N. Fonteneau, J.P. Gesson, Tetrahedron Lett. 42 (2001) 7229.
[145] F.C. Engelhardt, M.J. Schmitt, R.E. Taylor, Org. Lett. 3 (2001) 2209.
[146] A. Lera, C.J. Highes, Org. Lett. 3 (2001) 2765.
[147] A.K. Chatterjee, T.L. Choi, R.H. Grubbs, Synlett (2001) 1034.
[148] S. Randl, S. Gessler, H. Wakamatsu, S. Blechert, Synlett (2001) 430.
[149] J. Cossy, C. Willis, V. Bellosta, Synlett (2001) 1578.
[150] P.G. Breed, J.A. Ramsden, J.M. Brown, Can. J. Chem. 79 (2001) 1049.
[151] E. Sugiono, H. Detert, Synthesis (2001) 893.
[152] T. Yasuda, J. Abe, T. Iyoda, T. Kawai, Chem. Lett. (2001) 812.
[153] C. Böhm, O. Reiser, Org. Lett. 3 (2001) 1315.
[154] C.C. Lin, T. Subramanian, T.S. Hus, G.T. Fan, C.C. Lin, J. Chin. Chem. Soc. 48 (2001) 55.
[155] K.C. Nicolaou, R. Hughes, S.Y. Cho, N. Wissinger, H. Labischinski, R. Endermann, Chem. Eur. J. 7 (2001) 3824.
[156] N. Batoux, R. Benhaddou-Zerrouki, P. Bressolier, R. Granet, G. Laumont, A.M. Aubertin, P. Krausz, Tetrahedron Lett. 42 (2001) 1491.
[157] S. Faure, O. Piva, Tetrahedron Lett. 42 (2001) 255.
[158] A.B. Smith, III, C.M. Adams, S.A. Kozmin, D.V. Paone, J. Am. Chem. Soc. 123 (2001) 5925.
[159] A.B. Smith, III, C.M. Adams, S.A. Kozmin, J. Am. Chem. Soc. 123 (2001) 990.
[160] A. Fürstner, O.R. Thiel, L. Ackermann, Org. Lett. 3 (2001) 449.
[161] C.W. Lee, R.H. Grubbs, J. Org. Chem. 66 (2001) 7155.
[162] L.A. Paquette, J. Méndez-Andino, Tetrahedron Lett. 42 (2001) 967.
[163] M.C. Hewitt, P.H. Seeberger, J. Org. Chem. 66 (2001) 4233.
[164] M.C. Hewitt, P.H. Seeberger, Org. Lett. 3 (2001) 3699.
[165] D. Spitzner, K. Oesterreich, Eur. J. Org. Chem. (2002) 1883.
[166] M. Nevalainen, A.M.P. Koskinen, Angew. Chem. Int. Ed. 40 (2001) 4060.
[167] M.K. Gurjar, S.V. Ravindranadh, S. Karmaker, Chem. Commun. (2001) 241.
[168] J. Ravn, P. Nielson, J. Chem. Soc. Perkin Trans. 1 (2001) 985.
[169] R. Naasz, L.A. Arnold, A.J. Minaard, B.L. Feringa, Chem. Commun. (2001) 735.
[170] P.S. Aburel, C. Rømming, K. Ma, K. Undheim, J. Chem. Soc. Perkin Trans. 1 (2001) 1458.
[171] F.D. Boyer, I. Hanna, Tetrahedron Lett. 42 (2001) 1275.
[172] P.R. Skaanderup, R. Madsen, Chem. Commun. (2001) 1106.
[173] D.C. Braddock, A.J. Wildsmith, Tetrahedron Lett. 42 (2001) 3239.
[174] C. Agami, F. Couty, N. Rabasso, Tetrahedron Lett. 42 (2001) 4633.
[175] J.A. Burlison, J.M. Gray, D.G.J. Young, Tetrahedron Lett. 42 (2001) 5363.
[176] J.R. Green, Synlett (2001) 353.
[177] K.S. Huang, E.C. Wang, Tetrahedron Lett. 42 (2001) 6155.
[178] P.A. Evans, L.J. Kennedy, Tetrahedron Lett. 42 (2001) 7015.
[179] A. Okada, T. Oshima, M. Shibasaki, Tetrahedron Lett. 42 (2001) 8023.
[180] A. Nishikawa, S. Saito, Y. Hashimoto, K. Koga, R. Shirai, Tetrahedron Lett. 42 (2001) 9195.
[181] M. Jorgensen, E.H. Iversen, A.L. Paulsen, R. Madsen, J. Org. Chem. 66 (2001) 4630.
[182] K. Kadota, M. Takeuchi, T. Taniguchi, K. Ogasawara, Org. Lett. 3 (2001) 1769.
[183] H. Ovaa, G.A. van der Marel, J.H. van Boom, Tetrahedron Lett. 42 (2001) 5749.
[184] K. Lee, C. Cass, K.A. Jacobson, Org. Lett. 3 (2001) 597.
[185] W.J. Choi, J.G. Park, S.J. Yoo, H.O. Kim, H.R. Moon, M.W. Chun, Y.H. Jung, L.S. Jeon, J. Org. Chem. 66 (2001) 6490.
[186] I. Gillaizeau, S. Charamon, L.A. Agrofoglio, Tetrahedron Lett. 42 (2001) 8817.
[187] E.M. Codesido, L. Castedo, J.R. Granja, Org. Lett. 3 (2001) 1483.
[188] H. Tang, N. Yusaff, J.L. Wood, Org. Lett. 3 (2001) 1563.
[189] J.G. Boiteau, P. Van de Weghe, J. Eustache, Org. Lett. 3 (2001) 2737.
[190] S. Liras, M.P. Allen, J.F. Blake, Org. Lett. 3 (2001) 3483.
[191] S. Liras, J.E. Davoren, J. Bordner, Org. Lett. 3 (2001) 703.
[192] M.T. Crimmins, E.A. Tabet, J. Org. Chem. 66 (2001) 4012.
[193] M.E. Krafft, M. Sugiura, K.A. Abboud, J. Am. Chem. Soc. 123 (2001) 9174.
[194] R.C. Hughes, C.A. Dvorak, A.I. Myers, J. Org. Chem. 66 (2001) 5545.
[195] F.D. Boyer, I. Hanna, S.P. Nolan, J. Org. Chem. 66 (2001) 4094.
[196] M.E. Krafft, Y.Y. Cheung, K.A. Abboud, J. Org. Chem. 66 (2001) 7443.
[197] C.S. Callum, T.S. Lowary, J. Org. Chem. 66 (2001) 8961.

[198] A. Srikrishna, M.S. Rao, S.J. Gharpure, N.C. Babu, Synlett (2001) 1986.
[199] G. Sabitha, C.S. Reddy, B.S. Babu, J.S. Yadav, Synlett (2001) 1787.
[200] S. Cuiard, M. Santelli, J.L. Parrain, Synlett (2001) 553.
[201] S. Krikstolaityté, A. Sackus, C. Rømming, K. Undheim, Tetrahedron: Asymmetry 12 (2001) 393.
[202] S. Kotha, N. Sreenivasachary, K. Mohanraja, S. Durani, Bioorg. Med. Chem. Lett. 11 (2001) 1421.
[203] D.C. Harrowven, M.C. Lucas, P.D. Howes, Tetrahedron 57 (2001) 9157.
[204] L.A. Paquette, I. Efremov, J. Am. Chem. Soc. 123 (2001) 4492.
[205] L. Belvisi, L. Colombo, M. Colombo, M. di Giacomo, L. Manzoni, B. Vodopivec, C. Scolastico, Tetrahedron 57 (2001) 6463.
[206] A. Boto, R. Hernández, Y. de Leon, E. Suárez, J. Org. Chem. 66 (2001) 7796.
[207] B.B. Snider, N.A. Hawryluk, Org. Lett. 3 (2001) 569.
[208] S.H. Lim, M.D. Curtis, P. Beak, Org. Lett. 3 (2001) 711.
[209] J. Tesler, R. Beumer, A.A. Bell, S.M. Ceccarelli, D. Monti, C. Gennari, Tetrahedron Lett. 42 (2001) 9187.
[210] K. Pachamuthu, Y.D. Vankar, J. Organomet. Chem. 624 (2001) 359; Erratum: J. Organomet. Chem. 648 (2002) 307.
[211] Y. Banba, C. Abe, H. Nemoto, A. Kato, I. Adachi, H. Takahata, Tetrahedron: Asymmetry 12 (2001) 817.
[212] S.N. Osipov, O.I. Artyushin, A.F. Kolomiets, C. Bruneau, M. Picquet, P.H. Dixneuf, Eur. J. Org. Chem. (2001) 3891.
[213] K.L. Lee, J.B. Goh, S.F. Martin, Tetrahedon Lett. 42 (2001) 1635.
[214] H. Suzuki, N. Yamazaki, C. Kibayashi, Tetrahedron Lett. 42 (2001) 3013.
[215] T. Subramanian, C.C. Lin, C.C. Lin, Tetrahedron Lett. 42 (2001) 4079.
[216] S. Fustero, A. Navarro, B. Pina, J.G. Soler, A. Bartolomé, A. Asensio, A. Simón, P. Bravo, G. Fronza, A. Volonterio, M. Zanda, Org. Lett. 3 (2001) 2621.
[217] C. Agami, F. Couty, N. Rabasso, Tetrahedron 57 (2001) 5393.
[218] M. Sabat, C.R. Johnson, Tetrahedron Lett. 42 (2001) 1209.
[219] Y. Du, D.F. Wiemar, Tetrahedron Lett. 42 (2001) 6069.
[220] M. Arisawa, C. Theeraladanon, A. Nishida, M. Nakayama, Tetrahedron Lett. 42 (2001) 8029.
[221] P.A. Evans, J.E. Robinson, K.K. Moffett, Org. Lett. 3 (2001) 3269.
[222] C.J. Creighton, A.B. Reitz, Org. Lett. 3 (2001) 893.
[223] R.G. Arrayás, M. Alcudia, L.S. Liebeskind, Org. Lett. 3 (2001) 3381.
[224] G. Vo-Thanh, V. Boucard, H. Sauriat-Dorizon, F. Guibé, Synlett (2001) 37.
[225] E.C. Wang, K.S. Huang, B.W. Lin, J.R. Lin, M.K. Hsu, J. Chin. Chem. Soc. 48 (2001) 83.
[226] W.H. Pearson, A. Aponik, Org. Lett. 3 (2001) 1327.
[227] A.B. Smith, III, Y.S. Cho, L.E. Zawacki, R. Hirschmann, G.R. Pettit, Org. Lett. 3 (2001) 4063.
[228] S.S. Kinderman, J.H. van Maarseveen, H.E. Schoemaker, H. Hiemstra, F.P.J.T. Rutjes, Org. Lett. 3 (2001) 2045.
[229] D.J. Wallace, J.M. Goodman, D.J. Kennedy, A.J. Davies, C.J. Cowden, M.S. Ashwood, I.F. Cottrell, U.H. Dolling, P.J. Reider, Org. Lett. 3 (2001) 671.
[230] D.J. Wallace, P.G. Bulger, D.J. Kennedy, M.S. Ashwood, I.F. Cottrell, U.H. Dolling, Synlett (2001) 357.
[231] C. Paolucci, L. Mattioli, J. Org. Chem. 66 (2001) 4787.
[232] C.F. Klitzke, R.A. Pilli, Tetrahedron Lett. 42 (2001) 5605.
[233] B. Alcaide, P. Almendros, J.M. Alonso, M.F. Aly, M.C. Redondo, Synlett (2001) 773.
[234] R. Stürmer, B. Schäfer, V. Wolfart, H. Stahr, U. Kazmaier, G. Helchen, Synthesis (2001) 46.
[235] H. Mues, U. Kazmaier, Synthesis (2001) 487.
[236] T. Hoffmann, H. Lanig, R. Weibl, P. Gmeiner, Angew. Chem. Int. Ed. 40 (2001) 3361.
[237] L. Rambaud, P. Compain, O.R. Martin, Tetrahedron: Asymmetry 12 (2001) 1807.
[238] S.H. Park, K. Kang, S. Ko, S. Park, S. Chang, Tetrahedron: Asymmetry 12 (2001) 2621.
[239] A.I. Meyers, S.V. Downing, M.J. Weiser, J. Org. Chem. 66 (2001) 1413.
[240] L.A. Paquette, C.S. Ra, J.D. Schloss, S.M. Leit, J.C. Gallucci, J. Org. Chem. 66 (2001) 3564.
[241] H.A. Dondas, G. Balme, B. Clique, R. Grigg, A. Hodgeson, J. Morris, V. Sridharan, Tetrahedron Lett. 42 (2001) 8673.
[242] F.X. Felpin, S. Girard, G. Vo-Thanh, R.J. Robbins, J. Villiéras, J. Lebreton, J. Org. Chem. 66 (2001) 6305.
[243] S.H. Lim, S. Ma, P. Beak, J. Org. Chem. 66 (2001) 9056.
[244] N. Papaioannou, C.A. Evans, J.T. Blank, S.J. Miller, Org. Lett. 3 (2001) 2879.
[245] M.G. Banwell, A.M. Bray, A.J. Edwards, D.J. Wong, New J. Chem. 25 (2001) 1347.
[246] M.V.R. Reddy, H.C. Brown, P.V. Ramachandran, J. Organomet. Chem. 624 (2001) 239.
[247] C. Herld, R. Fröhlich, P. Metz, Angew. Chem. Int. Ed. 40 (2001) 1058.
[248] M.V.R. Reddy, A.J. Yucel, P.V. Ramachandran, J. Org. Chem. 66 (2001) 2512.
[249] M.V.R. Reddy, J.P. Rearick, N. Hoch, P.V. Ramachandran, Org. Lett. 3 (2001) 19.
[250] J. Cossy, F. Pradaux, S. Bouzbouz, Org. Lett. 3 (2001) 2233.
[251] P. de Armas, F. García-Tellado, J.J. Marrero-Tellado, Eur. J. Org. Chem. (2001) 4423.
[252] P. Langer, T. Eckhardt, N.N.R. Saleh, I. Karimé, P. Müller, Eur. J. Org. Chem. (2001) 3657.
[253] M.T. Crimmins, K.A. Emmitte, J. Am. Chem. Soc. 123 (2001) 1533.
[254] I. Kadota, A. Ohno, K. Matsuda, Y. Yamamoto, J. Am. Chem. Soc. 123 (2001) 6702.
[255] J.D. Ranier, J.M. Cox, S.P. Allwein, Tetrahedon Lett. 42 (2001) 179.
[256] H. Imai, H. Uehara, M. Inoue, H. Oguri, T. Oishi, M. Hirama, Tetrahedron Lett. 42 (2001) 6219.
[257] J.D. Ranier, S.P. Allwein, J.M. Cox, J. Org. Chem. 66 (2001) 1380.
[258] T. Oishi, S.I. Tanaka, Y. Ogasawara, K. Maeda, H. Oguri, M. Hirama, Synlett (2001) 952.
[259] M. Maruyama, K. Maeda, T. Oishi, H. Oguri, M. Hirama, Heterocycles 54 (2001) 93.
[260] M. Hirama, T. Oishi, H. Uehara, M. Inoue, M. Maruyama, H. Guri, M. Satake, Science 294 (2001) 1904.
[261] D.L.J. Clive, H. Cheng, Chem. Commun. (2001) 605.
[262] A. Fürstner, K. Radkowski, Chem. Commun. (2001) 671.
[263] P.A.V. van Hooft, G.A. van der Marel, C.A.A. van Boeckel, J.H. van Boom, Tetrahedron Lett. 42 (2001) 1769.
[264] B.C. Maity, V.M. Swamy, A. Sarkar, Tetrahedron Lett. 42 (2001) 4373.
[265] E.A. Voight, C. Rein, S.D. Burke, Tetrahedron Lett. 42 (2001) 8747.
[266] S.D. Burke, E.A. Voight, Org. Lett. 3 (2001) 237.
[267] M.P. Heck, C. Baylon, S.P. Nolan, C. Mioskowki, Org. Lett. 3 (2001) 1989.
[268] G. Ki, S.Y. Jeon, Bull. Korean Chem. Soc. 22 (2001) 1156.
[269] A. Ahmed, E. Öhler, J. Mulzer, Synthesis (2001) 2007.
[270] B. Schmidt, D. Costisella, R. Roggenback, M. Westhus, H. Wildemann, P. Eilbracht, J. Org. Chem. 66 (2001) 7658.
[271] L. Liu, M.H.D. Postema, J. Am. Chem. Soc. 123 (2001) 8602.
[272] A. Schnaars, C. Schultz, Tetrahedron 57 (2001) 519.
[273] G.T. Nadolski, B.S. Davidson, Tetrahedron Lett. 42 (2001) 797.
[274] B.T. Messenger, B.S. Davidson, Tetrahedon Lett. 42 (2001) 801.

[275] A.K. Ghosh, Y. Wang, J.T. Kim, J. Org. Chem. 66 (2001) 8973.
[276] H.W. Lee, C.S. Jeong, S.H. Yoon, I.Y.C. Lee, Bull. Korean Chem. Soc. 22 (2001) 791.
[277] H.W. Lee, S.H. Yoon, I.Y.C. Lee, B.Y. Chung, Bull. Korean Chem. Soc. 22 (2001) 1179.
[278] T. Taniguchi, K. Ogasawara, Tetrahedron Lett. 42 (2001) 3359.
[279] Y. Baba, G. Saha, S. Nakao, C. Iwata, T. Tanaka, T. Ibukara, H. Ohishi, Y. Takemoto, J. Org. Chem. 66 (2001) 81.
[280] A.J. Locke, C. Jones, C.J. Richards, J. Organomet. Chem. 637–639 (2001) 669.
[281] A.M. Sørensen, K.E. Nielsen, B. Vogg, P.J. Jacobsen, P. Nielsen, Tetrahedron 57 (2001) 10191.
[282] M.S.M. Timmer, H. Ovaa, D.V. Filippov, G.A. van der Marel, J.H. van Boom, Tetrahedron Lett. 42 (2001) 8231.
[283] D.S. Stoianova, P.R. Hanson, Org. Lett. 3 (2001) 3285.
[284] K.T. Sprott, M.D. McReynolds, P.R. Hanson, Org. Lett. 3 (2001) 3939.
[285] K.T. Sprott, M.D. McReynolds, P.R. Hanson, Synthesis (2001) 612.
[286] J.D. Moore, K.T. Sprott, P.R. Hanson, Synlett (2001) 605.
[287] J.G. Boiteau, P. Van de Weghe, J. Eustache, Tetrahedon Lett. 42 (2001) 239.
[288] S.E. Denmark, S.M. Yang, Org. Lett. 3 (2001) 1749.
[289] R.E. Taylor, F.C. Engelhardt, M.J. Schmitt, H. Yuan, J. Am. Chem. Soc. 123 (2001) 2964.
[290] B.A. Harrison, G.L. Verdine, Org. Lett. 3 (2001) 2157.
[291] Y. Landais, S.S. Surange, Tetrahedron Lett. 42 (2001) 581.
[292] S. Kuroda, F. Dekura, Y. Sato, M. Mori, J. Am. Chem. Soc. 123 (2001) 4139.
[293] K. Koide, J.M. Finkelstein, Z. Ball, G.L. Verdine, J. Am. Chem. Soc. 123 (2001) 398.
[294] P.E. Harrington, M.A. Tius, J. Am. Chem. Soc. 123 (2001) 8509.
[295] D.L. Boger, J. Hong, J. Am. Chem. Soc. 123 (2001) 8515.
[296] R.M. Garbaccio, S.J. Stochel, D.K. Baeschlin, S.J. Danishefsky, J. Am. Chem. Soc. 123 (2001) 10903.
[297] J. Louie, C.W. Bielawski, R.H. Grubbs, J. Am. Chem. Soc. 123 (2001) 11312.
[298] G.I. Georg, Y.M. Ahn, B. Blackman, F. Farokhi, P.T. Flaherty, C.J. Mossman, S. Roy, K.L. Yang, Chem. Commun. (2001) 255.
[299] D. Lebrecque, S. Charron, R. Rej, C. Blais, S. Lamothe, Tetrahedron Lett. 42 (2001) 2645.
[300] B.B. Snider, F. Song, Org. Lett. 3 (2001) 1749.
[301] A.B. Smith, III, J. Zheng, Synlett (2001) 1019.
[302] A. Fürstner, T. Dierkes, R.R. Thiel, G. Blanda, Chem. Eur. J. 7 (2001) 5286.
[303] S.C. Sinha, J. Sun, G.P. Miller, M. Wartmann, R.A. Lerner, Chem. Eur. J. 7 (2001) 1691.
[304] E.N. Prabhakaran, V. Rajesh, S. Dubey, J. Iqbal, Tetrahedron Lett. 42 (2001) 339.
[305] H.E. Blackwell, J.D. Sadowsky, R.J. Howard, J.N. Sampson, J.A. Chao, W.E. Steinmetz, D.J. O'Leary, R.H. Grubbs, J. Org. Chem. 66 (2001) 5291.
[306] Y. Gao, J. Voigt, J.X. Wu, D. Yang, T.R. Burke, Jr., Bioorg. Med. Chem. Lett. (2001) 1889.
[307] B. Kaptein, Q.B. Broxterman, H.E. Schoemaker, F.P.J.T. Rutjes, J.J.N. Veerman, J. Kamphuis, C. Peggion, F. Formaggio, C. Toniolo, Tetrahedron 57 (2001) 6567.
[308] Y. Gao, C.Q. Wei, T.R. Burke, Jr., Org. Lett. 3 (2001) 1617.
[309] Q. Tang, J.R. Wareing, Tetrahedron Lett. 42 (2001) 1399.
[310] Y. Sakamoto, M. Okazaki, K. Miyamoto, T. Nakata, Tetrahedron Lett. 42 (2001) 7633.
[311] J.D. White, P.R. Blakemore, E.A. Korf, A.F.T. Yokochi, Org. Lett. 3 (2001) 413.
[312] B.B. Mataferia, J. Hoch, T.E. Glass, S.L. Bane, S.K. Chatterjee, J.P. Snyder, A. Lakdamala, B. Cornett, D.G.I. Kingston, Org. Lett. 3 (2001) 2461.
[313] D.J. Dixon, A.C. Foster, S.V. Ley, Can. J. Chem. 79 (2001) 1668.
[314] W.W. Lee, H.J. Shin, S. Chang, Tetrahedron: Asymmetry 12 (2001) 29.
[315] D.A. Leigh, P.J. Lusby, S.J. Teat, A.J. Wilson, J.K.Y. Wong, Angew. Chem. Int. Ed. 40 (2001) 1538.
[316] L.G. Schultz, Y. Zhao, S.C. Zimmerman, Angew. Chem. Int. Ed. 40 (2001) 1962.
[317] K. Wada, D. Izuhara, K. Yamada, M. Shiotsuki, T. Kondo, T.A. Mitsudo, Chem. Commun. (2001) 1802.
[318] A.G.M. Barrett, D. Mamprecht, R.A. James, M. Okhubo, P.A. Procopiou, M.A. Toledo, A.J.P. White, D.J. Williams, J. Org. Chem. 66 (2001) 2187.
[319] E.P. Balskus, J. Méndez-Andino, R.M. Arbit, L.A. Paquette, J. Org. Chem. 66 (2001) 6695.
[320] H.E. Blackwell, P.A. Clemons, S.L. Schreiber, Org. Lett. 3 (2001) 1185.
[321] B.X. Zhao, S. Blechert, Chem. J. Chin. Univ. 22 (2001) 2045.
[322] M.R. Heinrich, W. Steglitch, Tetrahedron Lett. 42 (2001) 3287.
[323] M.R. Heinrich, Y. Kashman, P. Spiteller, W. Steglich, Tetrahedron 57 (2001) 9973.
[324] S. Rodríguez-Conesa, P. Candal, C. Jiménez, J. Rodriguez, Tetrahedron Lett. 42 (2001) 6699.
[325] G. Zhang, A. Graham, M. Shibata, J.R. Missert, A.R. Oseroff, T.J. Dougherty, R.K. Pandey, J. Org. Chem. 66 (2001) 8709.
[326] I. Ahmad, M.L. Halck-Pedersen, K. Undheim, J. Organomet. Chem. 625 (2001) 160.
[327] D. Sémeril, M. Cléran, C. Bruneau, P.H. Dixneuf, Adv. Synth. Catal. 343 (2001) 184.
[328] M.P. Schramm, D.S. Reddy, S.A. Kozmin, Angew. Chem. Int. Ed. 40 (2001) 4274.
[329] R. Duboc, C. Hénaut, M. Savignac, J.P. Genet, N. Bhatnagar, Tetrahedron Lett. 42 (2001) 2461.
[330] J.S. Clark, R.J. Townsend, A.J. Blake, S.J. Teat, A. Johns, Tetrahedron Lett. 42 (2001) 3235.
[331] M. Rosillo, L. Casarrubios, G. Domínguez, J. Pérez-Castells, Tetrahedron Lett. 42 (2001) 7029.
[332] L. Ackermann, C. Bruneau, P.H. Dixneuf, Synlett (2001) 397.
[333] M. Moreno-Mañas, R. Pleixats, A. Santamaria, Synlett (2001) 1784.
[334] M. Mori, T. Kitamura, Y. Sato, Synthesis (2001) 654.
[335] T. Kitamura, M. Mori, Org. Lett. 3 (2001) 1161.
[336] J.A. Smulik, S.T. Diver, Tetrahedron Lett. 42 (2001) 171.
[337] J. Efskind, C. Römming, K. Undheim, J. Chem. Soc. Perkin Trans. 1 (2001) 2697.
[338] Q. Yao, Org. Lett. 3 (2001) 2069.
[339] F.D. Boyer, I. Hanna, L. Ricard, Org. Lett. 3 (2001) 3095.
[340] T.L. Choi, R.H. Grubbs, Chem. Commun. (2001) 2648.
[341] A. Rückert, D. Eisele, S. Blechert, Tetrahedron Lett. 42 (2001) 5245.
[342] T. Kitamura, Y. Sato, M. Mori, Chem. Commun. (2001) 1258.
[343] J. Marco-Contelles, N. Arroyo, J. Ruiz-Caro, Synlett (2001) 652.
[344] T.M. Trnka, M.W. Day, R.H. Grubbs, Organometalics 20 (2001) 3845.
[345] C. Pietraszuk, H. Fischer, Organometallics 22 (2001) 4641.
[346] B. Alcaide, P. Almeadros, J.M. Alonso, M.F. Aly, Org. Lett. 3 (2001) 3781.
[347] M.K. Gurjar, P. Yakambram, Tetrahedron Lett. 42 (2001) 3633.
[348] D.M. Lynn, R.H. Grubbs, J. Am. Chem. Soc. 123 (2001) 3187.
[349] J.N. Coalter, III, J.C. Huffman, K.G. Caulton, Chem. Commun. (2001) 1158.
[350] M.S. Stanford, J.A. Love, R.H. Grubbs, Organometallics 20 (2001) 5314.
[351] H. Kunkely, A. Vogler, Inorg. Chim. Acta 325 (2001) 179.
[352] S.D. Drouin, F. Zamanian, D.E. Fogg, Organometallics 20 (2001) 5495.

[353] M.A. Rahim, H. Sasaki, J. Saito, T. Fujiwara, T. Takeda, Chem. Commun. (2001) 625.
[354] T. Fujiwara, K. Yanai, K. Shimane, M. Takamori, T. Takeda, Eur. J. Org. Chem. (2001) 155.
[355] T. Fujiwara, T. Takeda, Tetrahedron Lett. 42 (2001) 3369.
[356] T. Oishii, H. Uehara, Y. Nagumo, M. Shoji, J.Y. Le Brazidec, M. Kosaka, M. Hirama, Chem. Commun. (2001) 381.
[357] J.M. Cox, J.D. Ranier, Org. Lett. 3 (2001) 2919.
[358] C. Santamaría, R. Beckhaus, D. Haase, R. Koch, W. Saak, I. Strauss, Organometallics 20 (2001) 1354.
[359] M.D. Fryzuk, P.B. Duval, B.O. Patrick, S.J. Rettig, Organometallics 20 (2001) 1608.
[360] K. Aparna, R.P. Kamalesh Babu, R. McDonald, R.G. Clavell, Angew. Chem. Int. Ed. 40 (2001) 4400.
[361] P.N. Riley, P.E. Fanwick, I.P. Rothwell, J. Chem. Soc. Dalton Trans. (2001) 181.
[362] C. Viliers, A. Vandais, M. Ephritikhine, J. Organomet. Chem. 617–618 (2001) 744.
[363] C. Villiers, M. Ephritikhine, Chem. Eur. J. 7 (2001) 3043.
[364] L.A. Watson, D.V. Yandulov, K.G. Caulton, J. Am. Chem. Soc. 123 (2001) 603.
[365] S. Courtenay, D.W. Stephan, Organometallics 20 (2001) 1442.
[366] C. Copéret, O. Maury, J. Thivolle-Cazat, J.M. Basset, Angew. Chem. Int. Ed. 40 (2001) 2331.
[367] M. Chabanas, E.A. Quadrelli, B. Fenet, C. Copéret, J. Thivolle-Cazat, J.M. Basset, A. Lesage, L. Emsley, Angew. Chem. Int. Ed. 40 (2001) 4493.
[368] S.W. Schweiger, M.M. Salberg, A.L. Pulvirenti, E.E. Freeman, P.E. Fanwick, I.P. Rothwell, J. Chem. Soc. Dalton Trans. (2001) 2020.
[369] S.I. Wolke, R. Buffon, U.P. Rodrigues, J. Organomet. Chem. 625 (2001) 101.
[370] A.S. Veige, P.T. Wolczanski, E.B. Lobkovsky, Angew. Chem. Int. Ed. 40 (2001) 3629.
[371] J.B. Diminnie, J.R. Blanton, H. Cai, K.T. Quisenberry, Z. Xue, Organometallics 20 (2001) 1504.
[372] K.S. Cook, W.E. Piers, T.K. Woo, R. McDonald, Organometallics 20 (2001) 3927.
[373] J.A.R. Schmidt, S.A. Chmura, J. Arnold, Organometallics 20 (2001) 1062.
[374] J.A.R. Schmidt, J. Arnold, J. Am. Chem. Soc. 123 (2001) 8424.
[375] A.J. Sillanpää, K.E. Laasonen, Organometallics 20 (2001) 1334.
[376] G. Guillemot, E. Solari, R. Scopelliti, C. Floriani, Organometallics 20 (2001) 2446.
[377] P. Schollhammer, N. Cabon, J.F. Capon, F.Y. Pétillon, K.W. Muir, Organometallics 20 (2001) 1230.
[378] R.R. Schrock, C. Rosenberger, S.W. Seidel, K.Y. Shih, W.M. Davis, A.L. Odom, J. Organomet. Chem. 617–618 (2001) 495.
[379] Y.H. Shen, Y.D. Wu, J. Am. Chem. Soc. 123 (2001) 6662.
[380] J.C. Green, C.M. Jardine, J. Chem. Soc. Dalton Trans. (2001) 274.
[381] W.W. Schoeller, A.J.B. Rozhenko, A. Alijah, J. Organomet. Chem. 617–618 (2001) 435.
[382] M. Landman, H. Görls, S. Lotz, Eur. J. Inorg. Chem. (2001) 233.
[383] M. Landman, H. Görls, S. Lotz, J. Organomet. Chem. 617–618 (2001) 280.
[384] P.D. Woodgate, H.S. Sutherland, C.E.F. Rickard, J. Organomet. Chem. 626 (2001) 199.
[385] T.W. Stringfield, R.E. Shepherd, Inorg. Chim. Acta 325 (2001) 51.
[386] A. de Meijere, S. Müller, T. Labahn, J. Organomet. Chem. 617–618 (2001) 318.
[387] H.B. Friedrich, M.O. Onani, O.Q. Munro, J. Organomet. Chem. 633 (2001) 39.
[388] E. Licandro, S. Maiorana, B. Vandoni, D. Perdichia, P. Paravidino, C. Baldoli, Synlett (2001) 757.
[389] J. Barluenga, A.L. Súarez-Sobrino, M. Tomás, S. García-Granda, R. Santiagp-García, J. Am. Chem. Soc. 123 (2001) 10494.
[390] M.A. Sierra, J.C. del Amo, M.J. Mancheño, M. Gómez-Gallego, Tetrahedron Lett. 42 (2001) 5435.
[391] P.D. Woodgate, H.S. Sutherland, J. Organomet. Chem. 628 (2001) 155.
[392] J. Barluenga, S. López, A.A. Trabanco, J. Flórez, Chem. Eur. J. 7 (2001) 4723.
[393] H. Rudler, T. Durand-Réville, J. Organomet. Chem. 617–618 (2001) 571.
[394] K.H. Dötz, F. Otto, M. Nieger, J. Organomet. Chem. 621 (2001) 77.
[395] R.P. Hsung, W.D. Wulff, S. Chamberlin, Y. Liu, R.Y. Liu, H. Wang, J.F. Quinn, S.L.B. Wang, A.L. Rheingold, Synthesis (2001) 200.
[396] L. Fogel, R.P. Hsung, W.D. Wulff, R.D. Sommer, A.L. Rheingold, J. Am. Chem. Soc. 123 (2001) 5580.
[397] A.V. Vorogushin, W.D. Wulff, H.J. Hansen, Org. Lett. 3 (2001) 2641.
[398] M.W. Davies, C.N. Johnson, J.P.A. Harrity, J. Org. Chem. 66 (2001) 3525.
[399] J.J. Caldwell, R. Colman, W.J. Kerr, E.J. Magennis, Synlett (2001) 1428.
[400] X. Xie, M.C. Kozlowski, Org. Lett. 3 (2001) 2661.
[401] M. Zora, E.U. Güngör, Tetrahedron Lett. 42 (2001) 4733.
[402] W.H. Moser, L. Sun, J.C. Huffman, Org. Lett. 3 (2001) 3389.
[403] P.D. Woodgate, H.S. Sutherland, C.E.F. Rickard, J. Organomet. Chem. 627 (2001) 206.
[404] P.D. Woodgate, H.S. Sutherland, J. Organomet. Chem. 629 (2001) 131.
[405] I. Göttker-Schnetmann, R. Aumann, Organometallics 20 (2001) 346.
[406] B.L. Flynn, H. Schirmer, M. Beutsch, A. de Meijere, J. Org. Chem. 66 (2001) 1747.
[407] B.K. Ghorai, J.W. Herndon, Y.F. Lam, Org. Lett. 3 (2001) 3535.
[408] Y. Zhang, J.W. Herndon, Tetrahedron Lett. 42 (2001) 777.
[409] T.J. Jackson, J.W. Herndon, Tetrahedron 57 (2001) 3859.
[410] H. Rudler, A. Parlier, V. Certal, J.C. Frison, Tetrahedron Lett. 42 (2001) 5235H. Rudler, A. Parlier, V. Certal. J.C. Frison, C.R. Acad. Sci., Ser. IIC 4 (2001) 671..
[411] M. Zora, J.W. Herndon, Y. Li, J. Rossi, Tetrahedron 57 (2001) 5097.
[412] R. Alcázar, P. Ramírez, R. Vicente, M.J. Mancheño, M.A. Sierra, M. Gómez-Gallego, Heterocycles 55 (2001) 511.
[413] P.D. Woodgate, H.S. Sutherland, C.E.F. Rickard, J. Organomet. Chem. 629 (2001) 114.
[414] M.A. Sierra, M.J. Mancheño, R. Vicente, M. Gómez-Gallego, J. Org. Chem. 66 (2001) 8920.
[415] K.O. Doyle, M.L. Gallagher, M.T. Pryce, A.D. Rooney, J. Organomet. Chem. 617–618 (2001) 269.
[416] C.A. Merlic, C.C. Aldrich, J. Albaneze-Walker, A. Saghatelian, J. Mammen, J. Org. Chem. 66 (2001) 1297.
[417] C.A. Merlic, Y. Tou, D.M. McInnes, A.L. Zechman, M.M. Miller, Tetrahedron 57 (2001) 5199.
[418] I. Ferbnandez, M.A. Sierra, M.J. Mancheño, M. Gómez-Gallego, S. Ricart, Organometallics 20 (2001) 4304.
[419] J.M. Moreto, S. Ricart, J. Organomet. Chem. 617–618 (2001) 334.
[420] J. Barluenga, M.A. Fernández-Rodríguez, E. Aguilar, F. Fernández-Marí, A. Salinas, B. Olano, Chem. Eur. J. 7 (2001) 3533. Erratum: Chem. Eur. J. 7 (2001) 4323.
[421] H.P. Wu, R. Aumann, R. Fröhlich, E. Wegelius, Organometallics 20 (2001) 2183.
[422] R. Aumann, I. Göttker-Schnetmann, R. Frölich, P. Saarenketo, C. Holst, Chem. Eur. J. 7 (2001) 711.

[423] H.P. Wu, R. Aumann, R. Frölich, P. Saarenketo, Chem. Eur. J. 7 (2001) 700.
[424] Y.T. Wu, H. Schirmer, M. Noltemeyer, A. de Meijere, Eur. J. Org. Chem. (2001) 2501.
[425] H.P. Wu, R. Aumann, R. Fröhlich, B. Wibbeling, O. Kataeva, Chem. Eur. J. 7 (2001) 5084.
[426] J. Barluenga, F. Aznar, M.A. Palomero, Chem. Eur. J. 7 (2001) 5318.
[427] I. Göttker-Schnettman, R. Aumann, O. Kataeva, C. Holst, R. Frölich, Organometallics 20 (2001) 2889.
[428] I. Göttker-Schnettman, R. Aumann, O.K. Bergander, Organometallics 20 (2001) 3574.
[429] J. Barluenga, M. Tomás, A. Ballesteros, J. Santamaría, R. Corzo-Suárez, S. García-Granda, New J. Chem. 25 (2001) 8.
[430] R. Aumann, K. Roths, R. Frölich, J. Organomet. Chem. 617–618 (2001) 322.
[431] C.F. Bernasconi, M. Ali, Organometallics 20 (2001) 3383.
[432] F.E. McDonald, K. Subba Reddy, J. Organomet. Chem. 617–618 (2001) 444.
[433] F.E. McDonald, K.S. Reddy, Angew. Chem. Int. Ed. 40 (2001) 3653.
[434] N. Iwasawa, M. Shido, H. Kusama, J. Am. Chem. Soc. 123 (2001) 5814.
[435] N. Iwasawa, K. Maeyuma, H. Kusama, Org. Lett. 3 (2001) 3871.
[436] R.J. Madhushaw, C.L. Li, K.H. Shen, C.C. Hu, R.S. Liu, J. Am. Chem. Soc. 123 (2001) 7427.
[437] B. Liu, M.J. Chen, C.Y. Lo, R.S. Liu, Tetrahedron Lett. 42 (2001) 2533.
[438] H.L. Huang, W.H. Sung, R.S. Liu, J. Org. Chem. 66 (2001) 6193.
[439] C.C. Karl, S. Joneleit, K. Weissenbach, H. Fischer, J. Organomet. Chem. 617–618 (2001) 464.
[440] H. Fischer, F. Kirchenbauer, A. Früh, M.M. Abd-Elzaher, G. Roth, C.C. Karl, M. Dede, J. Organomet. Chem. 620 (2001) 165.
[441] K. Ulrich, V. Guerchais, K.H. Dötz, L. Topet, H. Le Bozec, Eur. J. Inorg. Chem. (2001) 725.
[442] J. Ipaktschi, S. Ulhig, A. Dülmer, Organometallics 20 (2001) 4840.
[443] T. Szymánska-Buzar, K. Kern, J. Organomet. Chem. 622 (2001) 74.
[444] M. Tamm, T. Bannenberg, A. Grzegorzewski, R. Frölich, J. Organomet. Chem. 617–618 (2001) 640.
[445] E. Licandro, S. Maiorama, L. Capella, R. Manzotti, A. Papagni, B. Vandoni, A. Albinati, S.H. Chuang, J.-R. Hwu, Organometallics 20 (2001) 485.
[446] E. Licandro, S. Maiorana, D. Perdicchia, C. Baldoli, C. Graiff, A. Tiripicchio, J. Organomet. Chem. 617–618 (2001) 399.
[447] E. Janes, K.H. Dötz, J. Organomet. Chem. 622 (2001) 251.
[448] F.R.L. Guen, P.L. Paul, B. Caro, R. Pinchon, N. Kervarec, J. Organomet. Chem. 626 (2001) 37.
[449] A. Papagni, S. Maiorama, E. Licandro, R. Manzotti, C. Baldoli, Eur. J. Org. Chem. (2001) 1149.
[450] J.M. Moretó, S. Ricart, K.H. Dötz, E. Molins, Organometallics 20 (2001) 62.
[451] M. Salmain, E. Licandro, C. Baldoli, S. Maiorama, H. Tran-Huy, G. Jaouen, J. Organomet. Chem. 617–618 (2001) 376.
[452] J. Barluenga, S. Martínez, A.L. Súarez-Sobrino, M. Tomás, J. Am. Chem. Soc. 123 (2001) 11113.
[453] A.S. Jepsen, N.J. Vogeley, P.S. White, J.L. Templeton, J. Organomet. Chem. 617–618 (2001) 520.
[454] M.A. Sierra, J.C. del Arno, M.J. Mancheño, M. Gómez-Gallego, J. Am. Chem. Soc. 123 (2001) 851.
[455] R. Stumpf, M. Jaeger, H. Fischer, Organometallics 20 (2001) 4040.
[456] R. Stumpf, H. Fischer, J. Organomet. Chem. 634 (2001) 209.
[457] H. Kagoshima, T. Okamura, T. Akiyama, J. Am. Chem. Soc. 123 (2001) 7182.
[458] R. Streubel, S. Priemer, J. Jeske, P.G. Jones, J. Organomet. Chem. 617–618 (2001) 423.
[459] L. Weber, M. Meyer, H.G. Stammler, B. Neumann, Chem. Eur. J. 7 (2001) 5401.
[460] C.J. Beddows, A.D. Burrows, N.G. Connely, M. Green, J.M. Lynans, T.J. Paget, Organometallics 20 (2001) 231.
[461] H. Ishino, S. Kuwata, Y. Ishii, M. Hidai, Organometallics 20 (2001) 13.
[462] C.S. Adams, P. Legzdins, W.S. McNeil, Organometallics 20 (2001) 4939.
[463] C.S. Adams, P. Legzdins, E. Tran, J. Am. Chem. Soc. 123 (2001) 612.
[464] P. Legzdins, K.M. Smith, S.J. Rettig, Can. J. Chem. 79 (2001) 502.
[465] N. Iwasawa, M. Saitou, H. Kusama, J. Organomet. Chem. 617–618 (2001) 741.
[466] K.N. Jayaprakash, D. Harza, K.S. Hagen, U. Samanta, M.M. Bhadbhade, V.K. Puranik, A. Sarkar, J. Organomet. Chem. 617–618 (2001) 709.
[467] S.F. Hwang, Y. Chi, S.J. Chiang, S.M. Peng, G.H. Lee, Organometallics 20 (2001) 215.
[468] L.Y. Goh, Z. Weng, W.K. Leong, P.H. Leung, Angew. Chem. Int. Ed. 40 (2001) 3236.
[469] S. Leelasubchareen, K.C. Lam, T.E. Concolino, A.L. Rheingold, K.H. Theopold, Organometallics 20 (2001) 182.
[470] C.P. Casey, S. Kraft, D.R. Powell, Organometallics 20 (2001) 2651.
[471] C.P. Casey, S. Kraft, M. Kavana, Organometallics 20 (2001) 3795.
[472] C.P. Casey, S. Kraft, D.R. Powell, M. Kavana, J. Organomet. Chem. 617–618 (2001) 723.
[473] Y. Ortin, Y. Copped, N. Lugan, R. Mathieu, M.J. McGlinchney, Chem. Commun. (2001) 2636.
[474] G. Maas, D. Mayer, J. Organomet. Chem. 617–618 (2001) 339.
[475] A. Rabier, N. Lugan, R. Mathieu, J. Organomet. Chem. 617–618 (2001) 681.
[476] K. Weissenbach, H. Fischer, J. Organomet. Chem. 621 (2001) 344.
[477] H.G. Raubenheimer, A. Neveling, S. Cronje, D.C. Billing, Polyhedron 20 (2001) 1089.
[478] C.F. Bernasconi, M.L. Ragains, J. Am. Chem. Soc. 123 (2001) 11890.
[479] W.E. Meyer, A.J. Amoroso, C.R. Horn, M. Jaeger, J.A. Gladysz, Organometallics 20 (2001) 1115.
[480] C. Bianchini, N. Mantovani, L. Marvelli, M. Peruzzini, R. Rossi, A. Romerosa, J. Organomet. Chem. 617–618 (2001) 233.
[481] J.K. Bera, P.E. Fanwick, R.A. Walton, J. Chem. Soc. Dalton Trans. (2001) 109.
[482] L.J. Morris, A.J. Downs, T.M. Greene, G.S. McGrady, W.A. Hermann, P. Sirsch, W. Scherer, O. Groper, Organometallics 20 (2001) 2344.
[483] Q. Wang, M.M. Hossain, J. Organomet. Chem. 617–618 (2001) 751.
[484] S. Ishii, S. Zhao, G. Mehta, C.J. Knors, P. Helquist, J. Org. Chem. 66 (2001) 3449.
[485] M.F. Semmelhack, A. Linderschmidt, D. Ho, Organometallics 20 (2001) 4114.
[486] R. Wang, Q. Xu, J. Sun, L.C. Song, J. Chen, Organometallics 20 (2001) 4092.
[487] K. Ferré, G. Poignant, L. Toupet, V. Guerchais, J. Organomet. Chem. 629 (2001) 19.
[488] T. Hayashida, H. Nagashima, Organometallics 20 (2001) 4996.
[489] R. Castarlenus, M.A. Esteruelas, E. Oñate, Organometallics 20 (2001) 2294.
[490] E. Rüba, K. Mereiter, R. Schmid, K. Kirchner, Chem. Commun. (2001) 1996.

[491] E. Becker, E. Rüba, K. Mereiter, R. Schmid, K. Kirchner, Organometallics 20 (2001) 3851.
[492] C. Ernst, O. Walton, E. Dinjas, J. Organomet. Chem. 627 (2001) 249.
[493] E. Rüba, K. Mereiter, R. Schmid, K. Kirchner, H. Schottenberger, J. Organomet. Chem. 637–639 (2001) 70.
[494] B.M. Trost, M.T. Rudd, J. Am. Chem. Soc. 123 (2001) 8862.
[495] C.G. Hamaker, J.P. Djukic, D.A. Smith, L.K. Woo, Organometallics 20 (2001) 5189.
[496] S. Bachmann, M. Furler, A. Mezzetti, Organometallics 20 (2001) 2102.
[497] C.G. Hamaker, G.A. Mirafzal, L.K. Woo, Organometallics 20 (2001) 5171.
[498] C.M. Che, J.S. Huang, F.W. Lee, Y. Li, T.S. Lai, H.L. Kwang, P.F. Teng, W.S. Lee, W.C. Lo, S.M. Peng, Z.Y. Zhou, J. Am. Chem. Soc. 123 (2001) 4119.
[499] Y. Li, J.S. Huang, Z.Y. Zhou, C.M. Che, J. Am. Chem. Soc. 123 (2001) 4843.
[500] V.A. Litosh, R.J. Saini, I.Y. Guzman-Jimenez, K.H. Whitmire, W.E. Billups, Org. Lett. 3 (2001) 65.
[501] M.S. Sanford, M.R. Valdez, R.H. Grubbs, Organometallics 20 (2001) 5455.
[502] V.F. Kuznetsov, G.P.A. Yap, H. Alper, Organometallics 20 (2001) 1300.
[503] P. Barrio, R. Casterlenas, M.A. Esteruelas, Organometallics 20 (2001) 2635.
[504] E. Bluell, B. Weberndörfer, H. Werner, J. Organomet. Chem. 617–618 (2001) 502.
[505] M. Lurtz, M. Haukka, T.A. Pakkanen, L.H. Gade, Organometallics 20 (2001) 2631.
[506] J.A. Cabeza, I. del Río, S. García-Granda, G. Lavigne, N. Lugan, M. Moreno, P. Nombel, M. Pérez-Priede, V. Riera, A. Rodríguez, M. Suárez, J.F. van der Maelen, Chem. Eur. J. 7 (2001) 2370.
[507] M. Akita, H. Musachi, S. Nakanishi, Y. Moro-oka, J. Organomet. Chem. 617–618 (2001) 254.
[508] A.V. Marchenko, H. Gerard, O. Eisenstein, K.G. Caulton, New J. Chem. 25 (2001) 1382.
[509] N. Dölker, G. Frenking, J. Organomet. Chem. 617–618 (2001) 225.
[510] Y. Chen, M. Hartmann, G. Frenking, Z. Anorg. Allg. Chem. 627 (2001) 984.
[511] L. Vyklický, H. Dvořáková, D. Dvořák, Organometallics 20 (2001) 5419.
[512] I. Rotrekl, L. Vyklický, D. Dvořák, J. Organomet. Chem. 617–618 (2001) 329.
[513] S. Zhang, Q. Xu, J. Sun, J. Chen, Organometallics 20 (2001) 2387.
[514] R. Schobert, J. Organomet. Chem. 617–618 (2001) 346.
[515] N. Le Gall, D. Luart, J.-Y. Salaün, H. des Abbayes, L. Toupet, J. Organomet. Chem. 617–618 (2001) 483.
[516] L.C. Song, G.L. Lu, Q.M. Hu, H.T. Fan, J. Chen, J. Sun, X.Y. Huang, J. Organomet. Chem. 627 (2001) 255.
[517] M. Baya, P. Crochet, M.A. Esteruelas, A.M. Lopéz, J. Modrego, E. Oñate, Organometallics 20 (2001) 4291.
[518] S.K. Hurst, M.P. Cifuentes, J.P.L. Morrall, N.T. Lucas, I.R. Whittall, M.G. Humphrey, I. Asselberghs, A. Persoons, M. Samoc, B. Luther-Davies, A.C. Willis, Organometallics 20 (2001) 4664.
[519] V.W.W. Yam, B.W.K. Chu, C.C. Ko, K.K. Cheung, J. Chem. Soc. Dalton Trans. (2001) 1911.
[520] V. Cadierno, M.P. Gamasa, J. Gimeno, B.M. Martín-Vaca, J. Organomet. Chem. 617–618 (2001) 261.
[521] S. Pavlik, C. Gemel, C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, J. Organomet. Chem. 617–618 (2001) 301.
[522] W. Baratta, A. Del Zotto, E. Herdtweck, S. Vuano, P. Rigo, J. Organomet. Chem. 617–618 (2001) 511.
[523] Y. Ajioka, Y. Matsushima, K. Onitsuka, H. Yamazaki, S. Takehashi, J. Organomet. Chem. 617–618 (2001) 601.
[524] V. Cadierno, M.P. Gamasa, J. Gimeno, J. Organomet. Chem. 617–618 (2001) 39.
[525] H. Matsuzaka, H. Okimura, Y. Sato, T. Ishii, M. Yamashita, M. Kondo, S. Kitagawa, M. Shiro, M. Yamasaki, J. Organomet. Chem. 625 (2001) 133.
[526] S.K. Hurst, N.T. Lucas, M.P. Cifuentes, M.G. Humphrey, M. Samoc, B. Luther-Davies, I. Asselberghs, R. van Boxel, A. Persoons, J. Organomet. Chem. 633 (2001) 114.
[527] L. Bonomo, C. Stern, E. Solari, R. Scopelliti, C. Floriani, Angew. Chem. Int. Ed. 40 (2001) 1449.
[528] S.K. Hurst, N.T. Lucas, M.G. Hunphrey, I. Asselberghs, R. Van Boxel, A. Persoons, Aust. J. Chem. 54 (2001) 447.
[529] H. Werner, P. Bachmann, M. Martin, Can. J. Chem. 79 (2001) 519.
[530] B. Gómez-Lor, A. Santos, M. Ruiz, A.M. Echavarren, Eur. J. Inorg. Chem. (2001) 2305.
[531] J.L. Fillaut, M. Price, A.L. Johnson, J. Perruchon, Chem. Commun. (2001) 739.
[532] C. Menéndez, D. Morales, J. Peréz, V. Rivera, D. Miguel, Organometallics 20 (2001) 2775.
[533] K.H. Chang, Y.C. Lin, Y.H. Liu, Y. Wang, J. Chem. Soc. Dalton Trans. (2001) 3154.
[534] M. Jiménez-Tenorio, M.C. Puerta, P. Valerga, F.J. Moreno-Dorado, F.M. Guerra, G.M. Massanet, Chem. Commun. (2001) 2324.
[535] T. Toman, D. Ooyama, T. Wada, K. Shiren, K. Tanaka, Chem. Commun. (2001) 1100.
[536] S. Jung, K. Ilg, J. Wolf, H. Werner, Organometallics 20 (2001) 2121.
[537] H. Werner, S. Jung, P. González-Herrero, K. Ilg, J. Wolf, Eur. J. Inorg. Chem. (2001) 1957.
[538] V. Cadierno, M.P. Gamasa, J. Gimeno, C. González-Bernado, E. Pérez-Carreño, S. García-Granda, Organometallics 20 (2001) 5177.
[539] C.E.F. Richard, W.R. Roper, S.D. Woodgate, L.I. Wright, J. Organomet. Chem. 623 (2001) 109.
[540] V. Cadierno, S. Conjero, M.P. Gamasa, E. Pérez-Carreño, S. Garciá-Granda, Organometallics 20 (2001) 3175.
[541] O.A. Kizas, V.V. Krivykh, E.V. Vorontsov, O.L. Tok, F.M. Dolgushin, A.A. Koridze, Organometallics 20 (2001) 4170.
[542] E. Bustelo, M. Jiménez-Tenorio, M.C. Puerta, P. Valerga, Eur. J. Inorg. Chem. (2001) 2391.
[543] F. Coat, P. Thominot, C. Lapinte, J. Organomet. Chem. 629 (2001) 39.
[544] C.J. den Reijer, D. Drago, P.S. Pregosin, Organometallics 20 (2001) 2982.
[545] S. Hartmann, R.F. Winter, T. Scheiring, M. Wanner, J. Organomet. Chem. 637–639 (2001) 240.
[546] R.F. Winter, K.W. Klinkhammer, S. Zális, Organometallics 20 (2001) 1317.
[547] S.M. Maddock, M.G. Finn, Angew. Chem. Int. Ed. 40 (2001) 2138.
[548] S. Rigaiut, O. Maury, D. Touchard, P.H. Dixneuf, Chem. Commun. (2001) 373.
[549] S. Rigaut, L. Le Pinchon, J.C. Daran, D. Touchard, P.H. Dixneuf, Chem. Commun. (2001) 1206.
[550] M. Gandelman, B. Rybtchinski, N. Ashkenazi, R.M. Gauvin, D. Milstein, J. Am. Chem. Soc. 123 (2001) 5372.
[551] E. Bleuel, P. Schwab, M. Laubender, H. Werner, J. Chem. Soc. Dalton Trans. (2001) 266.
[552] U. Herber, R.G. Sanchez, O. Gevert, M. Laubender, H. Werner, New J. Chem. 25 (2001) 396.
[553] D.H. Lee, J. Chen, J.W. Faller, R.H. Crabtree, Chem. Commun. (2001) 213.

[554] C. Slugovc, K. Mereiter, S. Trofimenko, E. Carmona, Helv. Chim. Acta 84 (2001) 2868.
[555] J.M. O'Connor, K. Hiibner, A. Closson, P. Gantzel, Organometallics 20 (2001) 1482.
[556] J.R. Bleeke, J.M.B. Blanchard, E. Donnay, Organometallics 20 (2001) 324.
[557] J.R. Bleeke, P.V. Hinkle, N.P. Rath, Organometallics 20 (2001) 1939.
[558] F. Locatelli, J.P. Candy, B. Didillon, G.P. Niccolai, D. Uzio, J.M. Basset, J. Am. Chem. Soc. 123 (2001) 1658.
[559] T. Ikeno, I. Iwakura, T. Yamada, Bull. Chem. Soc. Jpn. 74 (2001) 2151.
[560] H. Urtel, G.A. Bikzhanova, D.B. Grotjahn, P. Hofmann, Organometallics 20 (2001) 3938.
[561] H. Werner, E. Bluel, Angew. Chem. Int. Ed. 40 (2001) 145.
[562] C.E. Webster, M.B. Hall, Organometallics 20 (2001) 5606.
[563] K. Ilg, H. Werner, Organometallics 20 (2001) 3782.
[564] K. Ilg, H. Werner, Chem. Eur. J. 7 (2001) 4633.
[565] H. Werner, R. Wiedemann, M. Laubender, B. Windmüller, J. Wolf, Chem. Eur. J. 7 (2001) 1959.
[566] D. Moigno, W. Kiefer, B. Callejas-Gaspar, J. Gil-Rubio, H. Werner, New J. Chem. 25 (2001) 1389.
[567] J. Foerster, A. Kakoschke, R. Goddard, J. Rust, R. Wartchow, H. Butenschön, J. Organomet. Chem. 617–618 (2001) 412.
[568] H. Komatsu, Y. Suzuki, H. Yamazaki, Chem. Lett. (2001) 998.
[569] G. Fergusin, Y. Li, A.J. McAlees, R. McCrindle, E. Zang, J. Organomet. Chem. 617–618 (2001) 671.
[570] B. Martín-Matute, D.J. Cárdenas, A.M. Echevarren, Angew. Chem. Int. Ed. 40 (2001) 4754.
[571] B.M. Trost, A.S.K. Hashmi, R.G. Ball, Adv. Synth. Catal. 343 (2001) 490.
[572] S. Oi, I. Tsukamoto, T. Miyano, Y. Inoue, Organometallics 20 (2001) 3704.
[573] K. Nordhoff, D. Steinborn, Organometallics 20 (2001) 1408.
[574] T. Matsubara, Organometallics 20 (2001) 1462.
[575] F. Bernardi, A. Bottoni, G.P. Miscione, Organometallics 20 (2001) 2751.
[576] C. Rodríguez-García, A. Oliva, R.M. Ortuño, V. Branchadell, J. Am. Chem. Soc. 123 (2001) 6157.
[577] J. Barluenga, L.A. López, O. Löber, M. Tomás, S. García-Granda, C. Alvarez-Rúa, J. Borge, Angew. Chem. Int. Ed. 40 (2001) 3392.
[578] B.F. Straub, P. Hofmann, Angew. Chem. Int. Ed. 40 (2001) 1288.
[579] M. Bühl, F. Terstegen, F. Löffler, B. Meynhardt, S. Kierse, M. Müller, C. Näther, U. Lüning, Eur. J. Org. Chem. (2001) 2151.
[580] J.M. Fraille, J.I. Garcia, V. Martínez-Merino, J.A. Mayoral, L. Salvatella, J. Am. Chem. Soc. 123 (2001) 7616.
[581] J. Li, B.E. Bursten, M. Zhou, L. Andrews, Inorg. Chem. 40 (2001) 5448.
[582] R.R. Schrock, J. Chem. Soc. Dalton Trans. (2001) 2541.
[583] K.G. Caulton, J. Organomet. Chem. 617–618 (2001) 56.
[584] A.J.L. Pombeiro, M. Fátima, C.G. da Silva, J. Organomet. Chem. 617–618 (2001) 65.
[585] A.J.L. Pombeiro, Inorg. Chem. Commun. 4 (2001) 585.
[586] A.B. Zhang, H. Gong, S.M. Ma, Chin. J. Org. Chem. 21 (2001) 398.
[587] F.J. Fernández, M. Alfonso, H.W. Schmalle, H. Berke, Organometallics 20 (2001) 3123.
[588] N. Mantovani, L. Marvelli, R. Rossi, C. Bianchini, I. de los Rios, A. Romerosa, M. Peruzzini, J. Chem. Soc. Dalton Trans. (2001) 2353.
[589] P. González-Herrero, B. Weberndörfer, K. Ilg, J. Wolf, H. Werner, Organometallics 20 (2001) 3672.
[590] S. Jung, C.D. Brandt, H. Werner, New J. Chem. 25 (2001) 1101.
[591] R. Castarlenas, M.A. Esteruelas, E. Oñate, Organometallics 20 (2001) 3283.
[592] R. Castarlenas, M.A. Esteruelas, E. Gutiérrez-Puebla, E. Oñate, Organometallics 20 (2001) 1545.
[593] M. Baya, M.A. Esteruelas, E. Oñate, Organometallics 20 (2001) 4875.
[594] F.V. Cochran, R.R. Schrock, Organometallics 20 (2001) 2127.
[595] L.A. Friedman, W.D. Harman, J. Am. Chem. Soc. 123 (2001) 8967.
[596] T.B. Wen, Z.Y. Zhou, G. Jia, Angew. Chem. Int. Ed. 40 (2001) 1951.
[597] W.R. Roper, Angew. Chem. Int. Ed. 40 (2001) 2440.
[598] G. Ferrando, H. Gérard, G.J. Spivak, J.N. Coalter, III, J.C. Huffman, O. Eisenstein, K.G. Caulton, Inorg. Chem. 40 (2001) 6610.
[599] S. Fantacci, A. Sgamellotti, N. Re, C. Floriani, J. Chem. Soc. Dalton Trans (2001) 1718.
[600] A.E. Enriquez, P.S. White, J.L. Templeton, J. Am. Chem. Soc. 123 (2001) 4992.
[601] J.B. Greco, J.C. Peters, T.A. Baker, W.M. Davis, C.C. Cummins, G. Wu, J. Am. Chem. Soc. 123 (2001) 5003.
[602] S. Anderson, D.J. Cook, A.F. Hill, Organometallics 20 (2001) 2468.
[603] A.K. Hughes, J.M. Malget, A.E. Goeta, J. Chem. Soc. Dalton Trans. (1927).
[604] Y. Orfin, Y. Coppel, N. Lugan, R. Mathieu, M.J. McGlinchney, Chem. Commun. (2001) 1690.
[605] R. Wang, Q. Xu, Y. Souma, L.C. Song, J. Sun, J. Chen, Organometallics 20 (2001) 2226.
[606] K.H.A. Ostoja Starzewski, K. Weiss, M.O. Thuering, Chem. Abstr. 135 (2001) 273397.
[607] L. Weber, G. Dembeck, P. Lönneke, H.G. Stammler, B. Neumann, Organometallics 20 (2001) 2288.
[608] A.C. Filippou, P. Portius, C. Jankowski, J. Organomet. Chem. 617–618 (2001) 656.
[609] E. Bannwart, H. Jacobsen, R. Hübener, H.W. Schmalle, H. Bertz, J. Organomet. Chem. 622 (2001) 97.
[610] L. Zhang, M.F.C. Guedas da Silva, M.L. Kuznetsov, M.P. Gamasa, J. Gimeno, J.J.R. Fráusto da Silva, A.J.L. Pombeiro, Organometallics 20 (2001) 2782.
[611] M. Chabanas, A. Baudouin, C. Copéret, J.M. Basset, J. Am. Chem. Soc. 123 (2001) 2062.
[612] R.P. Saint-Arroman, M. Chabanas, A. Baudoin, C. Copéret, J.M. Basset, A. Lesage, L. Emsley, J. Am. Chem. Soc. 123 (2001) 3820.
[613] W. Steffan, B. Köhler, M. Altmann, U. Scherf, K. Stitzer, H.C. zur Loye, U.H.F. Bunz, Chem. Eur. J. 7 (2001) 117.
[614] W.Y. Huang, W. Gao, T.K. Kwei, Y. Okamoto, Macromolecules 34 (2001) 1570.
[615] D. Villemin, M. Héroux, V. Blot, Tetrahedron Lett. 42 (2001) 3701.
[616] A. Fürstner, C. Mathes, Org. Lett. 3 (2001) 221.
[617] A. Fürstner, C. Mathes, K. Krela, Chem. Commun. (2001) 1057.
[618] A. Fürstner, C. Mathes, C.W. Lehmann, Chem. Eur. J. 7 (2001) 5299.
[619] B. Aguilera, L.B. Wolf, P. Nieczypor, F.P.J.T. Rutjes, H.S. Overkleeft, J.C.M. van Hest, H.E. Schoemaker, B. Wang, J.C. Mol, A. Fürstner, M. Overhand, G.A. van der Marel, J.H. van Boom, J. Org. Chem. 66 (2001) 3584.