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The chemistry of the carbon–transition metal double and triple bond: annual survey covering the year 2000☆

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Abstract

This is a review of papers published in the year 2000 that focus on the synthesis, reactivity, or properties of compounds containing a carbon–transition metal double or triple bond.

Keywords: Carbon–transition metal; Alkenes; Alkynes; Carbene complexes; Carbyne complexes; Metathesis

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 [1] are not covered, unless there is some effort to characterize the carbene complex intermediate. 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 2000, have been included. Only compounds which 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 carbenes with transition metals have not been included; since the π-donation component of these complexes is minimal, there is no formal carbon–metal multiple bond [2,3]. 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. The metal carbene section has been organized according to metal, starting from the left side of the Periodic Table. The Ionic Model [4] 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.

Abbreviations (see also the front of issue no. 1 of the Journal of Organic Chemistry [5])

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)
Schrock Catalyst	Structure **3** (Fig. 1)

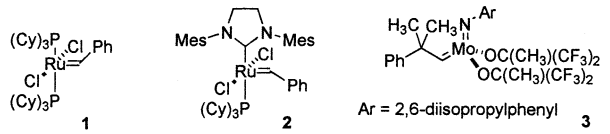


Fig. 1. Structures of alkene metathesis catalysts **1**–**3**.

2. Metal–carbene or metal–alkylidene complexes

2.1. Review articles

Several reviews covering aspects of metal–carbene complex chemistry appeared in 2000. Many reviews

focusing on some aspect of olefin metathesis were published, including the following specific subjects: (1) alkene metathesis with emphasis on catalyst design [6]; (2) synthesis of medium-sized rings through ring closing metathesis (RCM) [7]; (3) use of alkene metathesis in carbohydrate chemistry [8]; (4) use of carbene complexes to effect metathesis polymerization [9]; (5) ring opening metathesis polymerization (ROMP) of norbornene [10]; (6) transition–metal systems bearing a nucleophilic carbene ancillary ligand [11]; (7) olefin metathesis in carbohydrate chemistry [12]; and (8) metathesis for tandem asymmetric ring opening/intramolecular ring closure [13]. Other specific subjects have been reviewed in which there is a heavy focus on carbene complexes, including: (1) α,β-unsaturated metal carbene complexes in organic synthesis [14]; (2) metallahexatriene systems [15]; (3) use of Fischer carbene complexes for the synthesis of five-membered carbocyclic ring systems [16]; (4) metalloxy Fischer carbene complexes [17]; (5) titanium carbene complexes generated from dithioacetals [18]; (6) carbonyl olefination using dialkyltitanocene derivatives [19]; (7) ruthenium–vinylidene complexes in organic synthesis [20]; (8) nickel and palladium carbene complexes which contain stable carbene ligands [21]; (9) carbene complexes in organic synthesis [22]; (10) di- and polymetallic heteroatom-stabilized Fischer carbene complexes [23]; (11) the annual survey of the carbon metal double and triple bond for 1998 [24]; and (12) η^2-alkenylmetal complexes [25]. Although not directly focusing on the chemistry of metal–carbon multiply bonded systems, several reviews pertinent to this field have appeared, including reviews focusing on: (1) alkynylplatinum complexes, which contains several examples of vinylidene complexes [26]; (2) synthetic processes involving iron-substituted butenals [27]; (3) stoichiometric organotransition metal complexes in organic synthesis [28]; (4) catalytic applications of transition metals in organic synthesis [29]; (5) amino acid synthesis, including metathesis-based approaches [30–32]; (6) polymer-supported catalysts [33]; (7) synthesis of saturated oxygen heterocycles [34]; (8) synthesis of saturated nitrogen heterocycles [35]; (9) synthesis of diaryl ethers [36]; (10) polycyclic β-lactams [37]; (11) theoretical studies of transition metal-mediated processes of industrial and synthetic importance, including the Dötz reaction [38]; (12) complexes of metal–carbon σ-bonds of the groups iron to nickel, including carbene- and carbyne-complexes [39]; (13) complexes of metal–carbon σ-bonds of the groups titanium to manganese, including carbene- and carbyne-complexes [40]; (14) a review entitled 'miscellaneous complexes', which includes many examples of carbene complexes [41]; (15) complexes of *N*-heterocyclic carbenes [42,43]; (16) the past and future of organotransition metal chemistry [44]; (17) chromium reagents [45]; (18) metal complexes of di-phosphorus imines [46]; (19) the nature of bonding in transition metal compounds [47]; and (20) effects of metal coordination on the reactivity of enediynes [48].

2.2. Alkene metathesis

Alkene metathesis was the most common reaction process reported for metal–carbene complexes in 2000, and this special section is devoted to papers that focus on this process. Many examples of both polymerization (mostly 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.

2.2.1. General studies of alkene metathesis catalysts

Several mechanistic studies related to alkene metathesis appeared in 2000. Gas phase alkene metathesis has been studied by electrospray ionization mass spectrometry [49–51] using cationic catalysts (e.g. **4**–**7**, Fig. 2) and cationic alkene substrates (e.g. **8**). ROMP of norbornene-bound ammonium salts led to intermediates consistent with monophosphine–ruthenium complexes. A gas-phase comparison of several carbene–ruthenium catalysts revealed inconsistency with solution-phase metathesis reactivity data; monophosphine complex **5** proved to be the more reactive than complexes **6**–**7**.

Numerous attempts to develop new catalysts for alkene metathesis were reported in 2000; some representative examples are depicted in Fig. 3. Several derivatives of the Grubbs and Schrock catalysts were synthesized and tested in their ability to undergo either ROMP or RCM processes, including: (1) a ruthenium catalyst featuring alkoxy ligands (**9**), which can be transformed to a highly active catalyst upon treatment with HCl [52]; (2) various polymer- and silica-bound ruthenium catalysts [53–56] and molybdenum catalysts [57]; (3) phenoxycarbene complexes and S, Se, and Te analogs prepared from stoichiometric metathesis of phenyl vinyl ether derivatives with Grubbs catalyst I [58]; (4) water soluble analogs of Grubbs catalyst I (e.g. **10**) [59]; (5) recoverable analogs of Grubbs catalyst II

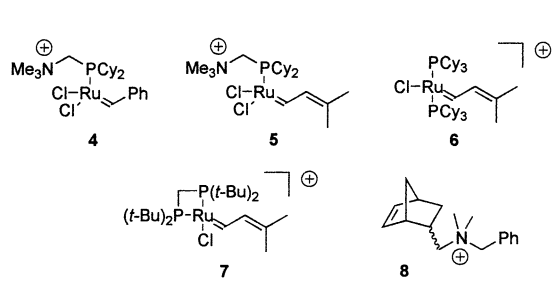


Fig. 2. Carbene complexes and monomers investigated in gas-phase metathesis reactions.

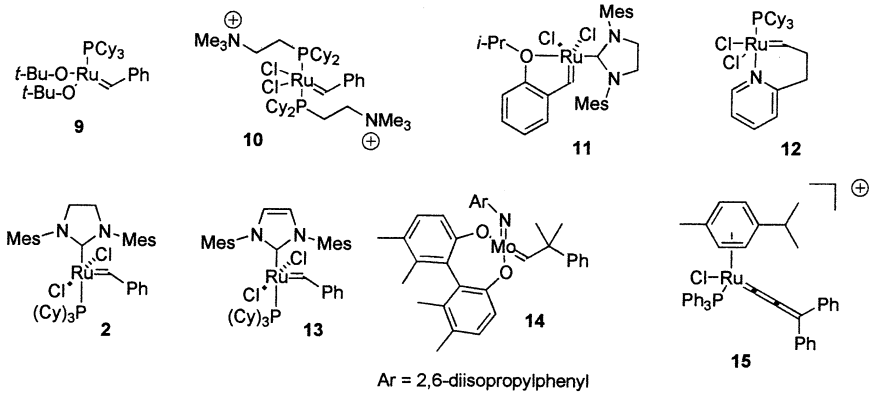


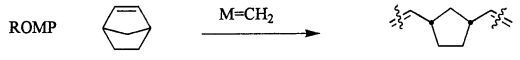
Fig. 3. Representative examples of new catalysts for alkene metathesis.

(e.g. **11**) [60,61]; (6) ruthenium catalysts containing an α-bromoester functionality which can initiate both metathesis and free radical polymerization reactions [62]; (7) a thiocarbene analog of Grubbs catalyst I and a catalyst featuring a pyridine ligand connected to the carbene ligand (**12**) [63]; (8) derivatives of the Grubbs catalyst featuring a heterocyclic carbene ligand in place of one of the phosphine ligands (e.g. **2**, **13**) [64–68]; (9) derivatives of Grubbs catalyst I featuring chelating sulfur ligands in place of the chloro and phosphine ligands [69]; (10) single enantiomer catalysts featuring chiral biphenyl ligands (e.g. **14**) [70]; (11) water-soluble derivatives of ruthenium–allenylidene monomers and dimers featuring sulfonated phosphine ligands [71]; (12) cationic ruthenium–allenylidene complexes (e.g. **15**) [72]; (13) vinylidene analogs of Grubbs catalyst I [73]; (14) analogs of Grubbs catalyst I featuring a chelating diphosphine in place of the tricyclohexylphosphine ligands [74,75]; (15) several examples of noncarbene-containing ruthenium and/or osmium complexes which are comparable to Grubbs catalyst I in their metathesis activity [76–79]; and (16) generation of an active metathesis catalyst by addition of trimethylsilyldiazomethane to cationic ruthenium-bridged phosphine–arene complexes [80]. An alternative synthesis for analogs of the Grubbs catalyst from a ruthenium hydride complex, HCl, and styrene was reported [81]. Several patents were issued for the synthesis and development of metal–carbene containing olefin metathesis catalysts [82–89].

Other general studies of alkene metathesis where carbene complexes were discussed include: (1) determination of catalyst activity for the RCM reaction using IR-thermographic screening [90]; (2) simulation of the alkene metathesis reaction using First Principles Molecular Dynamics [91]; (3) use of lead tetraacetate for the removal of highly colored byproducts from metathesis reactions using Grubbs catalyst I [92]; and (4) determination of active centers in metathesis reactions initiated by Re_2O_7–alumina [93].

2.2.2. Polymerization reactions

Initiation of the ROMP (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 2000 (Fig. 4). Examples of ROMP using metal carbene complexes include: (1) more facile ROMP using derivatives of Grubbs catalyst I where one heterocyclic carbene ligand replaces a phosphine ligand [94]; (2) ROMP of carbohydrate-linked norbornene derivatives (e.g. **16**) for the design of single multivalent receptors [95]; (3) use of ROMP to generate monolithic stationary media for chromatography [96,97]; (4) ring opening oligomerization of norbornene bound to a ruthenium porphyrin derivative [98]; (5) comparison of tacticity in the ROMP of methylnorbornene using various analogs of the Grubbs and the Schrock catalyst [99,100]; (6) ROMP of norbornenes linked to ferrocene–ammonium salts (e.g. **17**) [101]; (7) ROMP of norbornenes connected to thiophene derivatives [102,103]; (8) formation of *N*-hydroxysuccinimide-containing polymers via ROMP of *N*-hydroxysuccinnimide-containing oxanorbornene derivatives (e.g. **18**) [104]; (9) ROMP of norbornenecarboxamides [105]; (10) ROMP-based copolymerization of norbornene or 1,5-cyclooctadiene derivatives with 1,4-diacetoxy-2-butene [106–109]; (11) substituent effects on stereochemistry and tacticity for ROMP of norbornene derivatives using Grubbs catalyst I [110]; (13) ROMP of norbornene derivatives attached to self-assembled monolayers [111]; (15) ROMP of norbornene derivatives bound to a solid support through a peptide [112]; (16) ROMP of norbornene linked to a methacrylate ester for future crosslinking [113]; (17) ROMP of norbornene linked to a



Scheme 1.

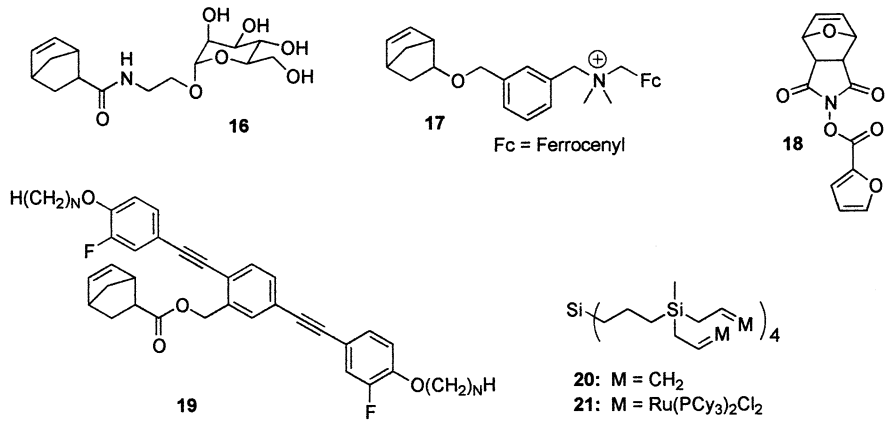
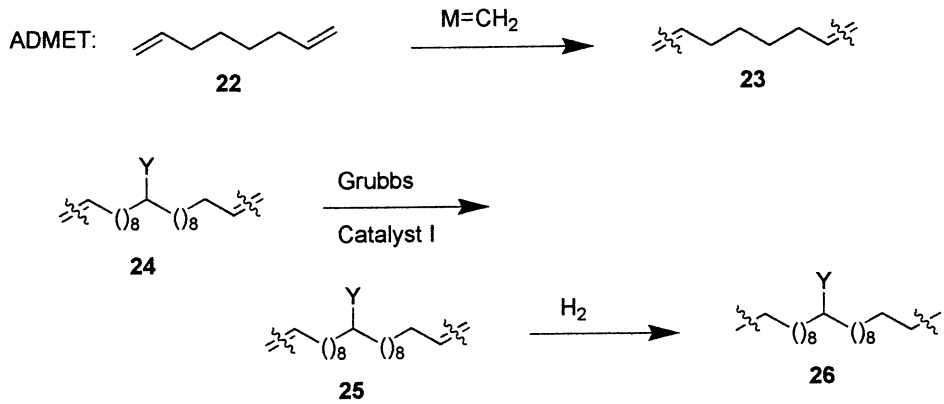


Fig. 4. Representative substrates for the ROMP reaction.



Scheme 2.

butadiene–styrene block copolymer [114]; (18) ROMP of norbornene bound to polyethylene glycol [115,116]; (19) preparation of liquid crystalline polynorbornenes through ROMP of norbornenes linked to complex arenes (e.g. **19**) [117]; (20) formation of block polyethylene copolymers using ROMP of norbornene derivatives and cyclopentene, followed by treatment with acetaldehyde and hydrogenation [118]; (21) formation of star polymers by stoichiometric reaction of diallylsilane derivative **20** with Grubbs catalyst I followed by ROMP of norbornene with the resulting bis(carbene) complex **21** [119]; (22) ROMP of norbornene carboximides and comparison of the tacticity in polymers derived from the *endo* and *exo* derivatives [120]; (23) use of ROMP to form copolymers of 1,5-cyclooctadiene and norbornene-containing amines [121]; (24) copolymerization of various norbornene and cyclooctene derivatives [122]; and (25) surface modification of polymer-bound alkenes through ROMP with norbornene [123].

An attempt to find the active species in the ROMP of norbornene by $W(CO)_6$–CCl_4 was reported [124]. The propagating species was reactive with benzaldehyde to afford carbonyl olefination products, suggesting a Schrock-type carbene complex as an intermediate. No signals attributable to the carbene complex were detected in the NMR analysis of the reaction, however signals attributable a metallacyclobutane were detected.

Several examples using carbene complexes to initiate acyclic diene metathesis (ADMET) polymerization reactions (Scheme 2) were reported in 2000, including: (1) copolymerization 1,7-octadiene and 9-decenyl acetate [125]; (2) synthesis of polyethylene of defined branching through ADMET polymerization of derivatives of **24** ($Y = CH_3$) followed by hydrogenation [126]; (3) net formation of vinyl acetate–ethylene copolymers through ADMET polymerization of derivatives of **24** ($Y = OAc$) followed by hydrogenation [127]; (4) net formation of functionalized ethylene–ethylene copolymers through ADMET polymerization of derivatives of **24** ($Y = Cl$, Ph, COOR, COOH) followed by hydrogenation [128]; (5) formation of liquid crystal polyesters through ADMET polymerization of steroid-linked 7-octenyl aryl ethers [129]; (6) formation of luminescent materials through ADMET polymerization of various divinylarene derivatives [130]; and (7) failure of the Schrock catalyst or Grubbs catalyst I to effect ADMET polymerization of tetravinylsilane and divinylsilane derivatives [131].

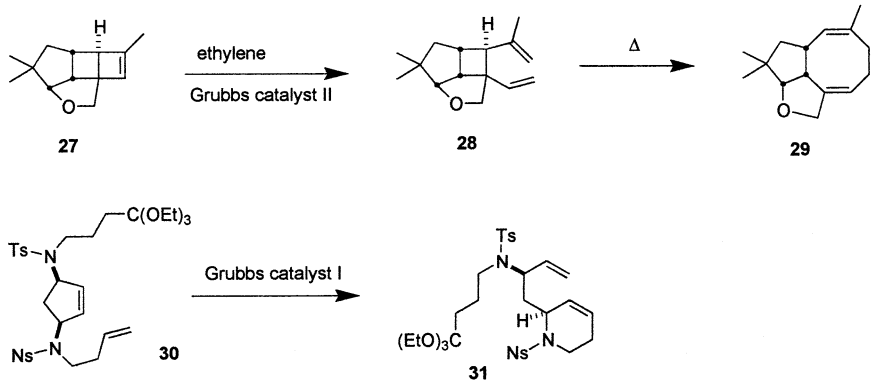
2.2.3. Nonpolymer-forming ring opening metathesis reactions

A tandem asymmetric ring opening metathesis–cross metathesis reaction sequence was reported using bicyclo[2.2.0]hexene derivatives (e.g. **27**, Scheme 3) and ethylene [132,133]. This reaction was the key step in a total synthesis of the eight-membered ring containing natural product asteriscanolide. Isoprostane derivatives were prepared using an analogous process using bicyclo[3.2.0]heptene ring systems [134]. A similar process was demonstrated in the cometathesis of ethylene and silicon-substituted norbornenes [135]. A tandem ring opening–RCM event was utilized for the construction of piperidine ring systems (e.g. **30**–**31**) [136–139]. A stoichiometric reaction of cyclohexene with carboalkoxycarbene–ruthenium complexes led to ring opening products [140].

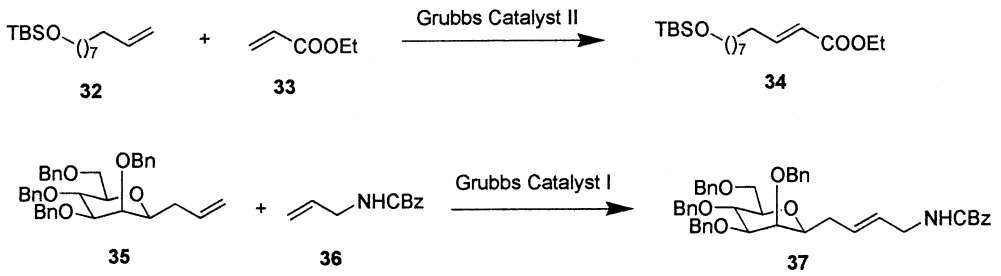
2.2.4. Cross metathesis and metathesis dimerization reactions

The cross metathesis reaction of various dissimilar monosubstituted alkenes was investigated (Scheme 4) including: (1) cross metathesis of simple monosubstituted alkenes (e.g. **32**) and α,β-unsaturated carbonyl compounds, which is only efficient and E-selective using Grubbs catalyst II [141]; (2) cross metathesis of vinylsilanes and styrene derivatives, which is highly selective even at high conversion [142]; (3) efficient cross metathesis of monosubstituted alkenes and symmetrical 1,2-disubstituted alkenes [143]; (4) cross metathesis–RCM in a highly ordered system for the conversion of a hydrogen-bonded assembly into a covalently-linked assembly [144]; (5) cross metathesis of ferrocenyl-substituted alkenes and simple monosubstituted alkenes [145]; (6) cross metathesis *C*-allyl glycosides (e.g. **35**) and allylamide derivatives [146,147]; and (7) competing cross metathesis and metathesis dimerization of diallyldibenzothiophenes and allylic amines [148].

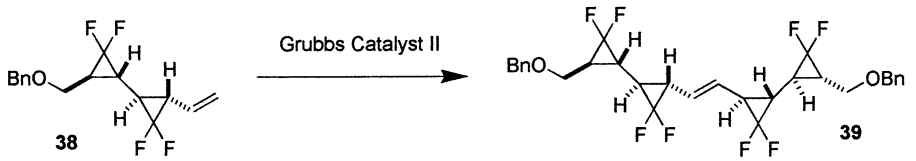
Several examples of dimerization via metathesis (Scheme 5) were reported in 2000, including: (1) dimerization of vinylcyclopropane derivatives (e.g. **38**) [149]; (2) dimerization of monosubstituted allenes [150]; and



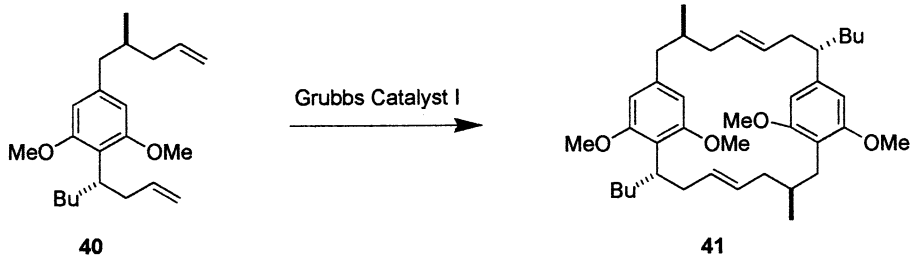
Scheme 3.



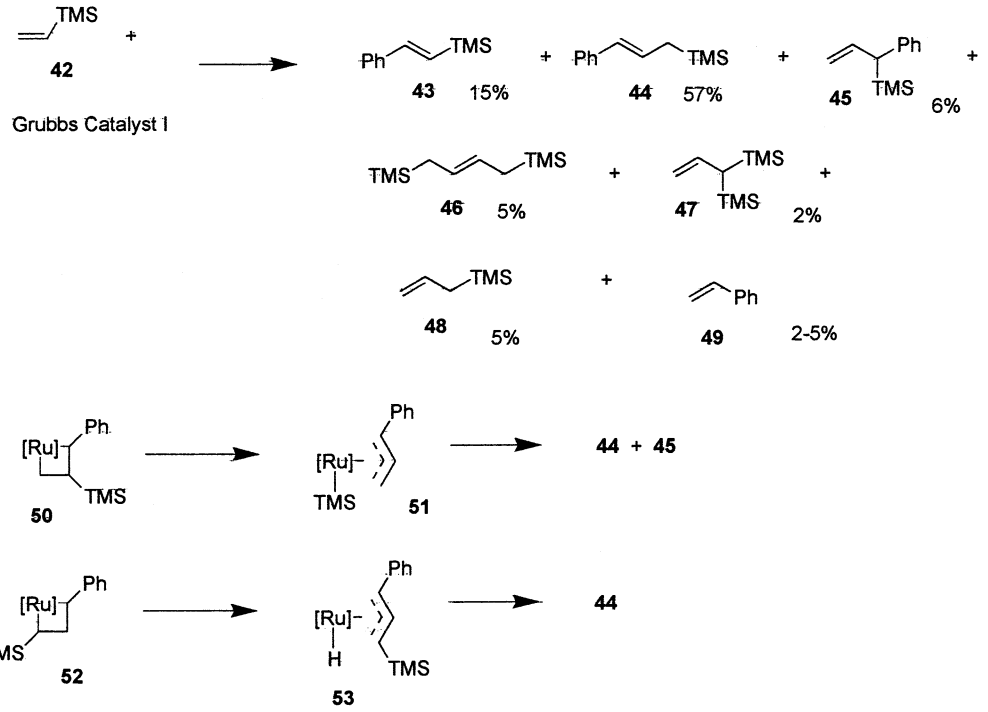
Scheme 4.



Scheme 5.



Scheme 6.



Scheme 7.

(3) dimerization of *O*-allyl carbohydrate derivatives [151].

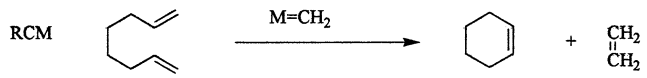
A tandem metathesis dimerization–RCM procedure was employed as a key step in the total synthesis of cylindrocyclophane derivatives (e.g. **41**, Scheme 6) [152]; the reaction was completely selective for formation of the head-to-tail isomer **41**. A related tandem metathesis dimerization–RCM procedure was reported for various sulfone-containing diene derivatives; in some cases the product as accompanied by the analogous trimeric systems [153].

A variety of compounds (**43**–**49**, Scheme 7) were produced in the stoichiometric reaction of Grubbs catalyst with vinyltrimethylsilane [154]. The major product, allylsilane **44**, arises from metallacyclobutane **50**, which undergoes β-silyl elimination followed by reductive elimination to afford **44** and **45**. An alternative mechanism involving β-hydride elimination from alternative ruthenacyclubutene **52** was not consistent with the deuterium labeling study.

2.2.5. Ring closing metathesis

The RCM reaction (Scheme 8) 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. 5, the indicated bond was formed via the RCM reaction). Examples include: (1) synthesis of eight-membered rings



Scheme 8.

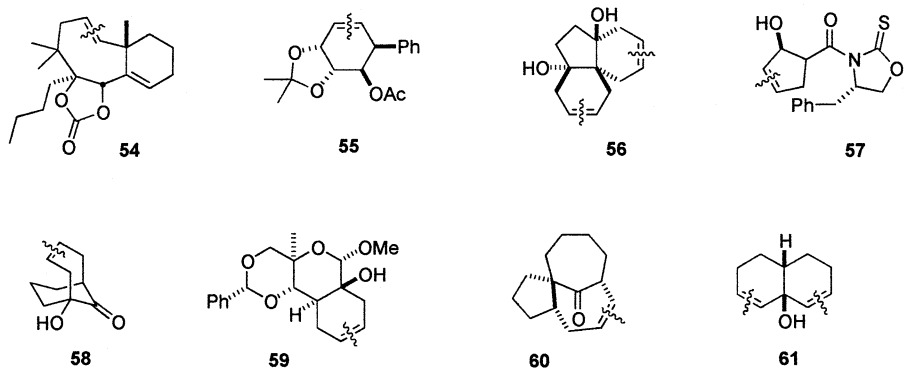


Fig. 5. Representative carbocycles produced through an RCM reaction (bond constructed through RCM indicated).

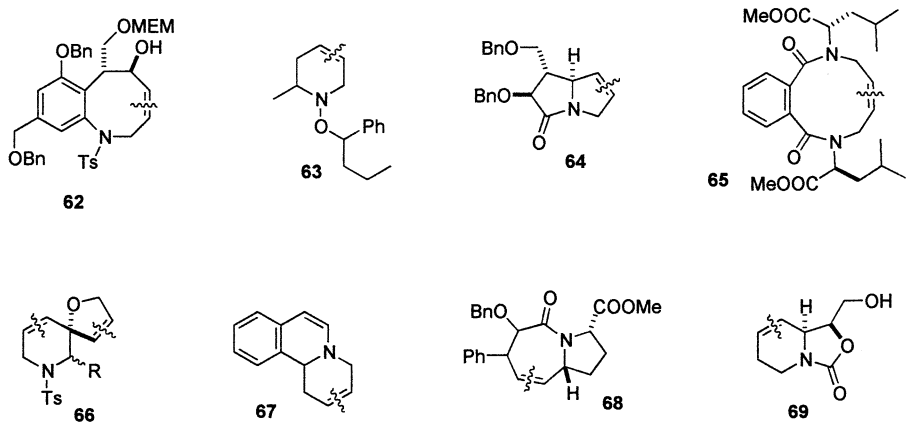


Fig. 6. Representative *N*-heterocycles produced through an RCM reaction (bond constructed through RCM indicated).

by RCM [155], including one system which results in the *trans*-cyclooctene derivative (**54**) [156] and a total synthesis of asteriscanolide [157]; (2) synthesis of highly oxygenated cyclohexene derivatives (e.g. **55**) [158–162]; (3) selective formation of fused ring systems (e.g. **56**) over spiro ring systems from tetraallylcyclopentane derivatives [163]; (4) synthesis of spirocycles connected to α-methylene–γ-butyrolactones [164]; (5) six-membered rings fused to cyclopropanes [165]; (6) release of carbohydrates from allylic alcohol-bound resins [166]; (7) synthesis of highly oxygenated cycloheptene derivatives [167–169]; (8) synthesis of cyclopentene derivatives for *C*-nucleoside synthesis (e.g. **57**) [170,171]; (9) synthesis of the bicyclo[3.3.1]nonenone and bicyclo[4.3.1]decenone ring systems (e.g. **58**) [172]; (10) synthesis of cyclohexadienes and cycloheptadienes containing a (diene)$Fe(CO)_3$ unit [173]; (11) synthesis of six-membered rings fused to carbohydrate ring systems (e.g. **59**) [174]; (12) synthesis of the ingenol ring system (e.g. **60**) [175]; (13) synthesis of six-membered rings fused to a piperidine ring [176]; (14) synthesis of six-membered rings spiro fused to the Schöllkopf chiral auxiliary [177]; (15) synthesis of *cis*-hexahydronaphthalenes (e.g. **61**) by RCM of tetraene derivatives [178]; and (16) formation of carbocycles in the depolymerization of polybutadiene using Grubbs catalyst I [179].

Numerous examples of the formation of nitrogen heterocycles using the RCM reaction (Fig. 6) were reported in 2000, including: (1) synthesis of an eight-membered ring cyclic *N*-tosylamide (**62**) for total synthesis of the antitumor antibiotic FR900482 [180]; (2) six-membered ring cyclic *N*-tosylamides [181,182]; (3) six-membered ring derivatives containing an *N*-alkoxy group (e.g. **63**) [183]; (4) eight-membered ring cyclic diamines [184]; (5) nitrogen heterocycles fused to β-lactam ring systems [185] and γ-lactam ring systems [186]; (6) an eight-membered ring nitrogen heterocycle for total synthesis of australine [187]; (7) synthesis of the pyrolizidine ring system (e.g. **64**) through RCM [188]; (9) synthesis of ten-membered ring cyclic diamides (e.g. **65**) [189]; (10) synthesis of the piperidine ring system in the presence of a protonated amine [190]; (11) synthesis of seven-membered ring amides for balanol total synthesis [191]; (12) diastereoselective formation of *N*-heterocycles spiro-fused to oxygen heterocycles (e.g. **66**) via RCM of tetraene derivatives [192]; (13) synthesis of six- to eight-membered nitrogen heterocycles fused to a cyclic enamine (e.g. **67**) [193]; (14) synthesis of *N*-heterocycles fused to oxazolones [194]; (15) simultaneous

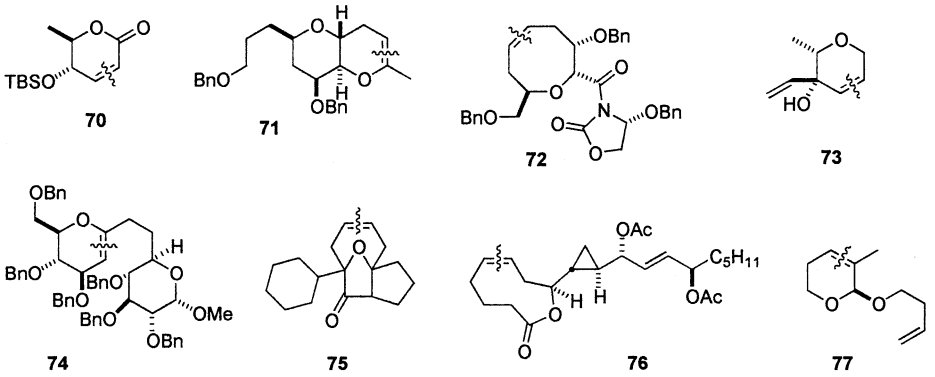


Fig. 7. Representative oxygen-heterocycles produced through an RCM reaction (bond constructed through RCM indicated).

RCM–Heck reaction using *N*,*N*-diallyl-*N*-*o*-bromophenylsulfonamides and the Grubbs catalyst and a palladium catalyst [195]; (16) synthesis of seven-membered ring cyclic amides (e.g. **68**) [196]; (17) synthesis of BOC-protected five-membered ring amines [197]; (18) synthesis of six-membered ring cyclic amides (e.g. **69**) for total synthesis of dihydrostreptazolin [198], sedamine [199], anabasine [200]; and (19) synthesis of phosphonate ester-containing cyclic amides [201].

Many examples of oxygen heterocycle synthesis using the RCM reaction were reported in 2000 (Fig. 7), including: (1) synthesis of α,β-unsaturated six-membered ring lactones (e.g. **70**), including examples for the total synthesis of everinomicin 13,384-1 [202], boronolide [203], and lanlimalide [204]; (2) synthesis of cyclic ethers for brevitoxin and ciguatoxin total synthesis (e.g. **71**) [205–208]; (3) synthesis of dihydrofuran derivatives for lankacyclinol total synthesis [209]; (4) synthesis of eight-membered ring cyclic ethers (e.g. **72**) [210–212]; (5) low-yield RCM of a 1,3-diaxial allyloxycyclohexane derivative [213]; (6) RCM using alkoxycarbene–chromium complexes [214]; (7) moderately diastereoselective RCM for the synthesis of six-membered rings (e.g. **73**) from trienes and tetraenes featuring diastereotopic vinyl groups [215–217]; (8) selective formation of a hydroxylated six-membered ring heterocycle from a triene [218]; (9) δ-lactone derivatives where the newly-constructed alkene is conjugated with the carbonyl group [219,220]; (10) synthesis of glycal derivatives of *C*-glycosides (e.g. **74**) [221]; (11) synthesis of six-membered ring cyclic ethers [222], including examples directed toward the total synthesis of laulimalide [223] and malyngolide [224]; (12) synthesis of the oxabicyclo[4.2.1]nonene ring system (e.g. **75**) [225]; (13) synthesis of a nine-membered ring cyclic ether (**76**) for the total synthesis of halicholactone [226]; (14) synthesis of the coumarin ring system [227]; (15) synthesis of six-membered ring cyclic ethers fused to a highly oxygenated ring system [228]; (16) enantioselective formation of five- and six-membered ring cyclic ethers (e.g. **77**) using the Schrock–Hoveyda catalyst [229]; (17) synthesis of seven-membered ring cyclic ethers [230]; and (18) synthesis of five-membered ring cyclic ethers [231–233].

Other heterocyclic compounds were also constructed via the RCM reaction (Fig. 8). Examples include: (1) heterocyclic phosphines (e.g. **78**), prepared from the RCM reaction of alkene-containing phosphine–borane complexes [234]; (2) stereoselective formation of phosphorus–nitrogen heterocycles (e.g. **79**) [235,236]; (3) silicon–oxygen heterocycles bound to carbohydrates (e.g. **80**) [237,238] and other cyclic siloxanes [239,240]; (4) cyclic phosphates [241–243]; (5) cyclic aminoboranes (e.g. **81**) [244]; and (6) cyclic sulfonamides (e.g. **82**) [245–247], including a simultaneous RCM resin-cleavage process [248].

Numerous examples of successful macrocyclic ring closure using the RCM reaction were reported in 2000 (Fig. 9), including: (1) synthesis of macrocyclic ring conjugated dienes through RCM of a conjugated diene and a simple alkene (e.g. **83**) [249,250]; (2) synthesis of the macrocyclic ester ring of salicylihalamide, zearalenone, and lasiodiplodin derivatives (e.g. **84**) [251–255]; (3) synthesis of macrocycle-bridged analogs of taxol [256]; (4) synthesis of chelating phosphine–metal complexes (e.g. **85**) using RCM of bis(remote alkenyl)phosphine complexes [257]; (5) synthesis of macrocycle-bridged dihydropyrrole derivatives [258]; (6) synthesis of macrocyclic *N*-tosylamides [259]; (7) synthesis of macrocyclic 1,5-diketones [260]; (8) synthesis of macrocyclic peptides [261,262]; (9) highly E-selective

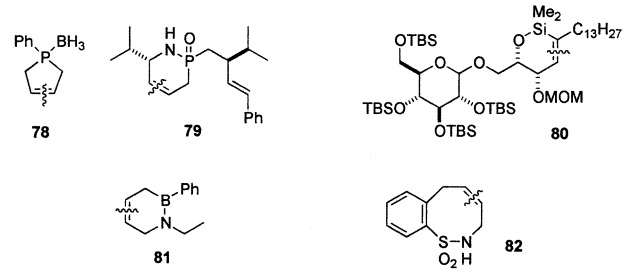


Fig. 8. Representative examples of other heterocycles prepared via the RCM reaction (bond constructed through RCM indicated).

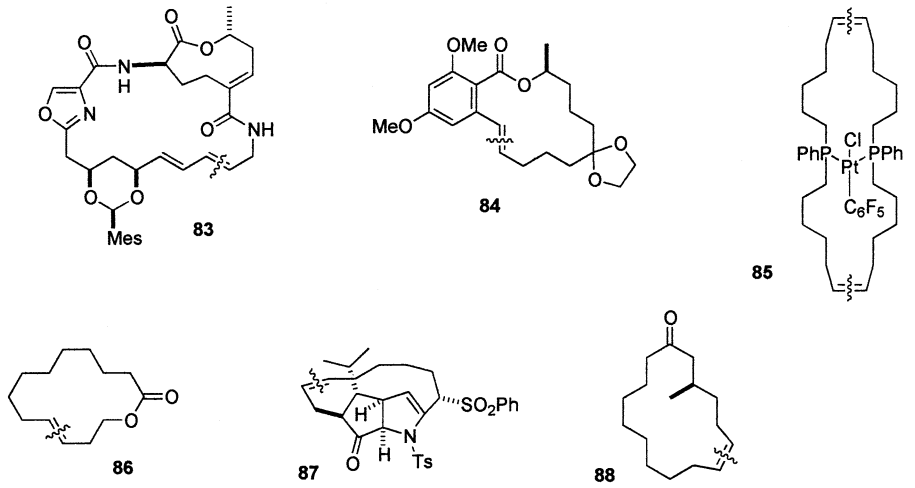
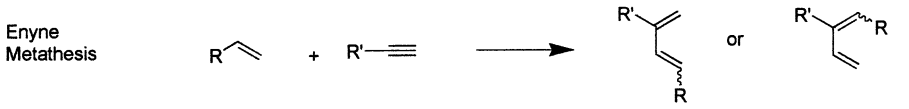


Fig. 9. Representative macrocycles (ring size >10) prepared using the RCM reaction (bond constructed through RCM indicated).



Scheme 9.

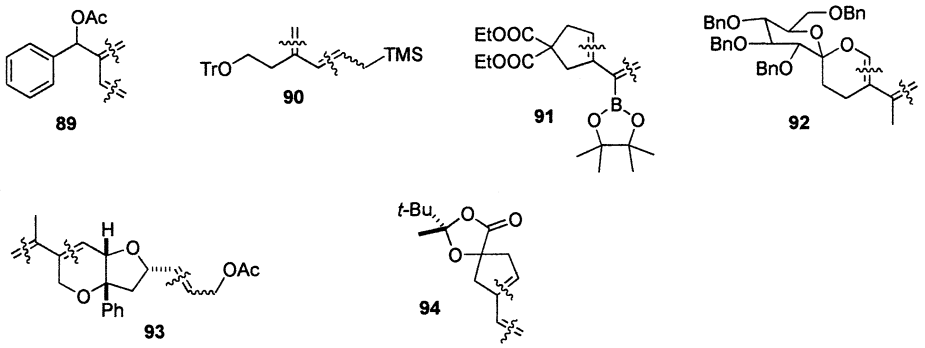
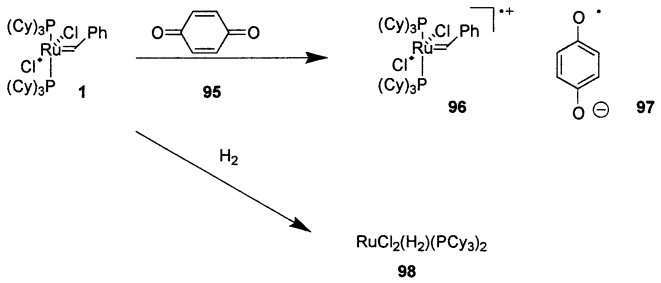


Fig. 10. Representative conjugated dienes prepared using an enyne metathesis reaction (bonds constructed through RCM indicated).

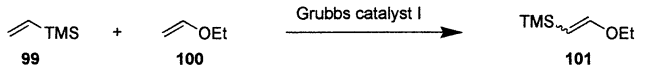
synthesis of macrocyclic esters (e.g. **86**) using Grubbs catalyst II [263]; (10) synthesis of highly oxygenated macrocyclic esters [264]; (11) synthesis of the macrocyclic ring of roseophilin (e.g. **87**) [265]; (12) synthesis of macrocyclic diamides [266], including an example where a resin is part of the macrocyclic ring system [267]; (13) synthesis of macrocycle-bridged carbohydrate derivatives [268,269]; (14) synthesis of a macrocyclic ketone (**88**) for muscone total synthesis [270]; (15) synthesis of 17-membered ring cyclic ketones [271]; and (16) synthesis of macrocyclic aryl ethers [272].

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 9) were reported in 2000. Examples of intermolecular enyne metathesis reactions (Fig. 10) include: (1) synthesis of isoprene derivatives (e.g. **89**) via the cometathesis of propargyl ethers or propargyl esters and ethylene [273,274]; (2) formation of pentadienylsilanes (e.g. **90**) via cometathesis of terminal alkynes and allyltrimethylsilane using Grubbs catalyst II [275]; and (3) cometathesis of propargylaminoacid derivatives and allyl acetate [276]. Examples of intramolecular enyne metathesis include: (1) five-membered ring formation (e.g. **91**) using alkynylboranes as the alkyne component [277]; (2) formation of the macrocyclic ring of rosephilin [278]; (3) synthesis of oxygen heterocycles spiro fused to the anomeric carbon of carbohydrate derivatives (e.g. **92**) [279]; (4) synthesis of eight-membered rings featuring two heteroatoms



Scheme 10.



Scheme 11.

[280]; (5) tandem ring opening-ring closing enyne metathesis followed by cross metathesis with allyl acetate, resulting in triene derivative **93** [281]; (4) formation of five-membered ring nitrogen heterocycles fused to six-membered rings in a tandem ring closing enyne metathesis–Diels–Alder sequence [282]; (5) stereoselective formation of vinylcyclopentene derivatives (e.g. **94**), which proceeds with a high degree of diastereoselectivity due to kinetic resolution in the enyne metathesis event [283]; and (6) synthesis of five-membered rings fused to γ-lactams [284].

2.2.7. Non-metathesis reaction processes involving the Grubbs catalyst

Reaction of Grubbs catalyst I with benzoquinone (**95**, Scheme 10) in dichloromethane led to the electron transfer product **96**, which could be observed by EPR [285]. No EPR signals were observed during the reaction in CCl_4. EPR signals were also observed in the ROMP of norbornadiene using Grubbs catalyst. Reaction of Grubbs catalyst I with hydrogen gas led to dihydrogen complex **98** [286].

The coupling of vinyltrimethylsilane and ethyl vinyl ether in the presence of Grubbs catalyst was studied (Scheme 11) [287]. Although an apparent cross metathesis product (**101**) was formed, deuterium labeling studies were not consistent with mechanism involving cross metathesis. A ruthenium-catalyzed silicon–hydrogen exchange process was proposed.

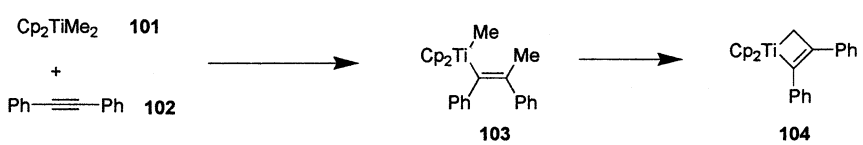
2.3. Individual carbene or alkylidene complexes classified according to metal

2.3.1. Group IV metal–carbene complexes

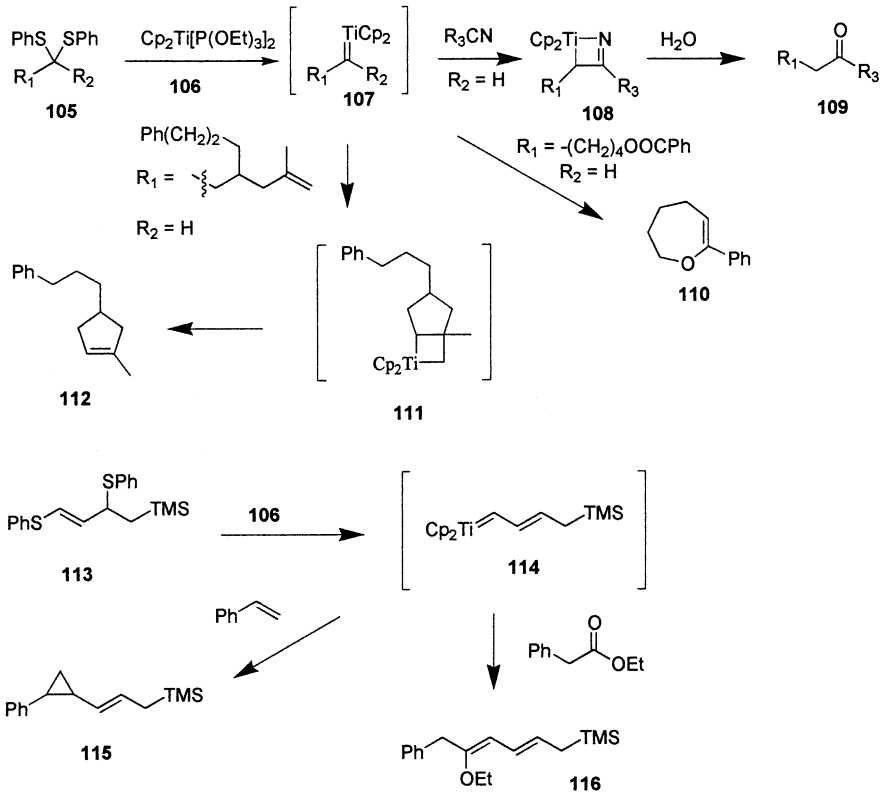
Both isolable titanium–carbene complexes and reactions that involve titanium alkylidene complexes are covered in this section. Routine uses of the Tebbe and Petassis reagents for carbonyl olefination are not covered in this section. Some alternative uses of these reagents were reported in 2000. The Tebbe reagent was an effective reagent for the reduction of sulfoxides to sulfides [288]. In the coupling of dimethyltitanocene with diphenylacetylene (Scheme 12), formation of the major product, titanacyclobutene **104**, was not consistent with involvement of titanium alkylidenes [289]. Alkyne insertion to form vinyltitanium species **103** (also isolated from the reaction) followed by oxidative addition into the γ-C–H bond and reductive elimination of methane was proposed.

Several examples of the generation of titanium alkylidene intermediates (**107**, Scheme 13) from dithioacetals (**105**) and low-valent titanium (**106**) were reported in 2000. Reaction of dithioacetals with titanium complex **106**, followed by a nitrile then water led to unsymmetrical ketone derivative **109**, via hydrolysis of azatitanacyclobutene intermediate **108** [290]. Tandem carbene formation–intramolecular carbonyl olefination was observed in the coupling an ester–dithioacetal with titanium complex **106**, resulting in cyclic enol ether **110** [291]. Tandem carbene formation–RCM resulting in cycloalkenes (e.g. **112**) was observed in the coupling alkene-dithioacetals with titanium complex **106** [292] and related systems [293]. Coupling of dithioacetals and resin-bound esters in the presence of titanium complex **106** led to resin-bound enol ethers, which were readily cleaved from the resin by acid hydrolysis of the enol ether [294]. Alkenylcarbene–titanium complex intermediates (e.g. **114**) were generated from the reaction of complex **106** with 1,3-bis(phenylthio)-1-alkene derivatives (e.g. **113**) [295]. Reaction with ketones and esters led to the expected carbonyl olefination products (e.g. **116**). Reaction with styrene led to alkenylcyclopropane derivatives (e.g. **115**).

Stable and isolable hafnium–alkylidene complexes featuring bridging phosphimine ligands (e.g. **117**, Scheme 14) were prepared and their reactivity profile examined [296,297]. Ligand exchange and alkylation reactions were reported for this complex, resulting in



Scheme 12.



Scheme 13.

addition products (e.g. **118**) or substitution products (e.g. **119**). Addition of isocyanates or imines afforded complexes resulting from [2 + 2] cycloaddition processes (e.g. **120**).

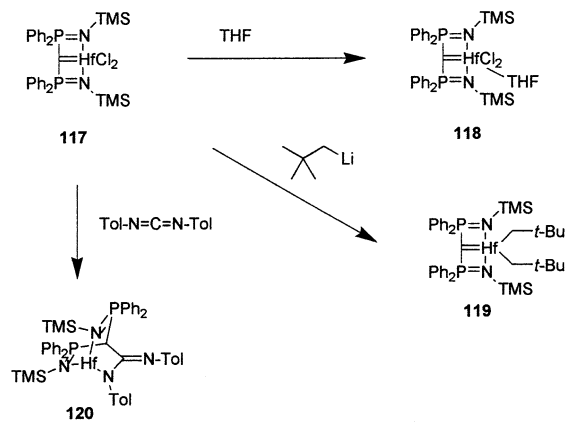
A patent was awarded for a zirconium–carbene olefin polymerization catalyst [298].

2.3.2. Group V metal–carbene complexes

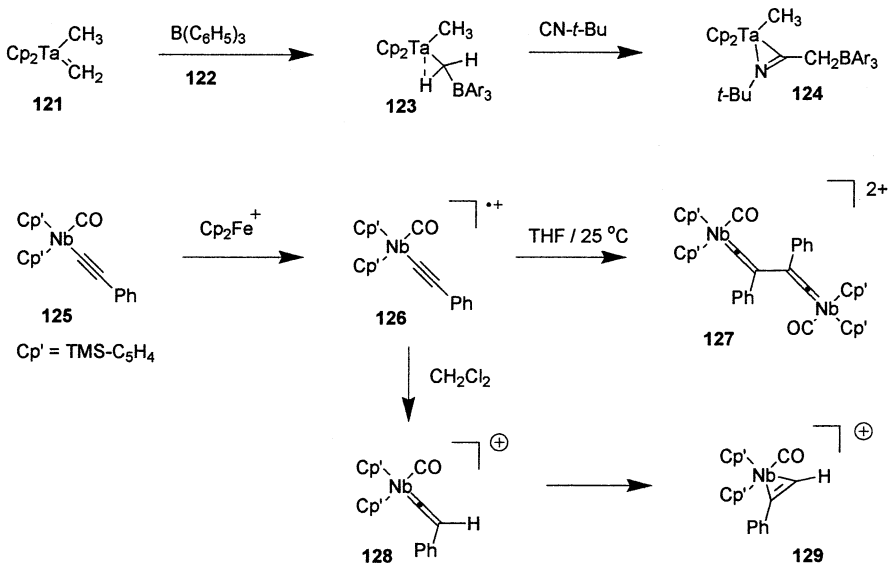
Several papers emphasizing the synthesis and reactivity of Group V metal–carbene complexes appeared in 2000. Reaction of tantalum–carbene complex **121** (Scheme 15) with tris(pentafluorophenyl)borane (**122**) led to the dialkyl complex **123** featuring an agostic interaction [299]. A series of cationic niobium–vinylidene complexes (e.g. **127**, **128**) were prepared through the protonation or oxidation processes of neutral alkynylniobium complexes (e.g. **125**) [300]. Alkynylniobium complex **125** undergoes one-electron oxidation to afford alkyne complex **126**, which then either abstracts a hydrogen atom from the solvent to afford the mononuclear vinylidene complex (e.g. **128**), or undergoes a dimerization to afford the dinuclear vinylidene complex (e.g. **127**). Silica-bound tantalum carbene complexes were produced from the reaction of *t*-BuCH=Ta(CH_2–*t*-Bu)$_3$ with dehydrated silica [301]. Mixtures of mono-linked and dilinked isomers were formed. Reaction of the silica-bound complexes with ethanol at 150 °C led to triethoxytantalum bound to silica. A tantalum carbene complex was obtained as a minor product in the reaction of an azadiene–tantalum complex with dibenzylmagnesium [302].

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

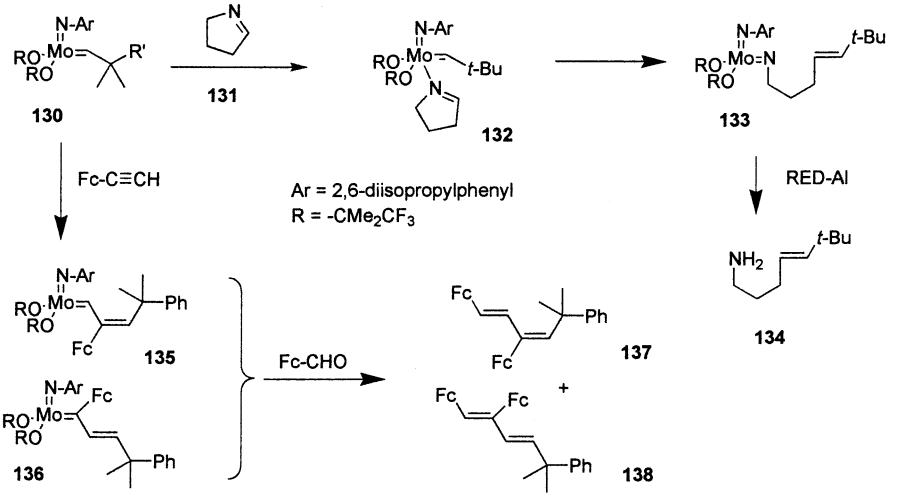
2.3.3.1. Schrock-type carbene complexes. A significant portion of this subject material has already been presented in the alkene metathesis section; the Schrock catalyst belongs to this class. Analogs of the Schrock catalyst featuring *N*,*N*′-disubstituted-2,2′-bisamido-1,1′-



Scheme 14.



Scheme 15.

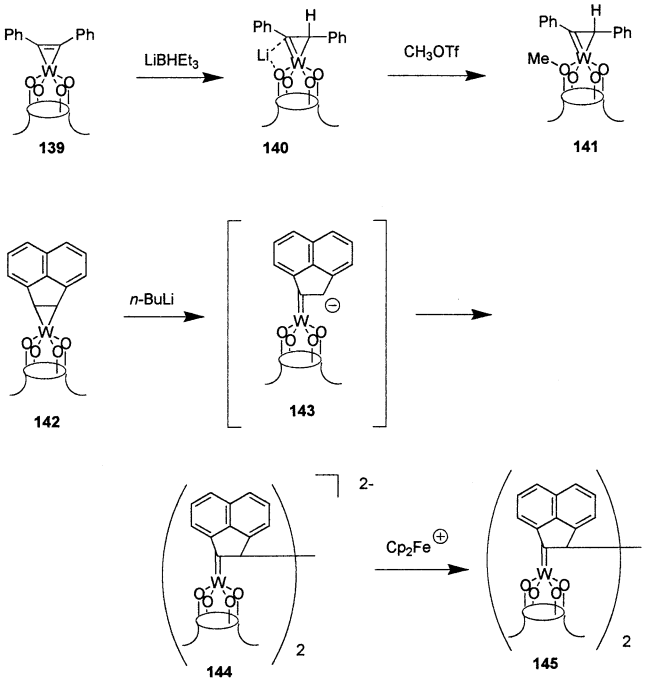


Scheme 16.

binaphthyl ligands were found to be surprisingly unreactive to alkenes and aldehydes [303]. A mechanistic study of the reaction of cyclic imines (e.g. **131**, Scheme 16) with derivatives of the Schrock catalyst (**130**, R′=CH_3) was reported [304]. Coupling of complex **130** with imine **131** led to aminoalkene **134** after reduction with RED-Al. A mechanism involving complexation followed by [2 + 2] cycloaddition, followed by retro [2 + 2] cycloaddition was proposed. The amine results from reduction of metal–imido complex **133**. Stoichiometric coupling of the Schrock catalyst with ethynylferrocene, followed by treatment of the resultant regioisomeric alkenylcarbene complexes (**135** and **136**) with ferrocenecarboxaldehyde led to diferrocenyl-substituted diene systems **137** and **138** [305]. A tungsten carbene–oxo complex was observed by NMR upon thermolysis of a dialkyltungsten complex [306].

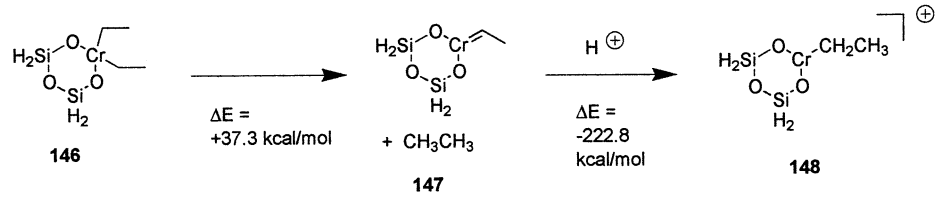
Tungsten calixarene alkyne complexes (e.g. **139**, Scheme 17) are transformed to the corresponding η^2-vinyl complexes (**140**) by reduction with lithium triethylborohydride [307]. A dimeric dicarbene complex (**144**) was produced from treatment of calixarene alkene tungsten complex **142**, which was transformed to the neutral complex **145** upon oxidation with ferrocenium cation.

The polymerization of ethylene using dialkylchromium(IV) species was studied by Density Functional Theory [308]. The energetically most reasonable pathway (Scheme 18) involves conversion of the dialkylchromium species (e.g. **146**) to a chromium carbene complex (e.g. **147**), followed by protonation to afford a cationic alkylmetal species (e.g. **148**), which is the active catalyst for polymerization.

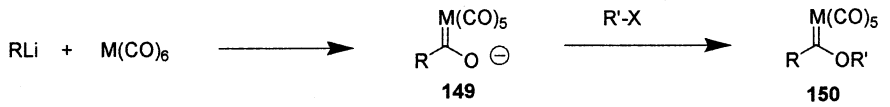


Scheme 17.

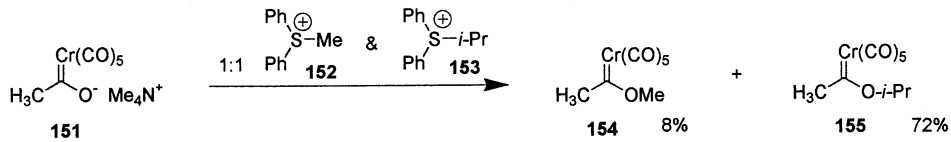
2.3.3.2. Publications focusing on synthesis or formation of Fischer carbene complexes of Group VI metals. The most common procedure used for the synthesis of Group VI metal–carbene complexes (e.g. **150**, Scheme 19) is the Fischer synthesis, which is depicted in Scheme 19 and involves coupling of an organolithium reagent with a Group VI metal carbonyl derivative, followed by alkylation of the resulting acylate (**149**). Sulfur ylides (e.g. **152**, **153**, Scheme 20) have been successfully utilized for the alkylation step of the Fischer synthesis [309]. This reaction was effective for transferring methyl, primary, and secondary groups to the acylate intermediate. Transfer of secondary groups was more facile than transfer of a methyl group as noted by the example in Scheme 20. Possible mechanisms considered for this process include: (1) an S_N2 process with lots of carbocation character; (2) addition of the acylate complex to sulfur followed by elimination of diphenyl sulfide; or (3) a radical chain process. Alkyl iodides were shown to be suitable reagents for the conversion of carbene acylates into alkoxycarbene complexes under phase transfer conditions [310].



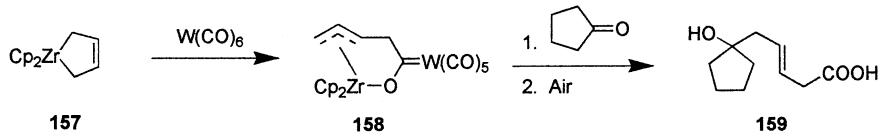
Scheme 18.



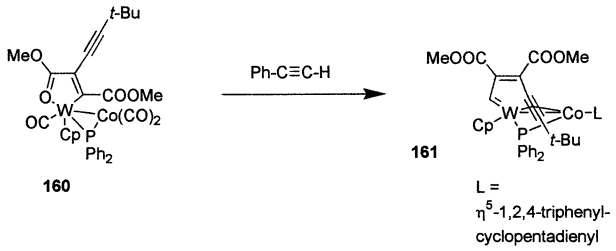
Scheme 19.



Scheme 20.



Scheme 21.

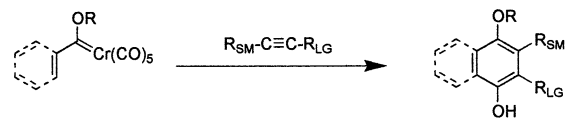


Scheme 22.

Zirconoxycarbene–tungsten complexes (e.g. **158**, Scheme 21) were prepared from the coupling of zirconacyclopentene (**157**) with tungsten hexacarbonyl [311]. Coupling of these complexes with ketones occurs at the allyl ligand to provide a hydroxy acid (e.g. **159**) upon oxidation. A tungsten–carbene complex bound to cobalt through a bridging alkyne (**161**, Scheme 22) was formed in the coupling of oxametallacyclopentadiene–tungsten complex **160** with phenylacetylene (Scheme 22) [312].

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.

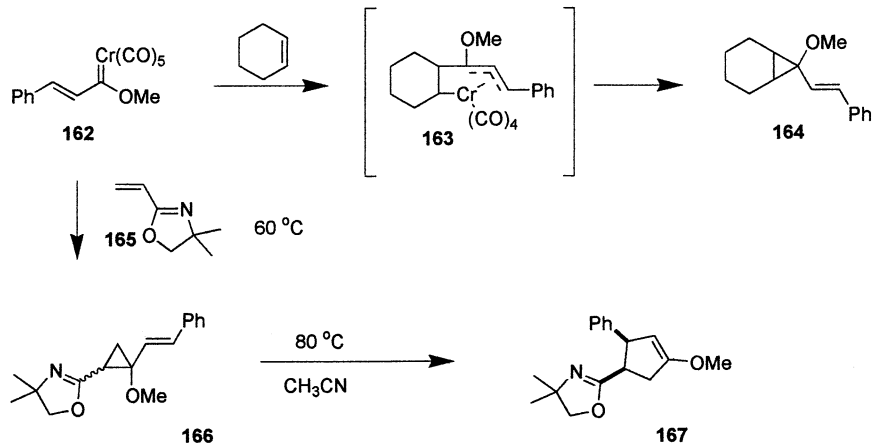
Successful cyclopropanation of unactivated alkenes was achieved using chromium complexes (e.g. **162**, Scheme 23) in refluxing DMF [313]. Only alkenylcarbene and heteroarylcarbene complexes were successful in this reaction. The cyclopropanation of cyclohexene required a 20-fold molar excess of cyclohexene. In cases



Scheme 24.

involving monosubstituted alkenes or *cis*-1,2-disubstituted alkenes, the cyclopropane stereoisomer where the methoxy group and the original alkene substituents are cis was produced with a high degree of stereoselectivity. A mechanism involving [2 + 2]-cycloaddition followed by conversion of the resulting σ- to a π-allyl complex (e.g. **163**) was proposed to account for the substrate limitations of this process. Reaction of α,β-unsaturated carbene complexes with 2-alkenyloxazoles (e.g. **165**) at 80 °C led to five-membered ring derivatives (e.g. **167**) [314]. At lower temperature the corresponding vinylcyclopropane derivatives (e.g. **166**) could be isolated, which isomerized to the five-membered ring derivatives at 80 °C in acetonitrile.

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 24) and alkynes (commonly known as the Dötz reaction) were reported in 2000. The formation of *m*- and *p*-cyclophanes (e.g. **169**, Scheme 25) was observed from the intramolecular coupling of alkyne-containing α,β-unsaturated carbene complexes (e.g. **168**) [315]. Coupling of tetracarbene complex **170** with 3-hexyne led to corresponding tetranaphthoxy ether derivative **171**; the crude product prior to decomplexation of chromium consisted of seven isomers [316]. Coupling of oxygenated arylcarbene–chromium complexes (e.g. **172**) with 1-hexyne was examined [317]. Serious competition with cyclopentannulation reactions was observed for complexes containing strongly electron donating groups in the para position. A complex

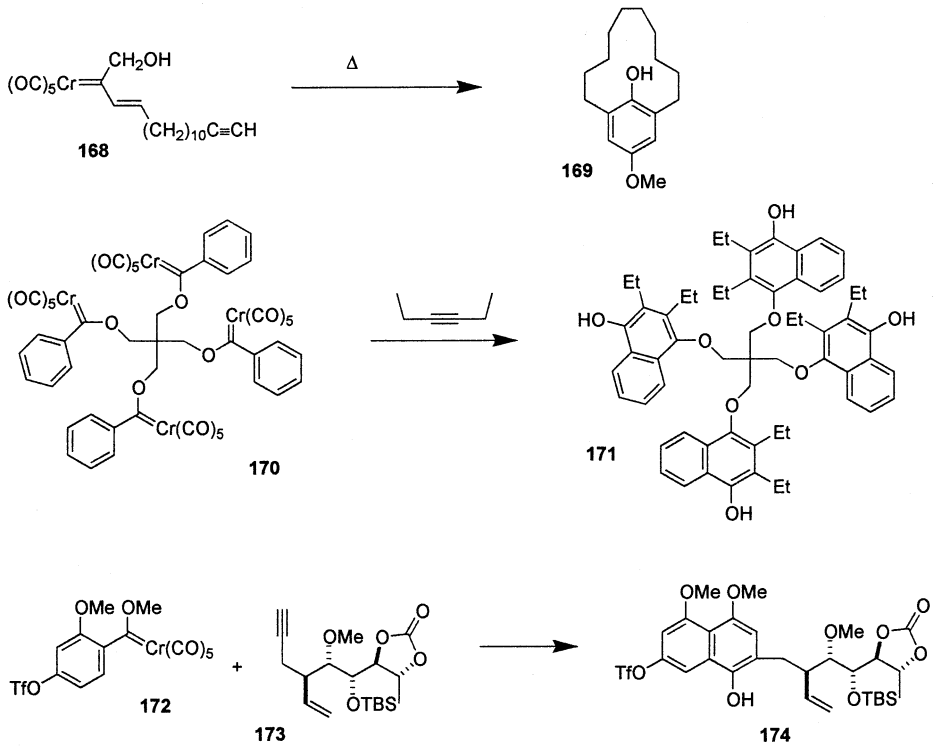


Scheme 23.

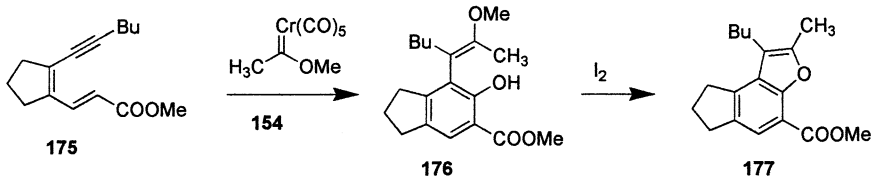
intermediate for olivin total synthesis (**174**) was prepared using similar complexes and a complex alkyne (**173**) in the Dötz reaction. A formal total synthesis of 7-methoxyeleutherin was reported which utilizes the Dötz reaction as the key step [318]. Aminobenzannulation reactions were observed in the coupling of β-carbomethoxy-α,β-unsaturated aminocarbene complexes with simple alkynes [319]. Cyclopentannulation reactions were observed when alkynoate esters were used.

Alternative benzannulation through the coupling of simple carbene complexes with fully conjugated dienylacetylenes (e.g. **175**, Scheme 26) was reported [320]. The initially expected phenol–enol ether derivatives (e.g. **176**) are converted to benzofurans (e.g. **177**) in the oxidative workup procedure. A related benzannulation process was observed in the coupling of conjugated enediynes (e.g. **178**, Scheme 27) with simple carbene complexes [321]. Formation of the aromatic ring involves conversion of an enyne–ketene intermediate (**179**) into diradical intermediate **180**. Through careful exclusion of hydrogen atom donors, selective remote functionalization processes occur, resulting in allylbenzene derivatives (e.g. **185**) as the major products. The diradical intermediates could also be captured through chlorine abstraction processes, resulting in chlorinated analogs (e.g. **187**).

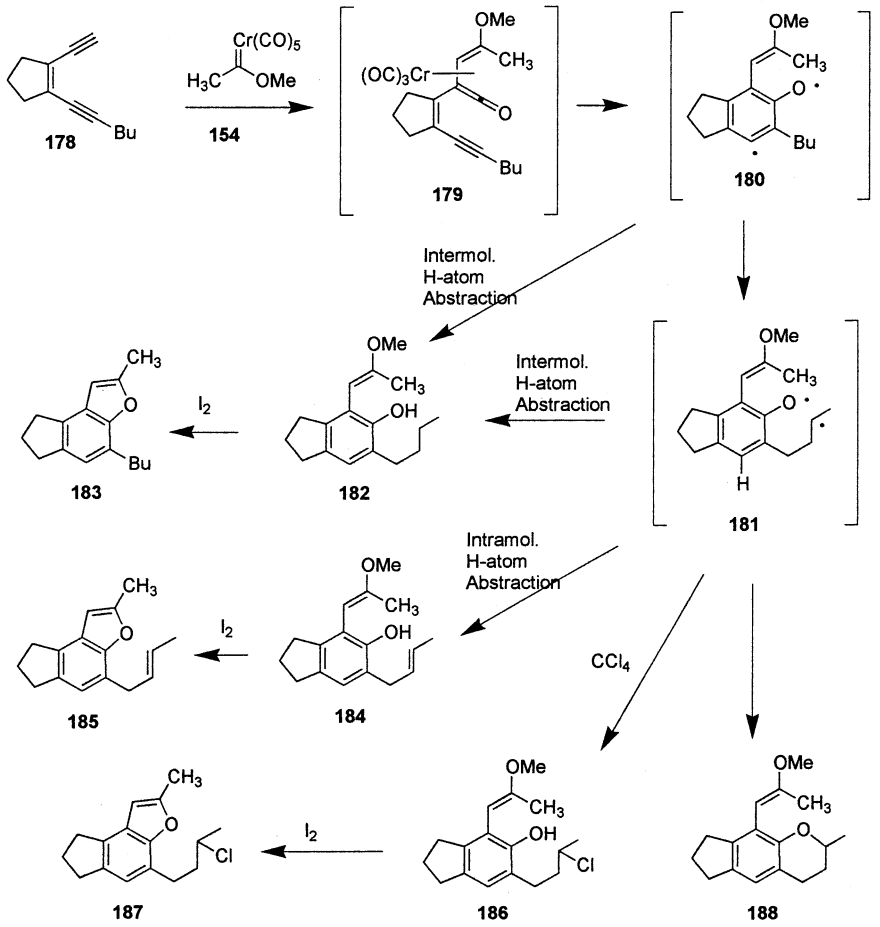
The stepwise Dötz reaction was demonstrated for the coupling of α,β-unsaturated aminocarbene complexes and dimethyl acetylene dicarboxylate (Scheme 28) [322]. Low-temperature photolysis of aminocarbene complexes (e.g. **189**) afforded the η^3-vinylcarbene complex (e.g. **190**), which reacted with DMAD to afford α,β,γ,δ-unsaturated carbene complex (e.g. **191**), which could be converted to the more stable pentacarbonyl species (e.g. **192**) upon treatment with CO. Complexes analogous to **192** could be characterized by X-ray crystallography. Thermolysis of complex **191** afforded cyclopentannulation product **193**. Thermolysis of analogous complexes derived from propiolic acid (e.g. **194**) led to benzannulation products (e.g. **196**).



Scheme 25.



Scheme 26.



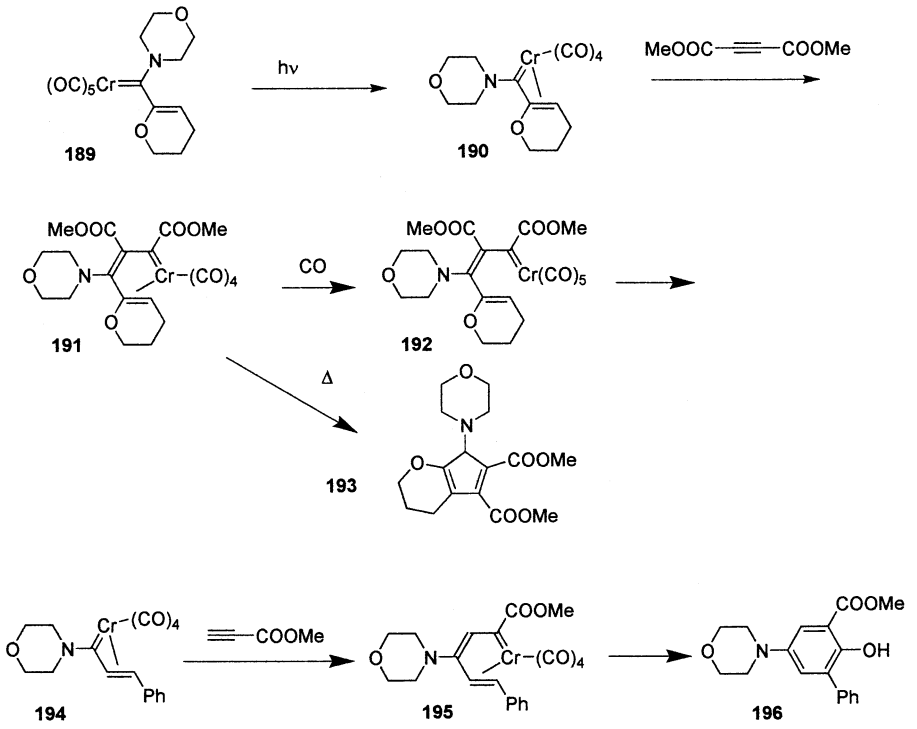
Scheme 27.

2.3.3.5. Nonbenzannulation reactions of Group VI metal–carbene complexes with alkynes. The coupling of β-amino-α,β-unsaturated carbene complexes (e.g. **197**, Scheme 29) with three moles of a terminal alkyne led to spiro[4.4]nonatriene derivatives (e.g. **205** and **206**) [323]. The proposed mechanism involves formation of the expected cyclopentannulation product (e.g. **198**) followed by conversion to a cyclopentadienylidene complex (e.g. **200**), which undergoes alkyne insertion and elimination of trimethylsilane to afford an alkoxycarbene complex intermediate (e.g. **202**). Insertion of a third equivalent of alkyne affords the expected cyclopentannulation product (e.g. **204**), which reacts with trimethylsilane to afford the observed products. This mechanism was supported through deuterium labeling studies.

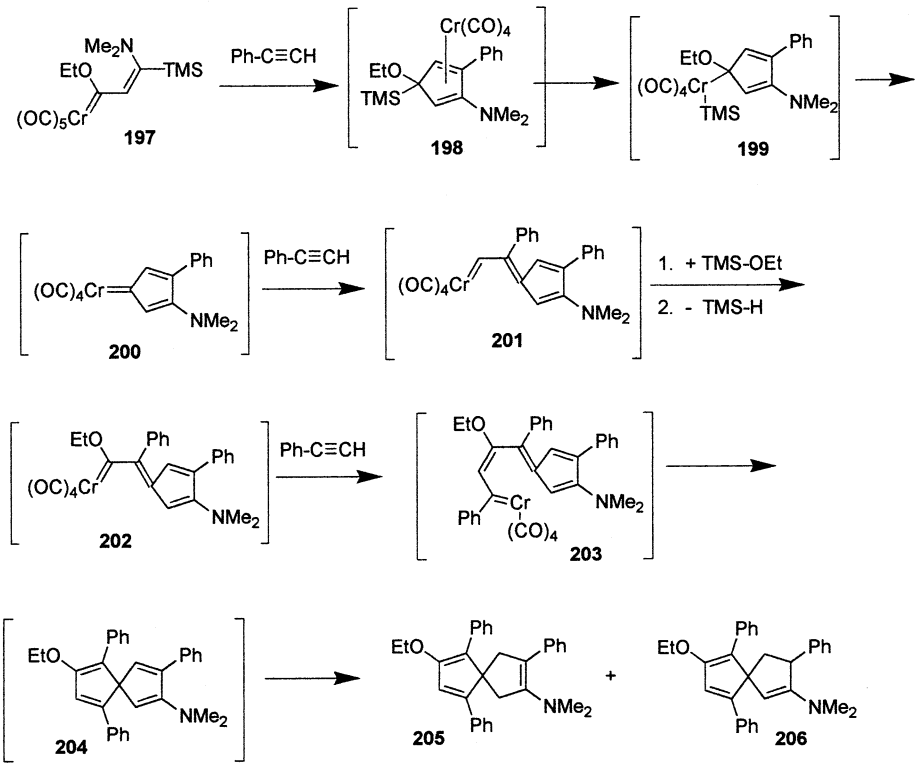
Other new cycloaddition processes that involve the coupling of metal–carbene complexes and alkynes were reported in 2000 (Scheme 30). Coupling of α,β,γ,δ-unsaturated carbene complexes (e.g. **207**) with monosubstituted acetylenes led to eight-membered ring derivatives (e.g. **208**) [324]. Analogs were the γ,δ-double bond is part of an aromatic ring (e.g. **209**) underwent Dötz-type chemistry, resulting in cyclohexadienone derivatives (e.g. **210**). Five-membered nitrogen heterocycles (e.g. **212**) were prepared from the coupling of alkenes or alkynes with iminocarbene complexes (e.g. **211**) under photolytic conditions [325]. Reaction of cyclopropylcarbene complexes (e.g. **213**) with propargyl ethers (e.g. **214**) and esters led to alkylidenecyclopentenone derivatives (e.g. **215**) [326]. Formation of a cyclopentadienide anion intermediate followed by elimination was the key step in these processes. Coupling of 1,4-dioxygenated-2-alkyne derivatives (e.g. **216**) with carbene complex **213** led to the formation of dialkylidenecyclopentenones (e.g. **217**) through a double elimination process.

Other processes involving the capture of vinylcarbene complexes generated from the coupling of carbene complexes and functionalized alkenes were reported in 2000 (Scheme 31). Coupling of carbene complexes with *o*-alkynylbenzaldehyde derivatives (e.g. **218**) led to the generation of isobenzofurans (e.g. **219**) [327]. Simple coupling of carbene with alkyne resulted in the formation of alkylidenephthalans (e.g. **223**) via a net 1,7-hydrogen shift followed by enol ether hydrolysis. A three-component coupling was observed if the reaction was conducted in the presence of electron-deficient

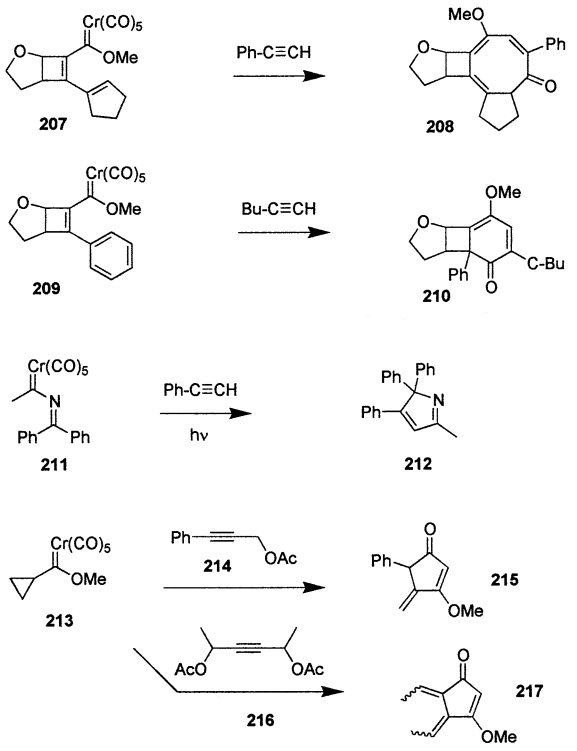
alkenes (e.g. **220**); the intermediate isobenzofuran undergoes a Diels–Alder reaction in this case. Processes involving capture of the corresponding vinylketenes were also reported (Scheme 32). The coupling of carbene complexes with dienyne derivatives (e.g. **224**) was examined as a possible synthetic route to taxol derivatives [328]. Coupling of **224** with methylcarbene complex **154** resulted in cyclobutenones (e.g. **227**) or cy-



Scheme 28.



Scheme 29.



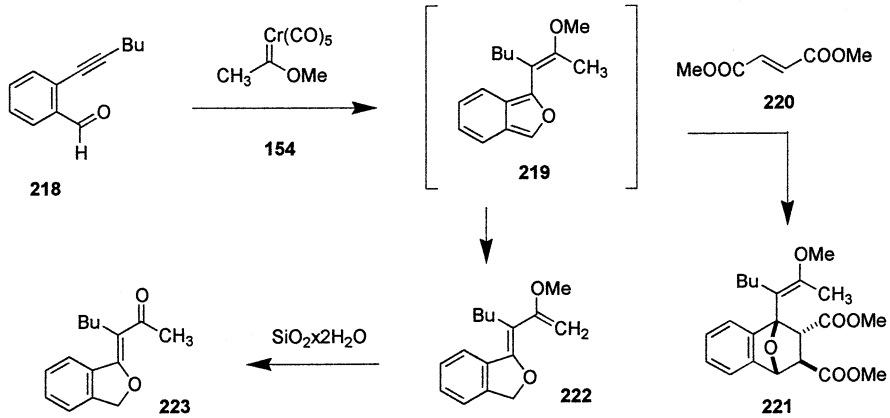
Scheme 30.

clobutenones (e.g. **226**). Formation of **226** is the desired process for taxol synthesis. A systematic study of this process involving aryloxycarbene complexes (e.g. **225**) revealed that electron-deficiency in the ketene favors the desired product. Coupling of hindered arylcarbene complex **228** with alkynols (e.g. **229**) led to the lactone derivatives (e.g. **230**) under thermal or sonication conditions [329].

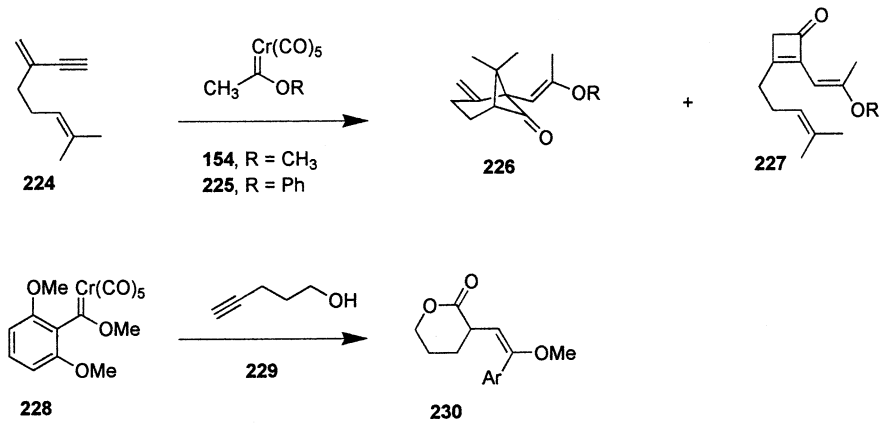
2.3.3.6. Photolysis reactions of Group VI metal–carbene complexes. Several publications concerning the formation of chromium ketene complexes (e.g. **232**, Scheme 33) through photolysis of Fischer carbene–chromium complexes appeared in 2000. Chromium carbene-derived cyclobutenones or β-lactams were used as starting materials for the synthesis of *C*-nucleosides (e.g. **234**) [330,331], cyclams (e.g. **236**) [332], and aminocyclitols [333]. Similar studies employing bis(carbene) complex species linked through the carbene oxygens were also reported [334]. A combined experimental–theoretical study of the photolytic formation of β-lactams from chromium carbene complexes and imines was reported [335]. The preferred mechanistic pathway is depicted in Scheme 34. The reaction is specific to complexes featuring all carbonyl ligands (e.g. **237**, L = CO) or one triphenylphosphine ligand (**237**, $L = PPh_3$), but is general not successful for complexes featuring a tributylphosphine ligand (**237**, $L = PBu_3$) or a chelating diphosphine. The calculations suggest that this effect can be attributed to widening of the HOMO–LUMO gap for complexes featuring an electron-rich phosphine ligand, which suppresses conversion to the vinylketene complex (e.g. **238**). The most energetically reasonable pathway for β-lactam formation involves a two-step process featuring conversion to chromium enolate (e.g. **240**) prior to ring closure. Laser flash photolysis studies of an alkoxycarbene–tungsten complex revealed that *E–Z* isomerization about the C–O bond and dissociation of a *cis*-CO ligand are the primary photochemical processes [336].

Photolysis of silylcarbene–tungsten complexes (e.g. **242**, **244**, Scheme 35) resulted in internally-chelated tetracarbonyltungsten–carbene analogs (e.g. **243**, **245**) [337]. The silicon–hydride analog resulted in a complex featuring an agostic Si–H ligand, while aminosilane and alkenylsilane derivatives afforded the expected internally-coordinated complexes.

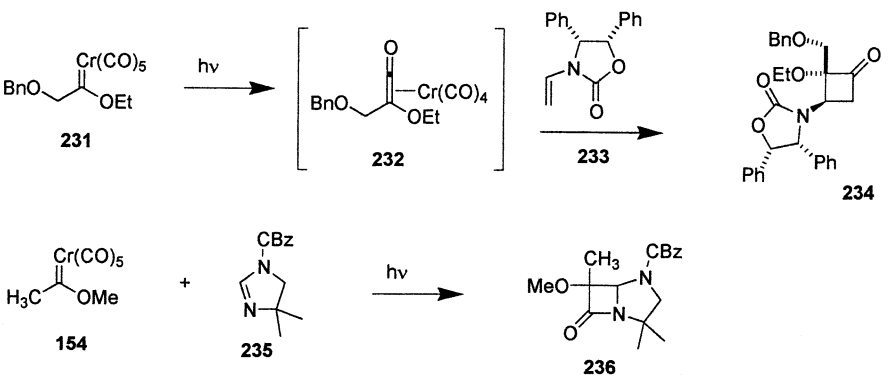
2.3.3.7. Reactions occurring at the conjugated C–C π-bond of α,β-unsaturated Group VI metal–carbene complexes. Numerous reaction processes were reported in 2000 where a carbene complex activates a π-bond for nucleophilic addition or cycloaddition reactions (i.e. the carbene complex is a surrogate for an 'activated ester').



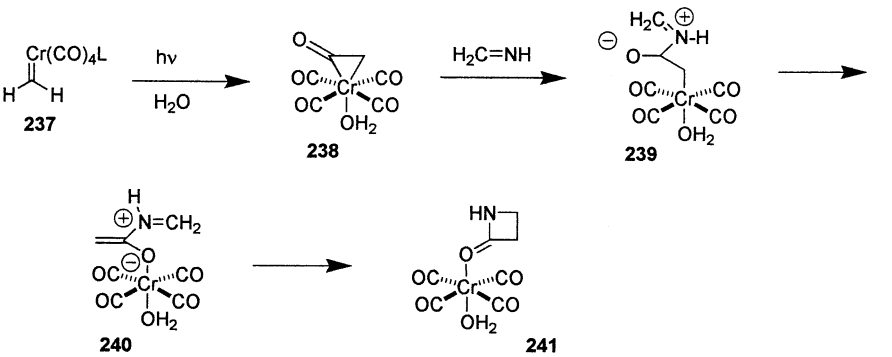
Scheme 31.



Scheme 32.

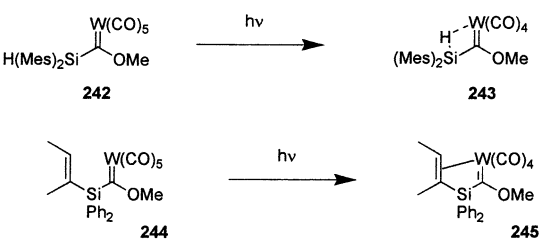


Scheme 33.

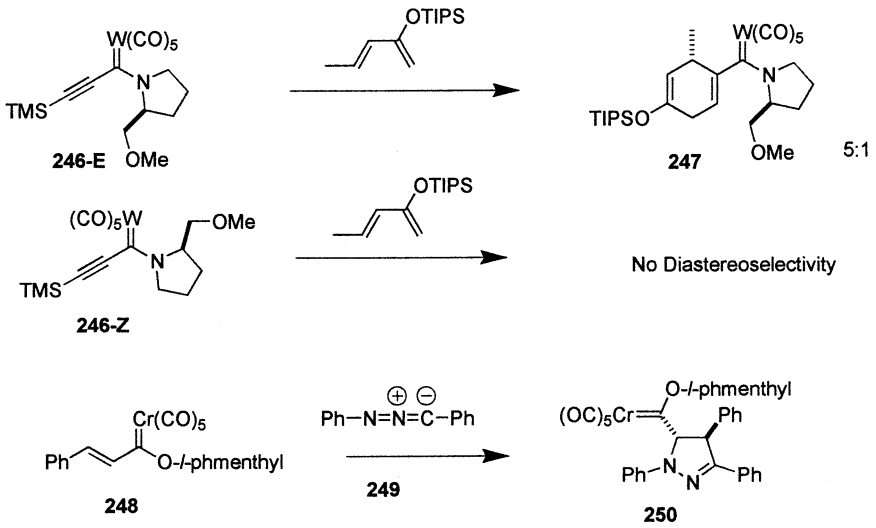


Scheme 34.

Representative examples of [N + 2] cycloaddition processes involving α,β-unsaturated carbene complexes as 2π components are depicted in Scheme 36. Moderately, diastereoselective Diels–Alder reactions were observed using alkynylcarbene complexes of general structure **246** [338]. The highest diastereoselectivity was achieved using the *E*-isomers of carbene complex **246**, no diastereoselectivity was observed using the *Z* isomers. The 1,3-dipolar cycloaddition was reported for α,β-unsaturated carbene complexes (e.g. **248**) and ni-



Scheme 35.



Scheme 36.

trones or diazo ylides (e.g. **249**) [339], and for the coupling of alkynylcarbene complexes with metal dithiolate complexes [340]. This process was highly diastereoselective using the L-phenylmenthyl chiral auxiliary. Coupling of enol ethers with *exo*-methylene cyclic carbene–chromium and –tungsten complexes resulted in a completely diastereoselective [2 + 2]-cycloaddition process [341].

In numerous cases, either nucleophilic addition or cycloaddition to the triple bond of an enynylcarbene or arylalkynylcarbene complex is followed by a secondary cyclization process of the resulting α,β,γ,δ-unsaturated carbene complex; examples are depicted in Scheme 37. Cyclopentannulation reactions were reported for the coupling of enynylcarbene complexes (e.g. **251**, Scheme 37) with sulfur nucleophiles [342]. Nucleophilic addition to the alkyne position affords the metallahexatriene (e.g. **253**), which spontaneously converts to the cyclopentadiene derivative (e.g. **254** or **257**). The observed products from thioacid addition are thioketone–tungsten complexes (e.g. **255**). A mechanistically similar process was observed in the coupling of enynylcarbene complexes with allylic thiols (e.g. **256**) [343]. In this case, the expected thio-substituted cyclopentadienes (e.g. **257**) undergo a thio-Claisen rearrangement to afford thiocyclopentenone derivatives featuring an allyl group in the α-position (e.g. **258**–**260**). Coupling of phenylethynylcarbene **261** with enamines (e.g. **262**) resulted in ring expanded products (e.g. **263**) or Michael addition–cyclization products (e.g. **264**–**266**), depending upon the conditions of the reaction [344]. The ring expansion products were favored in pentane; this process occurs via [2 + 2]-cycloaddition and ring opening. Michael addition products were favored using dichloromethane as the solvent. A net dimerization product (**267**) was formed in the coupling of enynylcarbene complex **251** with acetate ion [345]. Michael addition followed by cyclization affords a cyclopentadiene, which subsequently undergoes a [2 + 2]-cycloaddition with a second mole of carbene. Cyclization of cyclobutene derivative **267** then leads to the observed benzannulation product **268**. The observed benzannulation instead of cyclopentannulation was attributed to formation of the less strained product. Competitive benzannulation and cyclopentannulation were also observed in thermolysis for enynylcarbene complexes featuring an iron-bridging chalcogenide complexed to the central alkene [346].

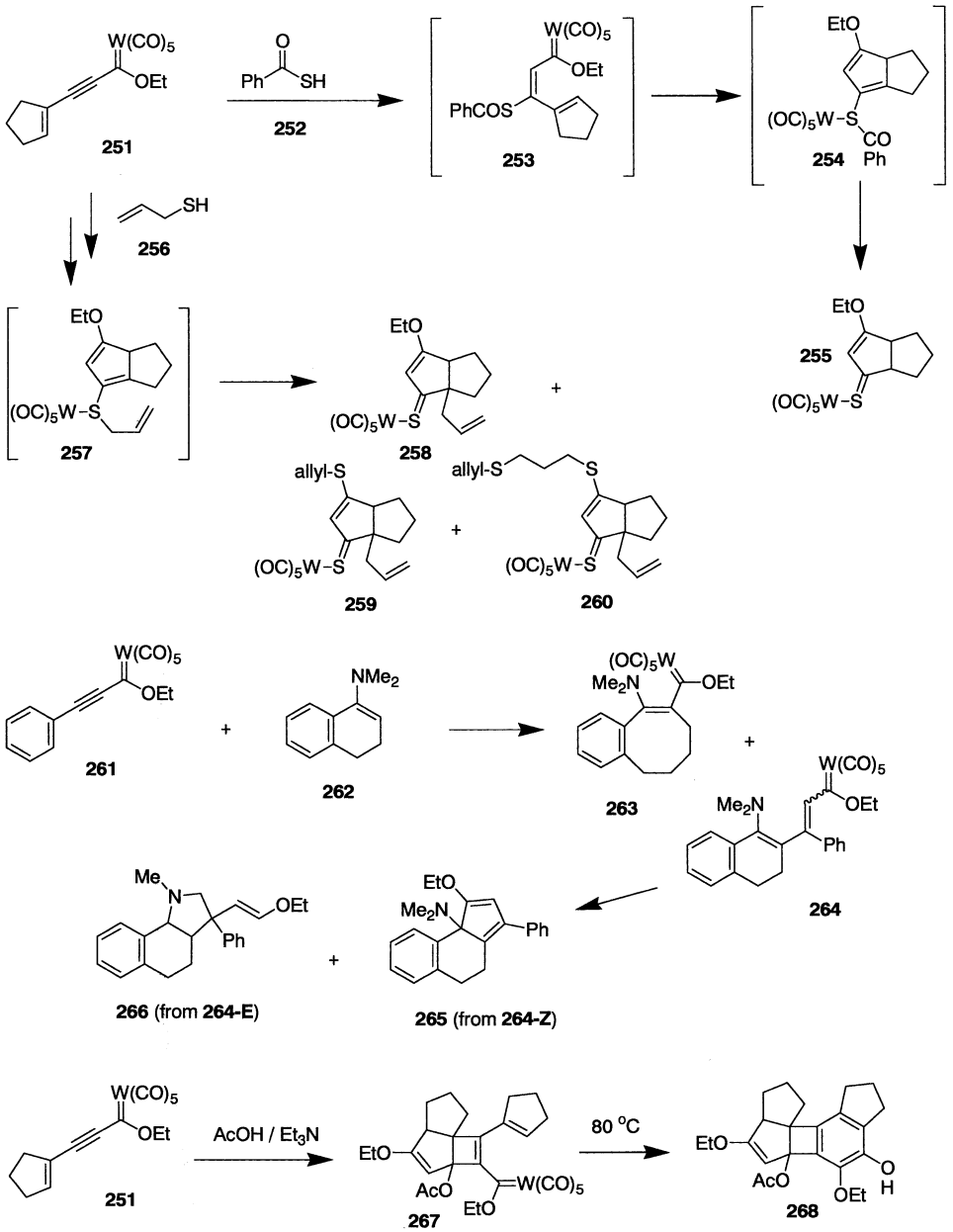
Coupling of α,β-unsaturated carbene complexes (e.g. **269**, Scheme 38) with enamines led to bicyclic structures **272** and **273** [347]. Initial reaction affords zwitterionic compound **271** through Michael addition, followed by proton transfer to afford an enamine–carbene complex, followed by 1,2-addition. Thermolysis of **271** leads to tricyclic compound **272**, while reaction with trifluoroacetic acid leads to bicyclic compound **273**. Coupling of α,β-unsaturated carbene complexes with methyl ketone enolates (e.g. **275**) led to cyclopentenol derivatives (e.g. **277**), which are easily hydrolyzed to cyclopentenones [348]. A mechanism involving 1,2-addition, followed by intramolecular addition of the resulting allylmetal complex **276** to the ketone and decomplexation was proposed. The reaction of enolates derived from methyl α,β-unsaturated ketones (e.g. **278**) led to seven-membered ring derivatives (e.g. **279**).

The coupling of pyranylidene-substituted carbene complexes (e.g. **280**, Scheme 39) with organolithium reagents was examined [349]. Reaction with alkyllithium reagents occurred by attack at the δ-carbon of the π-system. Quenching of the intermediate anion (e.g. **281**) at low temperature resulted in the addition product **282**. Rearrangement to a pyranylidene complex

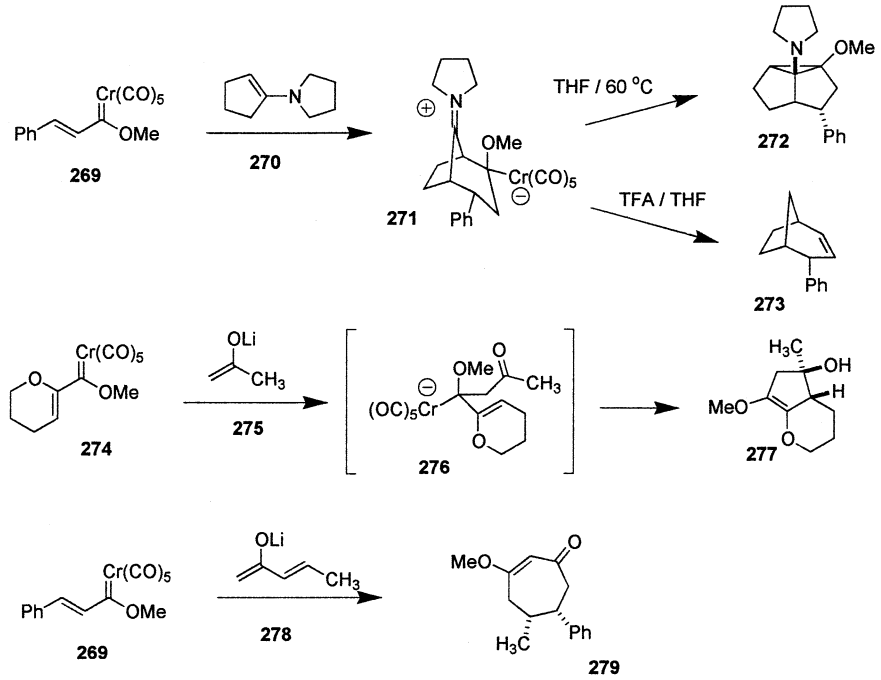
(e.g. **283**) was observed if the reaction was allowed to warm to room temperature prior to proton quench. Reaction with alkynyllithium reagents occurred through attack at the carbene carbon. Reaction with the anion derived from phenylacetylene led to carbene complex **284**.

The coupling of alkynylcarbene complexes (e.g. **261**, Scheme 40) with β-amino-α,β-unsaturated ketones (e.g. **285**) and β-hydroxy-α,β-unsaturated ketones (e.g. **288**) was reported [350]. Reaction with enaminones led to either ring expanded products (e.g. **286**) or cycloaddition products (e.g. **287**); for both **286** and **287**, a zwitterionic resonance form (not depicted) was more important as determined through X-ray and NMR studies. A mechanism involving [2 + 2]-cycloaddition followed by ring expansion was proposed for the formation of ring-expanded product **286**. For formation of **287**, Michael addition, followed by proton transfer, followed by intramolecular displacement of the ethoxy group was proposed. Reaction of these products with amines led to ring opened products (e.g. **288**). Reaction of 1,3-diketone enols led to either products resulting from Michael addition at O (e.g. **290**) or to C-addition products which later cyclized to carbene complexes of general structure **291**.

Reaction of carbohydrate-substituted α,β-unsaturated carbene complexes (e.g. **292**, Scheme 41) with radicals generated from epoxides and titanium(III) led



Scheme 37.



Scheme 38.

Scheme 39.

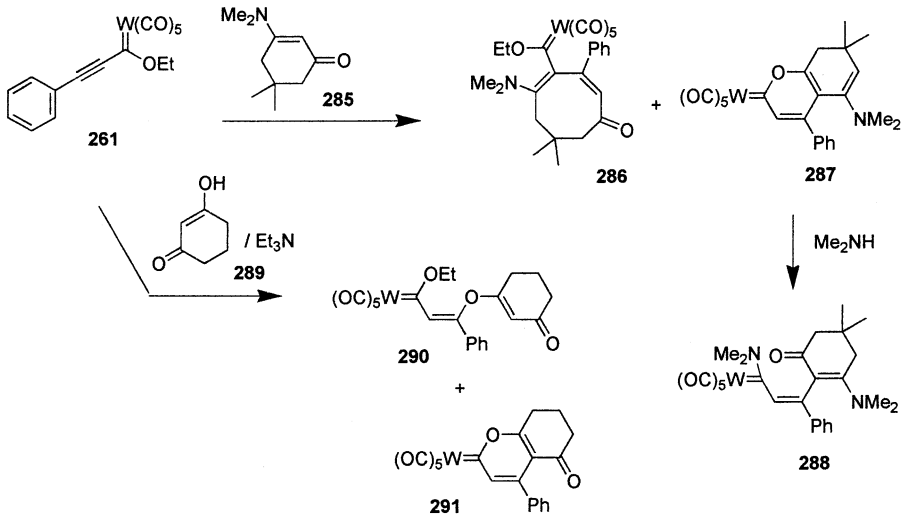
to cyclic carbene complexes (e.g. **294**) with a moderate degree of diastereoselectivity relative to the carbohydrate substituent [351]. Reaction of carbohydrate-epoxides with simple α,β-unsaturated carbene complexes was also reported.

2.3.3.8. Physical organic chemistry of Group VI Fischer carbene complexes. Several papers reporting on kinetic and thermodynamic analysis of nucleophilic acyl substitution reactions of carbene complexes were published in 2000.

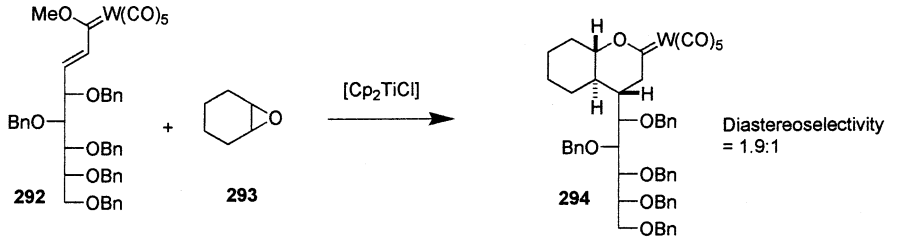
Kinetic and thermodynamic values for the hydrolysis of thiocarbene complexes (Scheme 42) were determined, assuming the mechanistic possibilities depicted in Scheme 42 [352]. The rate determining step was found to be very pH-dependent. At high pH (> 10) the rate determining step was step 1. At pH 6–10, there was no clear rate determining step, and the first step is a preequilibrium. At pH < 6, both the equilibrium constant of step 1 and k_2 were important in the rate equation.

The kinetics for reversible cyclization of carbene complexes of general structure **300** (Scheme 43) were studied [353]. A mechanism depicted in Scheme 43 has been proposed to account for the observations; formation of the tetrahedral adduct **302** could occur through the alkoxide **301** or could involve direct nucleophilic addition of an alcohol, depending on the pH. At equilibrium, the amount of tetrahedral species was greater for thiocarbene complexes (X = S), however the rate of formation of the tetrahedral intermediate was greater for alkoxycarbene complexes (X = O).

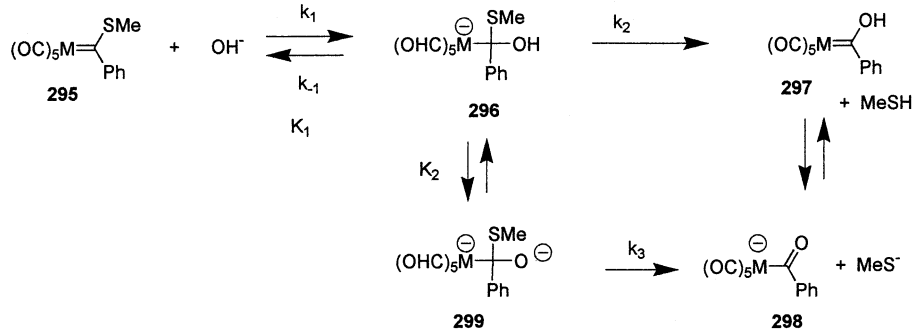
The kinetic and thermodynamic parameters for the addition of alkoxide ions (e.g. **304**, Scheme 44) of varying basicity to arylcarbene–chromium and –tungsten complexes (e.g. **303**) have been determined [354]. The data suggest that the transition state for the alkoxide anion addition is imbalanced in that charge delocal-



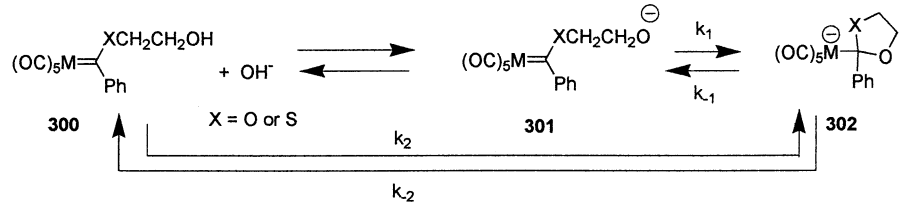
Scheme 40.



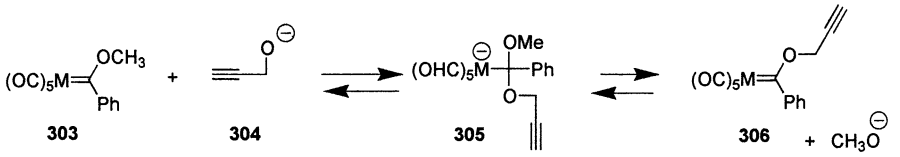
Scheme 41.



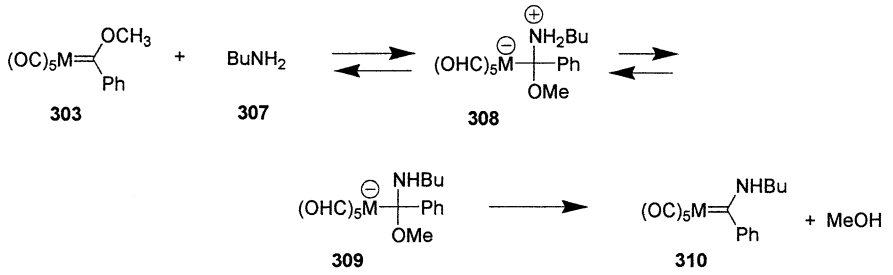
Scheme 42.



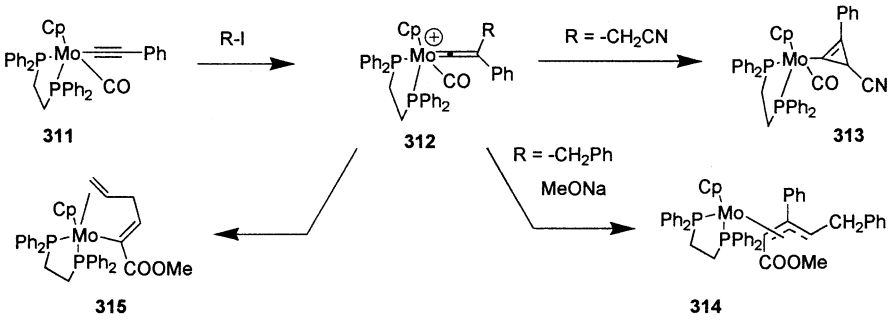
Scheme 43.



Scheme 44.



Scheme 45.



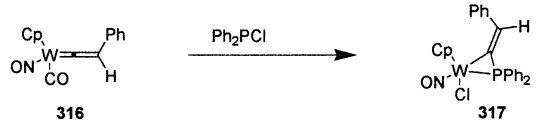
Scheme 46.

ization into the CO ligands lags behind C–O bond formation. A similar imbalance was noted for the acid-catalyzed decomposition of the tetrahedral intermediate.

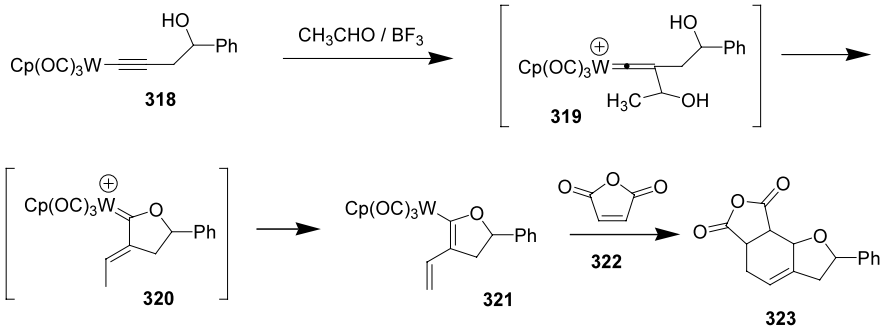
The kinetic parameters for the conversion of alkoxycarbene complexes (e.g. **303**, Scheme 45) to aminocarbene complexes (e.g. **310**) have been studied [355]. The observed studies are most consistent with a mechanism involving addition of the amine to form a tetrahedral intermediate, followed by proton transfer and loss of methoxy. At low amine–OH^- concentration, methoxide ion departure was rate limiting while at high amine–OH^- concentration nucleophilic attack was rate limiting. The tetrahedral intermediate could not be detected. A Hammett study using *p*-substituted analogs of **303** revealed a positive ρ value, which was attributed to destabilization of the starting carbene complex.

2.3.3.9. Synthesis and reactivity of Group VI metal–vinylidene complexes, and reactions that involve vinylidene–metal complexes as intermediates. The synthesis and reactivity of molybdenum–vinylidene complexes of general structure **312** (Scheme 46), prepared by alkylation of the corresponding molybdenum acetylide complex **311**, has been studied [356]. Reaction of allyl- or benzylvinylidene complexes with sodium methoxide proceeded by attack at the carbonyl ligand followed by coupling of the carbomethoxy and vinylidene ligands to give complexes **314** or **315**. Treatment of the cyanomethyl derivative of complex **312** with sodium methoxide led to the cyclopropenylmolybdenum complex **313**. Coupling of tungsten–vinylidene complexes (e.g. **316**, Scheme 47) with chlorophosphines led to the internally-coordinated vinylphosphine–tungsten complexes (e.g. **317**) [357]. Electrophilic attack at the α-carbon of the vinylidene ligand followed by intramolecular ligand substitution was proposed.

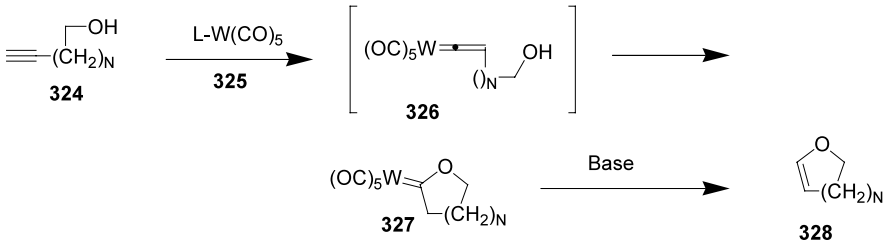
Coupling of alkynyltungsten complexes (e.g. **318**, Scheme 48) with aldehydes and Lewis acids resulted in



Scheme 47.



Scheme 48.



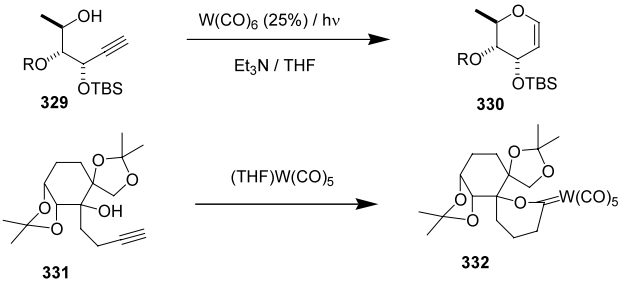
Scheme 49.

dihydrofuran derivatives (e.g. **321**) [358]. The reaction initially affords a vinylidene complex (e.g. **319**), which converts to a cyclic carbene (e.g. **320**) complex. If the reaction was conducted in the presence of triethylamine, the cyclic carbene complex is transformed to a diene. Diels–Alder reactions were demonstrated for these dienes. A similar study was reported of tosylamine analogs of the alkynols, resulting in dihydropyrrole derivatives [359], and for chiral and optically active polyhydroxylated analogs of **318** [360].

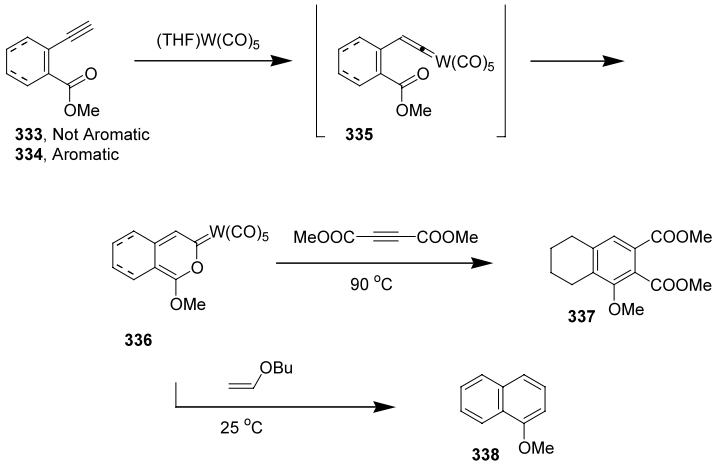
Many examples of the coupling of alkynes with Group VI metal pentacarbonyl sources (e.g. **325**, Scheme 49), which afford unstable metal–vinylidene intermediates (**326**), were reported in 2000. In many of these examples, the vinylidene intermediate is trapped, leading to the formation of a cyclic Fischer carbene complex (**327**), which can be converted to a cyclic enol ether (**328**) upon treatment with base. Highly oxygenated alkynol derivatives (e.g. **329**, Scheme 50) were converted to glycal derivatives (e.g. **330**) in a single step using a combination photolytic and thermal reaction with tungsten hexacarbonyl, presumably through the intermediacy of the tungsten vinylidene complex [361]. Cyclic carbene complexes (e.g. **332**) were produced in low yield from the coupling of $(THF)W(CO)_5$ with carbohydrate-containing alkynols (e.g. **331**) [362]. Dihydrothiophene derivatives were prepared by treatment of terminal alkyne–thiols with $(THF)W(CO)_5$ [363].

Coupling of $(THF)W(CO)_5$ with enyne esters (e.g. **333**, Scheme 51) and amides led to the pyranylidene complexes (e.g. **336**), which readily undergo Diels–Alder reaction with electron-deficient acetylenes followed by loss of tungsten hexacarbonyl to afford highly substituted aromatic rings (e.g. **337**) [364]. An analogous reaction process was reported for *o*-ethynylbenzoates and phenylketone analogs (e.g. **334**) [365]. The resulting *o*-quinoidal systems underwent Diels–Alder reactions with enamines and enol ethers to afford naphthalene ring systems. Reaction of the benzopyranylidine complexes with amines led to *o*-methylbenzophenone derivatives.

The electronic structure of chromium–vinylidene and cumulene complexes of general structure **339** (Scheme 52) has been studied by Density Functional Theory [366]. The back (π) donation of the cumulene ligand was found to be more important than the forward (σ) donation. The bond dissociation energy of the Cr=C bond was found to be independent of the chain length of the cumulene complex. The regioselectivity of nucleophilic and electrophilic attack was found to be frontier orbital controlled; the LUMO is localized on the odd carbons while the HOMO is localized on the even carbons.



Scheme 50.



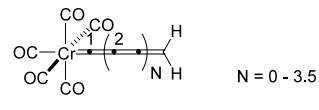
Scheme 51.

The coupling of molybdenum–alkyne complex **341** (Scheme 53), generated at low temperature, with imine **343** led to aminocarbene complexes **345** and **346** [367]. Formation of the cyclic carbene complex was attributed to nucleophilic addition of nitrogen to the carbene carbon followed by ring closure. Formation of **346** was attributed to direct [2 + 2]-cycloaddition involving alkyne complex **341** followed by an unusual hydrogen shift-ring opening process.

2.3.3.10. Reactions involving carbanions derived from Group VI metal–carbene complexes. Coupling of alkenyllithium reagents (e.g. **347**, Scheme 54) with chromium pentacarbonyl sources led to carbene complex-stabilized carbanions (e.g. **348**) [368]. Anions generated from glycals in this way were allylated with a high degree of diastereoselectivity in favor of the axial diastereomer (e.g. **350**). A β-elimination process resulting in unsaturated carbene complexes (e.g. **349**) was observed if **348** was allowed to warm above 0 °C.

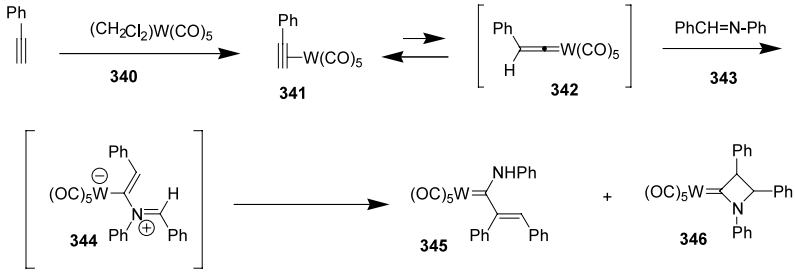
Examples of reactions that involve deprotonation of a Group VI Fischer carbene complex at the α-position, followed by reaction with an electrophile were reported in 2000 (Scheme 55). Moderately diastereoselective reaction of homochiral aminocarbene complex **351** with nitrostyrene derivatives (e.g. **352**) was a key step in the asymmetric total synthesis of baclofen [369]. Carbonyl insertion reactions were also reported for carbanions derived from Fischer carbene complexes [370]. Reaction of anion **356** with CH_3OH, Et_3N, then I_2 led to mixtures of ester **357** and iodide **358** with a high degree of stereoselectivity for the indicated isomers. The iodide product was avoided if silver triflate was added prior to iodine. Anions obtained from Michael addition reactions also underwent similar reaction processes.

2.3.3.11. Reactions involving the addition of nucleophiles to the carbene carbon. An in-depth study of the coupling of dihydropyridine derivatives (e.g. **359**, Scheme 56) with carbene–chromium or tungsten complexes was reported [371]. Common reaction pathways observed in these systems include initial formation of a stable tetrahedral complex (e.g. **360**) as a pyridinium salt followed by either in-situ generation of the nonheteroatom-stabilized carbene complex (e.g. **362**) and possibly formation of a stable pyridinium ylide complex (e.g. **363**) or CO insertion to generate the acylate complex (e.g. **361**). Optimization of the synthesis of pyridinium complexes, and coupling of these complexes with alkenes and alkynes was studied (Scheme 57). Reaction of the pyridinium salt complexes with electron-rich alkenes (e.g. **365**) led to cyclopropanation products (e.g. **366**) with a high degree of stereoselectivity for the depicted isomer. Direct cyclopropanation without isolation of the ylide complexes was observed in the reaction of δ,ω-unsaturated carbene complexes (e.g. **367**) with dihydropyridine derivatives; formation of cyclopropane derivative **368** proceeded with a high degree of stereoselectivity. Alkene-complexes which feature a shorter tether (e.g. **369**), afforded hydroxycyclopropanes (e.g. **370**) upon treatment with *N*-methyldihydropyridine via a CO insertion process. Reaction of alkyne–carbene tungsten complexes (e.g. **371**) with *N*-methyldihydropyridine led to CO insertion–cyclization products (e.g. **372**), while chromium analogs (e.g. **373**) afforded multiple CO-insertion products (e.g. **374**) [372]. A key step in the formation of compounds **372** and **374** is intramolecular alkyne-insertion reactions of chromium acylates (analogous to **361**, Scheme 56).

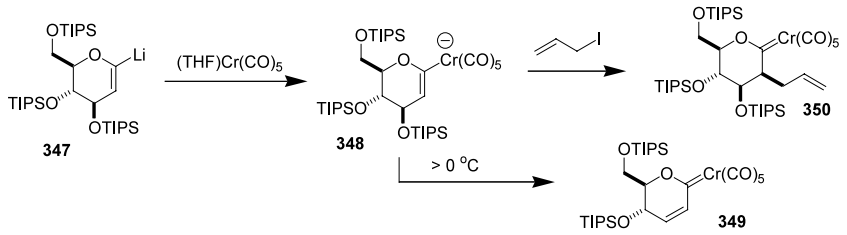


339

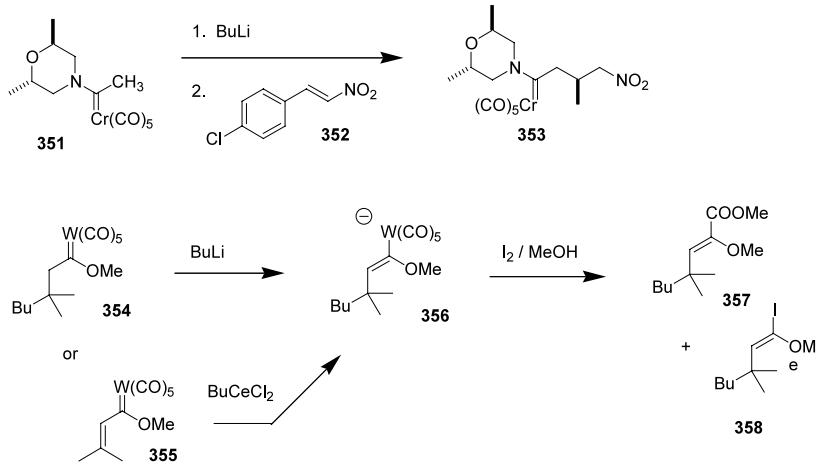
Scheme 52.



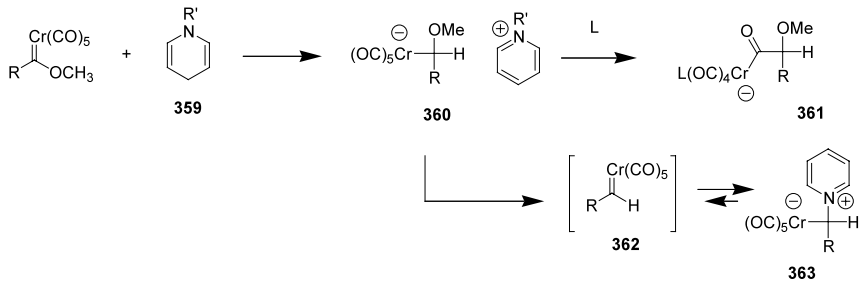
Scheme 53.



Scheme 54.



Scheme 55.



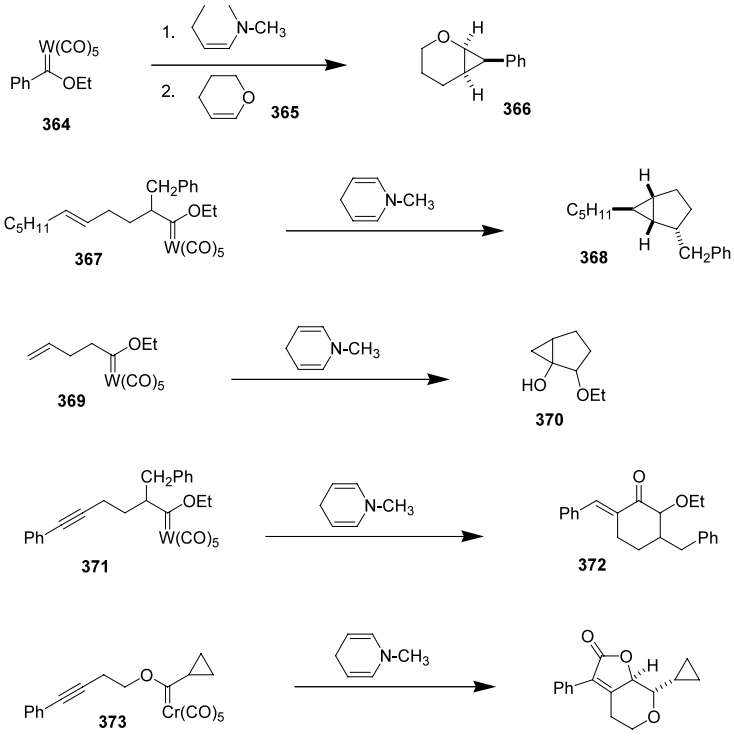
Scheme 56.

The addition of hydride nucleophiles to α,β-unsaturated carbene complexes (e.g. **375**, Scheme 58) has been studied [373]. Addition to alkenylcarbene complexes lead to alkenes **377** and **379**, which arise via initial addition of hydride to the carbene carbon, followed by reversible 1,3-rearrangement of the allylmetal and protonation. The high *Z* selectivity in the formation of enol ether **379** was attributed to coordination of the oxygen in the metal in the 1,3-rearranged intermediate. Addition to the alkynylcarbene complex **380** led to

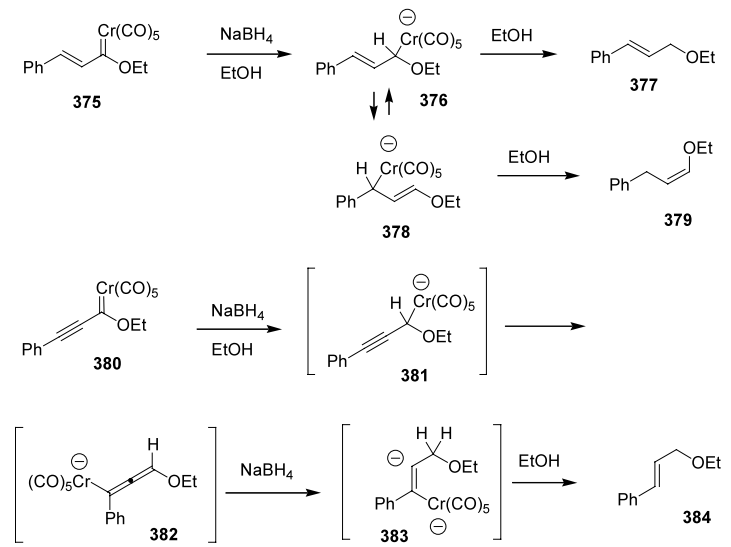
allylic ether derivative **384** by a mechanism involving addition of hydride to the carbene carbon, followed by rearrangement to an allenylmetal complex (**382**) followed by addition of a second hydride (resulting in dianion **383**) and protonation. The proposed mechanistic processes were supported through deuterium labeling studies.

Reaction of chromium carbene complex **385** (Scheme 59) with isonitriles led to aminonaphthalene derivatives (e.g. **387**), which were employed for the total synthesis of the calphostin natural products [374]. A carbene complex-containing polymer (**390**, Scheme 60) was formed from the coupling of carbon-tethered bis(carbene)complex **388** with hexamethylenediamine (**389**) [375].

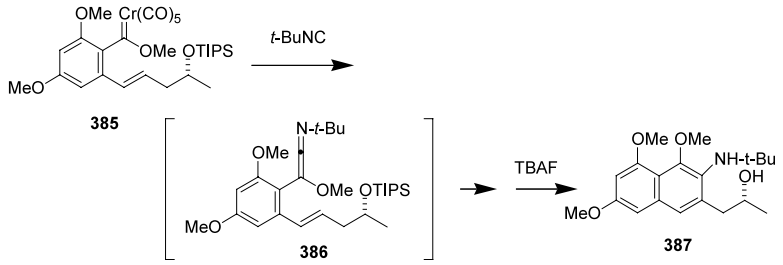
2.3.3.12. Other reactions of Group VI metal–carbene complexes. Thermal carbonylation of acylaminocarbene–chromium complexes (e.g. **391**, Scheme 61) led to the direct formation of munchone derivatives (e.g. **392**)



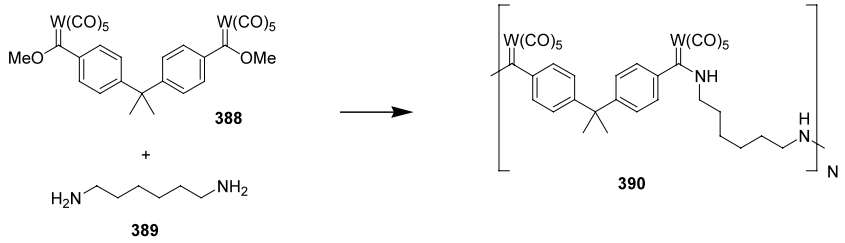
Scheme 57.



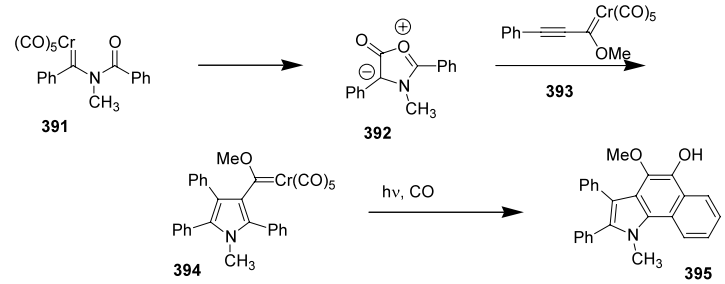
Scheme 58.



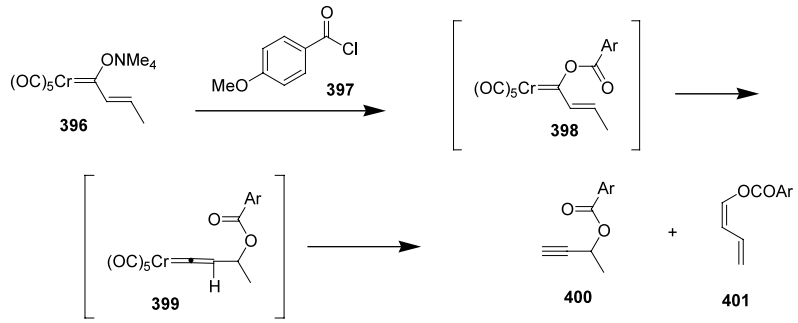
Scheme 59.



Scheme 60.



Scheme 61.

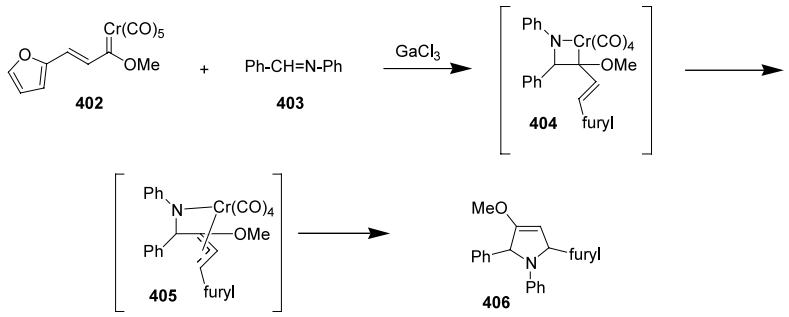


Scheme 62.

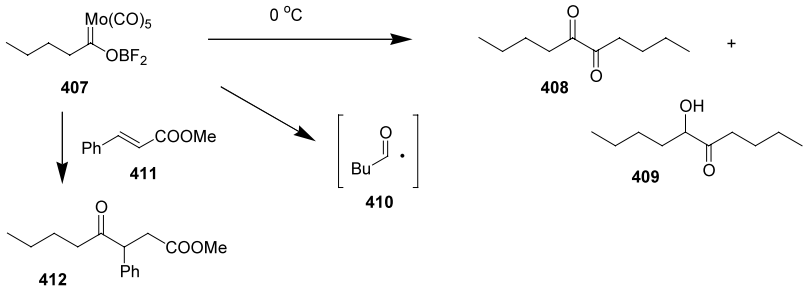
[376]. Coupling with a variety of dipolarophiles, including alkynylcarbene complexes (e.g. **393**), led to pyrrole derivatives (e.g. **394**). Carbene complex **394** underwent cyclization to the phenol derivative **395** upon photolysis in the presence of carbon monoxide.

The coupling of α,β-unsaturated acylate salts (e.g. **396**, Scheme 62) with acid chlorides has been examined [377]. This coupling resulted in a mixture of propargyl esters (e.g. **400**) and acyloxy diene derivatives (e.g. **401**). Formation of propargyl esters was proposed to arise through [3.3]-sigmatropic rearrangement of acyloxycarbene complexes (e.g. **398**) followed by conversion of the resulting vinylidene complexes (e.g. **399**) to a terminal alkyne. Formation of the acyloxydiene derivatives occurs via transfer of the γ-hydrogen to chromium in **398** followed by reductive elimination.

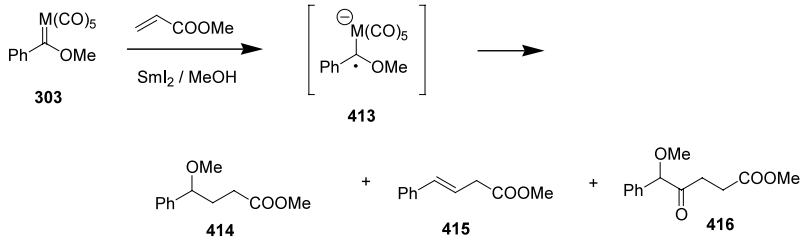
The nonphotochemical reaction of imines with α,β-unsaturated carbene complexes (e.g. **402**, Scheme 63) in the presence of gallium trichloride led to dihydropyrrole derivatives (e.g. **406**) [378]. A mechanism involv-



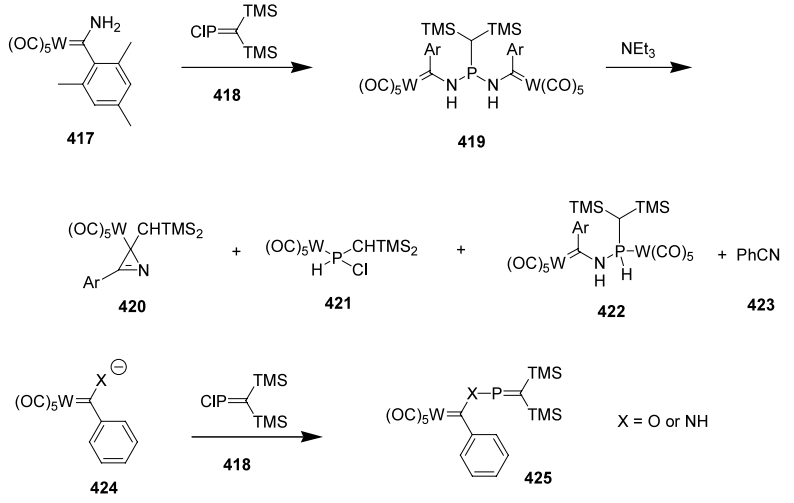
Scheme 63.



Scheme 64.



Scheme 65.



Scheme 66.

ing [2 + 2]-cycloaddition, followed by rearrangement of the σ-allyl complex (e.g. **404**) to the π-allyl complex (e.g. **405**), followed by reductive elimination was proposed.

Coupling of boryloxycarbene–molybdenum complexes (e.g. **407**, Scheme 64) with α,β-unsaturated esters and self decomposition reactions were reported [379]. Self-decomposition of the boryloxycarbene complexes led to 1,2-diketones (e.g. **408**), the corresponding alcohol (e.g. **409**), and some cases to decarbonylation–dimerization products. A mechanism involving conversion of complex **407** to an acyl radical (e.g. **410**) was proposed. The reaction with methyl cinnamate afforded γ-ketoester **412** in moderate yield. Reactions employing methyl methacrylate afforded five- and six-membered ring cyclic products resulting from multicomponent coupling processes.

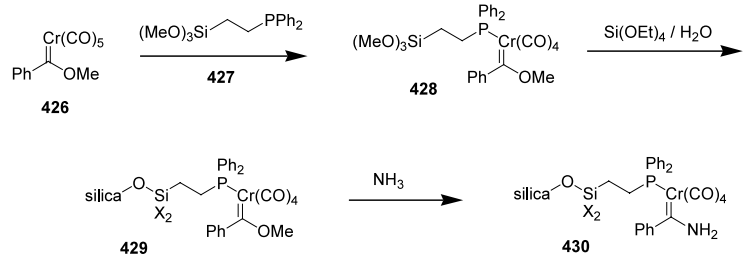
Reduction of carbene complexes with samarium(II) iodide was reported (Scheme 65) [380]. Reductive dimerization was noted for the reaction of carbene complex **303** (M=W) with samarium iodide in methanol. Coupling products (e.g. **414**–**416**) were observed if the reaction was conducted in the presence of ethyl acrylate. A mechanism involving one-electron reduction followed by addition of the radical to the alkene was reported. In coupling reactions involving alkylcarbene complexes, the major products were the CO-inserted complexes (e.g. **416**).

The coupling of aminocarbene–tungsten complexes (e.g. **417**, Scheme 66) with chlorophosphane **418** in the presence of triethylamine was reported [381]. The reaction led initially to diaminophosphine–dicarbene derivative **419**, which could be isolated. Further treatment with triethylamine led to azaphosphirene complex **420** and complexes **421** and **422**. A more sterically hindered analog of carbene complex **417** led only to analogs of complexes **420** and **421**. Complexes analogous to **425** (X = NH) are presumably intermediates in the formation of **419**, however they could only be isolated if prepared from the corresponding anions (e.g. **424**) [382].

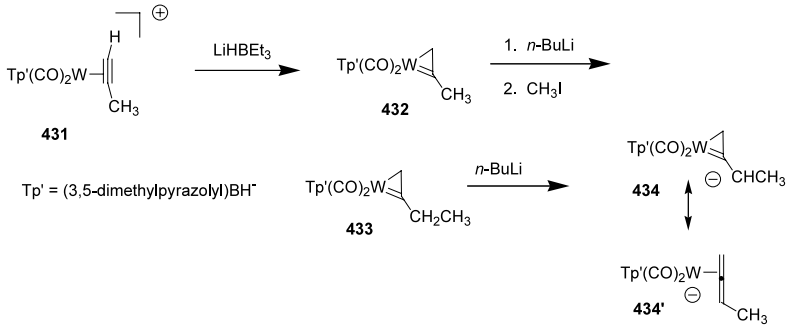
Silica-bound Fischer carbene complexes (e.g. **429**, **430**, Scheme 67) were prepared through reaction of a simple carbene complex (e.g. **426**) with phosphine–siloxane **427**, followed by treatment with triethoxysilane and water [383]. Aminolysis of the bound carbene complexes was also reported.

Synthesis and deprotonation reactions were reported for η^2-vinyltungsten complexes (e.g. **432**, **433**, Scheme 68) [384]. The title complexes were prepared most efficiently via hydride addition to a cationic alkyne complex (e.g. **431**). Deprotonation of the exocyclic allylic proton with *n*-butyllithium afforded a carbanion species (e.g. **434**) (resonance form is allene complex **434′**) that could be alkylated with methyl iodide or benzaldehyde.

Nucleophilic tungsten (0) carbene complexes were proposed as intermediates in the aldol condensation of cyclohexanone catalyzed by tungsten hexacarbonyl and light [385]. NMR signals consistent with tungsten– and molybdenum–carbene complexes were observed in the polymerization of *t*-butylacetylene by tungsten(II) and molybdenum(II) species [386]. Formation of a seven-coordinate tungsten–carbene complex (e.g. **436**, Scheme



Scheme 67.



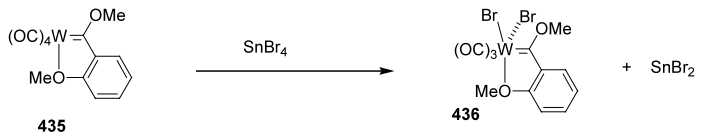
Scheme 68.

69) was observed in the reaction of complex **435** or the trimethylphosphine analog with $SnCl_4$ or $SnBr_4$ [387].

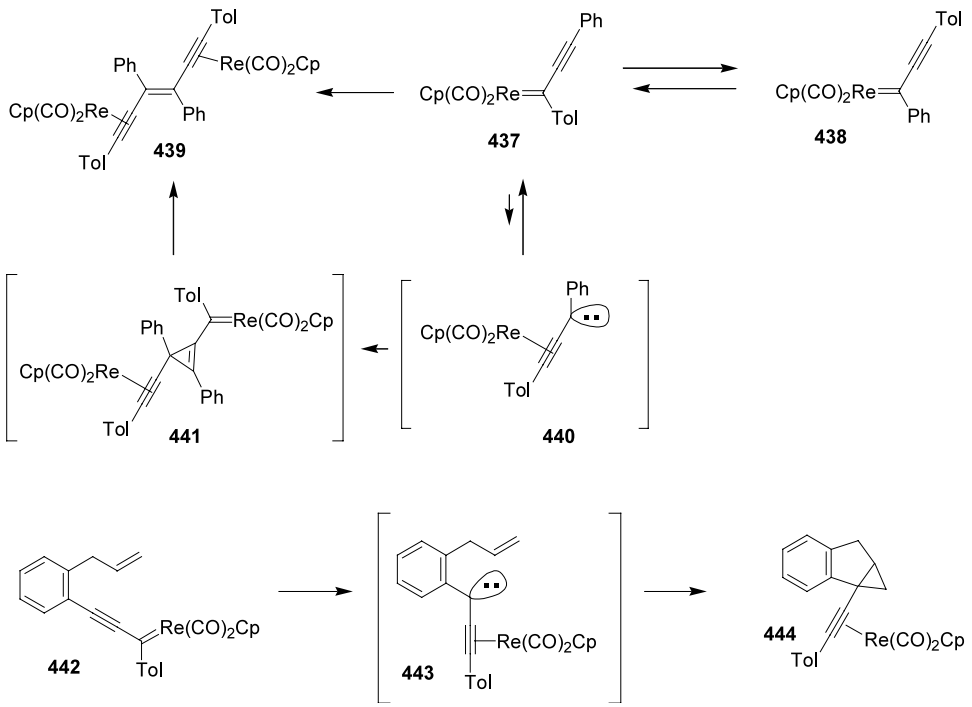
2.3.4. Group VII metal–carbene complexes

Thermolysis of alkynylcarbene–rhenium complex **437** (Scheme 70) led to dimeric enediyne complex **439** [388]. A slower thermal process involving a 1,3-shift of the carbene system was also observed, resulting in complex **438**. The mechanism for dimerization favored by the authors involves rearrangement to alkynylcarbene derivative **440**, followed by intermolecular cyclopropanation to give intermediate cyclopropene **441**, which rapidly converts to the observed product. This mechanism is supported by the facile rearrangement of simple cyclopropenylcarbene–rhenium complexes and by the ability of complex **442** to undergo an intramolecular cyclopropanation through a similar carbene intermediate.

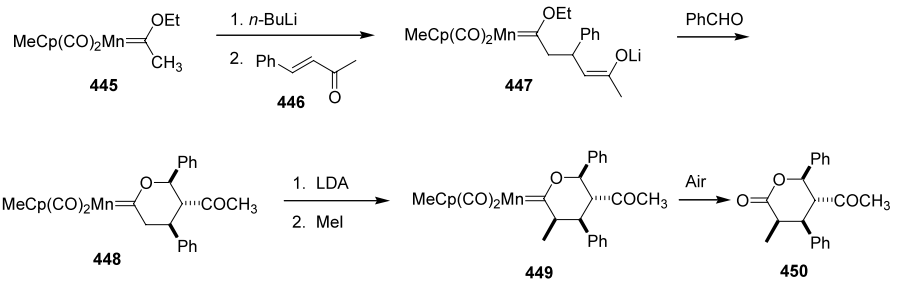
Deprotonation of Fischer carbene–manganese complex **445** (Scheme 71) followed by reaction with enones was reported [389]. Michael addition afforded a ketone enolate (e.g. **447**), which was stable with respect to internal proton transfer. Alkylation of the enolate with methyl triflate proceeded with a moderate degree of



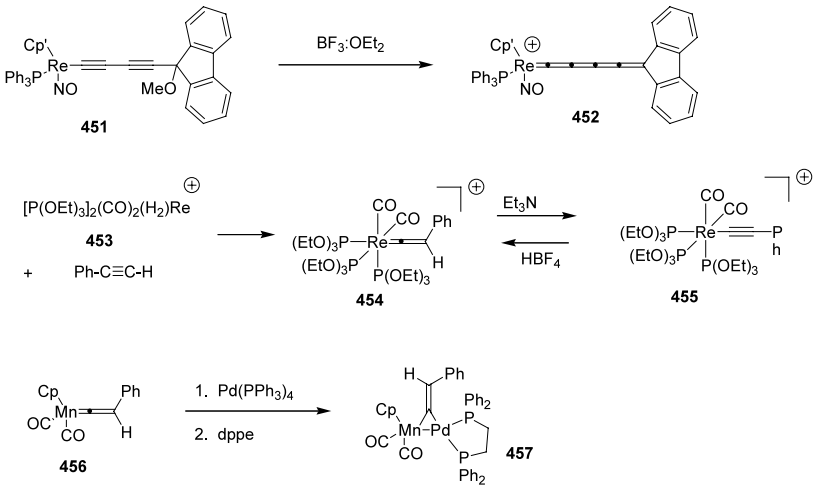
Scheme 69.



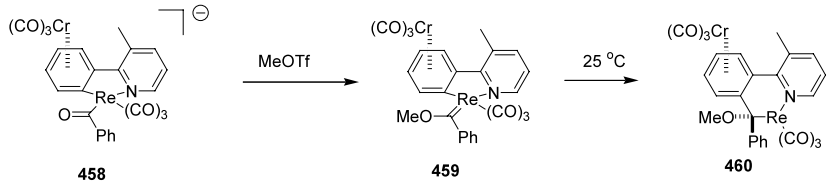
Scheme 70.



Scheme 71.



Scheme 72.



Scheme 73.

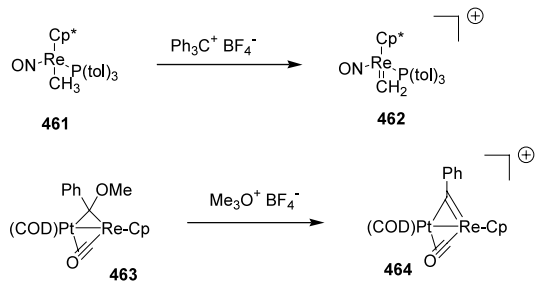
diastereoselectivity. Reaction with benzaldehyde proceeded with a high degree of diastereoselectivity and afforded cyclic carbene complexes (e.g. **448**), which could be alkylated stereoselectively. Air oxidation of cyclic carbene complexes led to the corresponding lactone derivatives (e.g. **450**).

Several examples of Group VII metal–cumulene complexes were reported in 2000 (Scheme 72). Rhenium–cumulene complexes (e.g. **452**) were prepared by treatment of dialkynylrhenium complexes (e.g. **451**) with BF_3 [390]. Cationic rhenium vinylidene complexes were prepared from reaction of phenylacetylene with rhenium–dihydrogen complex **453** [391]. The vinylidene complex (**454**) was deprotonated by triethylamine to afford the alkynylrhenium complex **455**. Vinylidene complex **454** could only be isolated if prepared by protonation of the alkynylrhenium complex. Treatment of manganese–vinylidene complex **456** with $Pd(PPh_3)_4$ followed by diphenylphosphinoethane led to bridging vinylidene complex **457** [392]. The chemical and electrochemical oxidation of four-carbon bridged rhenium bimetallic complexes revealed significant contribution from the cumulenediylidene resonance form for highly oxidized complexes [393].

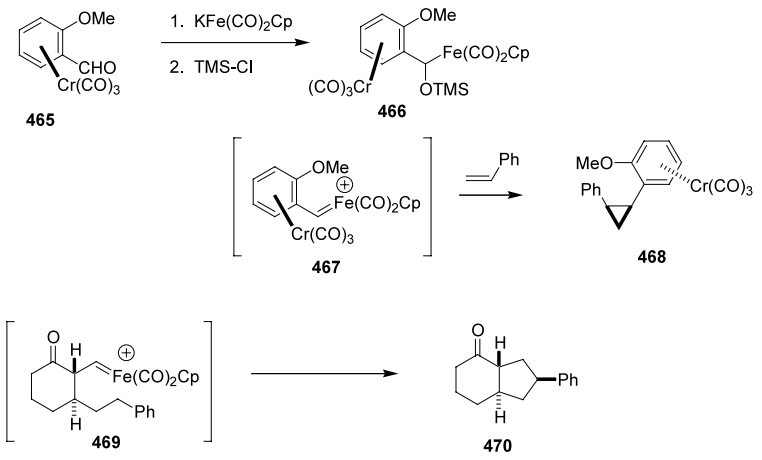
The coupling of aminocarbene–manganese complexes with chlorophosphanes in the presence of triethylamine was reported [394]; these studies are analogous to those reported in Scheme 66 involving Group VI metal–carbene complexes and chlorophosphanes.

Rhenium–carbene complexes (e.g. **459**, Scheme 73) could be generated in situ from rhenium acylate species (e.g. **458**) [395]. Upon warming to room temperature, migration of the carbene ligand occurs to provide ruthenium complex **460**. Alkylation of the manganese analog of **458** led to the manganese analog of complex **460** directly.

Other examples of Group VII metal carbene complexes are depicted in Scheme 74. A cationic rhenium–carbene complex (**462**) was prepared through hydride abstraction from methylrhenium complex **461** [396]. A bridging carbyne–rhenium complex (**464**) was formed when bridging methoxycarbene complex **463** was treated with trimethyloxonium tetrafluoroborate [397]. A theoretical study of the conversion of neutral η^2-allene–rhenium complexes to cationic η^2-alkenyl complexes by HCl was also reported [398].



Scheme 74.



Scheme 75.

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 (**467**, Scheme 75), generated in situ from a homochiral siloxyiron complex **466**, afforded chiral cyclopropane **468** with a high degree of diastereoselectivity [399]. Cyclopropane **468** was an intermediate in the enantioselective synthesis of cyclopropanecarboxylic acid derivatives. Stereoselective intramolecular C–H insertion processes were reported for cationic iron carbene complexes (e.g. **469**) [400]. Cationic iron carbene complexes $[Cp^*(CO)_2Fe{=}CHAr]^+$ were also generated from coupling of cationic alkoxycarbene complexes $[Cp^*(CO)_2Fe{=}CHOMe]^+$ with aryllithium reagents followed protonation of the resulting neutral alkoxyiron complexes [401].

2.3.5.2. Neutral nonheteroatom-substituted metal–carbene complexes that are not cumulenes. Numerous additional examples of the synthesis and reactivity of this class of compounds have been presented in the alkene metathesis section. The Grubbs catalyst falls into this classification.

Several reports of the preparation of Group VIII metal–carbene complexes directly from diazo compounds appeared in 2000 (Fig. 11). Examples include: (1) synthesis of ruthenium–dicarbene complex **472** from ethyl diazoacetate, which decomposes to dimethyl maleate and the starting complex **471** at room temperature [402]; (2) synthesis of iron carbene complex **474** from diphenyldiazomethane and an iron–calixarene complex (**473**) and air oxidation of **474** to benzophenone and an oxo-bridged iron dimer [403]; and (3) preparation of chiral ruthenium carbene complexes (e.g. **476**) from the coupling of ruthenium complexes (e.g. **475**) with ethyl diazoacetate and subsequent enantioselective cyclopropanation studies [404]. Ruthenium–carbene complexes are also suggested as intermediates in the formation of 1,3-dienes through the ruthenium-catalyzed addition of two carbene units (from diazo compounds) to alkynes [405].

Ruthenium carbene complexes (e.g. **479**, Scheme 76) could be isolated from the coupling of diazo compounds with ruthenium complexes (e.g. **478**) [406]. Coupling of carbene complex **479** with styrene resulted in the formation of a variety of compounds (**480**–**482**), which result from metallacyclobutane **483**. Competition between reductive elimination, β-hydride elimination, and retro [2 + 2]-cycloaddition accounts for the formation of the observed products. Osmium–carbene complexes (e.g. **485**) were prepared from diazo compounds and osmium complex **484** [407]. Ligand exchange processes were reported for this complex as well as coupling with vinylmagnesium bromide to afford π-allyl complex **486**.

Ruthenacyclopentadiene derivatives (e.g. **487**, Scheme 77) reacted with excess norbornene to afford the dicyclopropanation product **489** [408]. The reaction process was attributed to a substantial cyclopropanation through the dicarbene resonance structure (e.g. **488**). A catalytic process involving the direct conversion of 1,6-diynes to dicyclopropanes by way of ruthenacyclopentadienes was also reported.

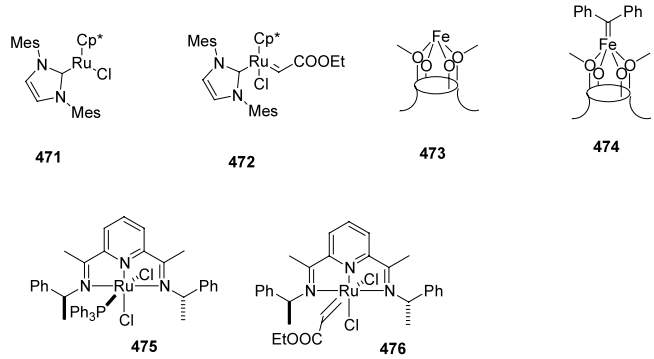
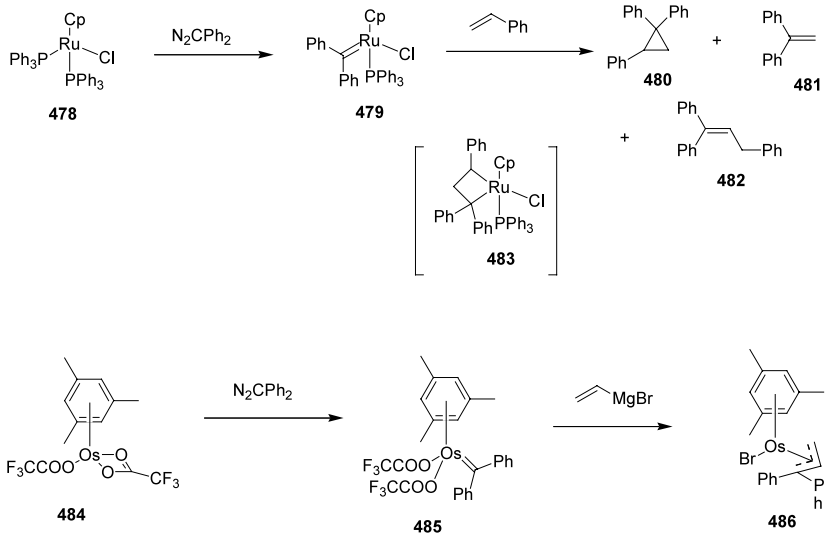
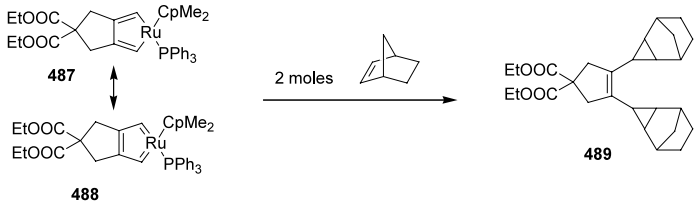


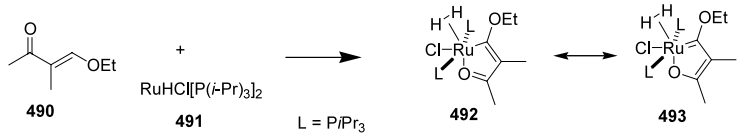
Fig. 11. Representative examples of Group VIII metal–carbene complexes prepared through coupling with diazo compounds.



Scheme 76.



Scheme 77.

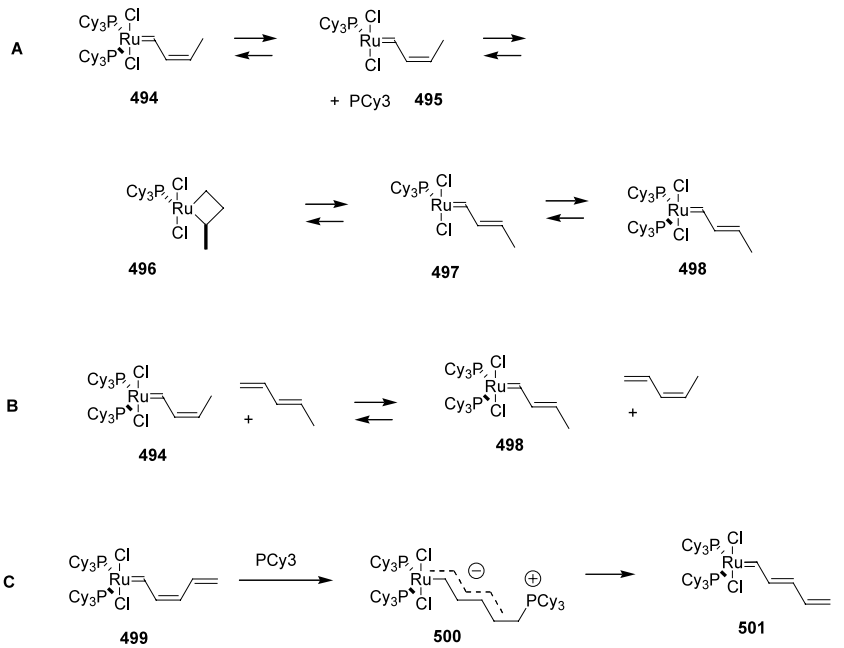


Scheme 78.

Ruthenium–carbene complexes (e.g. **493**, Scheme 78) were prepared from the coupling of ruthenium hydride complexes (e.g. **491**) with α,β-unsaturated ketones (e.g. **490**) [409]. A mechanism involving oxidative addition into the β-C–H bond followed by reductive elimination of hydrogen was proposed and supported via deuterium labeling studies. These studies were not consistent with the other mechanistic alternative involving hydrometallation of the alkene followed by α-hydride elimination and reductive elimination of hydrogen. The carbene resonance form was more important for alkoxy complex **493**, however the alkenylmetal resonance form analogous to **492** was more important for nitrogen analogs.

The *E*–*Z* isomerization of α,β-unsaturated ruthenium carbene complexes (e.g. **494**, **498**, **499**, **501**, Scheme 79) has been studied experimentally and by Density Functional Theory [410]. Numerous mechanistic possibilities for the isomerization were considered. Three potential mechanistic possibilities were considered to be most reasonable depending upon the situation. Mechanism A, involving dissociation of a phosphine and metallacyclobutene formation, followed by conversion back to a vinylcarbene complex, was considered for all of the compounds studied. Isomerization in the presence of added alkene was attributed to a metathesis process (mechanism B), while isomerization promoted by the nucleophilic addition of phosphine (mechanism C) was suggested for system where added phosphine induced the isomerization.

Other studies of carbene complexes in this category include: (1) demonstration of electrophilic aromatic substitution reactions for osmabenzene derivatives [411]; (2) preparation of a ruthenium–carbene complex resembling a quinone through deprotonation of *p*-phenoxyruthenium complex [412]; (3) coupling of cationic diiron–carbene complex with anionic metal–cyanide derivatives, which leads to trimetallic species bridged through a cyanide ligand [413], and related studies involving simpler nucleophiles [414]; (4) generation of

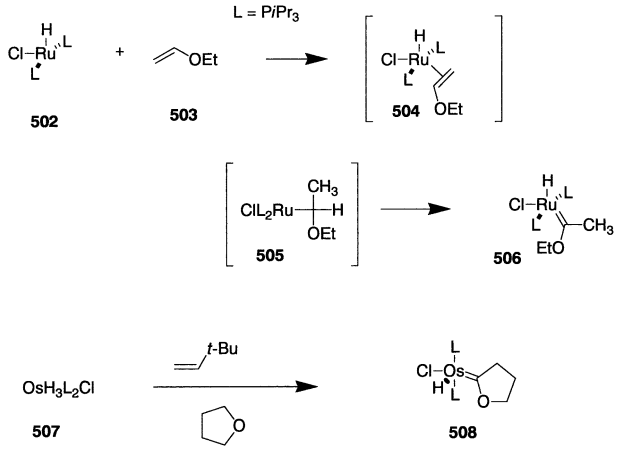


Scheme 79.

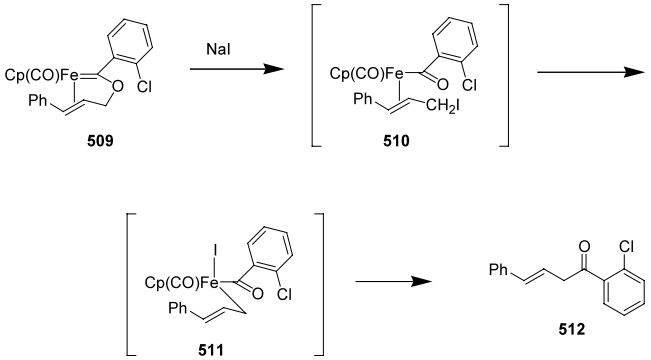
ruthenium carbene complexes from the treatment of ruthenium clusters with silica gel [415]; and (5) generation of a iron–cyclopropenylidene complex from the coupling of an iron–zirconium species with diphenylcyclopropenone [416].

2.3.5.3. Heteroatom-substituted Group VIII metal–carbene complexes. Coupling of ruthenium hydride complex **502** (Scheme 80) with vinyl ethers led to alkoxycarbene complexes (e.g. **506**) [417–419]. Deuterium labeling studies suggest a mechanism involving reversible hydrogen–deuterium exchange through alkene insertion leading to complex **505** followed by β-hydride elimination in competition with α-hydride elimination from alkoxyalkylruthenium complex **505** to afford carbene complex **506**. Coupling with *N*-vinylamides also led to carbene complexes, however less electron rich systems afforded η^2-alkene complexes analogous to complex **504**. Calculations suggest that an electron-rich heteroatom makes the carbene complex more stable than the π-olefin complex. Related studies of fluoro, triflate, and acac analogs of complex **502** were also reported [420] and for fluorocarbene analogs [421]. Cyclic carbene complexes were generated from THF and osmium-hydride (e.g. **507**) or ruthenium-hydride complexes [422]. Reaction with the osmium system required *t*-butylethylene as a coreactant to absorb hydrogen. A metallacyclic aminocarbene–osmium complex was generated through addition of methyl lithium to a phenyl isocyanide–osmium complex followed by intramolecular C–H activation [423].

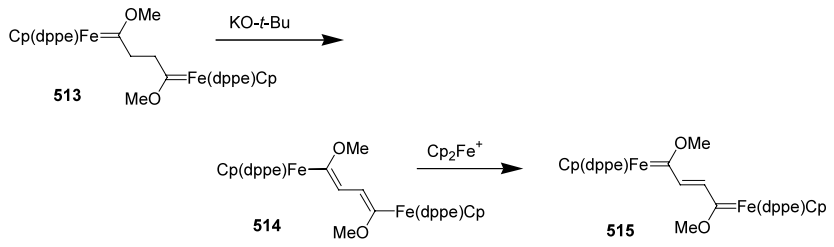
Reaction of allyloxycarbene–iron complexes (e.g. **509**, Scheme 81) with iodide resulted in β,γ-unsaturated ketone derivatives (e.g. **512**) [424]. No allylic rearrangement was observed in this transformation. A mecha-



Scheme 80.



Scheme 81.



Scheme 82.

nism involving iodide displacement of the metal acylate species, followed by formation of a σ-allyl complex (e.g. **511**), followed by reductive elimination was proposed.

The bis(carbene)–iron complex **515** (Scheme 82) was prepared from the saturated bis(carbene)–iron complex **513** [425]. Complex **515** was diamagnetic in solution at room temperature, however temperature-dependent magnetic susceptibility measurements showed antiferromagnetic behavior, and both high and low spin states could be observed by variable temperature Mössbauer spectroscopy.

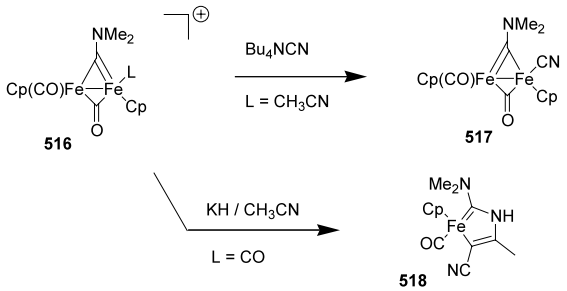
Ligand substitution processes were reported for bridging aminocarbyne–diiron (e.g. **517**, Scheme 83) complexes [426]. Reaction of similar complexes with acetonitrile anion led to a cyclic carbene complex (e.g. **518**) [427]. Trinuclear iron–carbene complexes were prepared by treatment of a trinuclear iron acylate with methyl triflate [428]. A structurally complex zirconoxycarbene–iron complex was generated from the coupling of a zirconium amide species with iron pentacarbonyl [429].

2.3.5.4. Group VIII metal–vinylidene complexes. Many examples of the formation of metal vinylidene complexes (e.g. **519**, Scheme 84) via coupling of coordinatively unsaturated Group VIII metal complexes with terminal or silylated alkynes were reported in 2000. Representative examples are depicted in Fig. 12. Common reaction pathways for these complexes include reaction with alcohols to form Fischer carbene complexes (**523**) or water to form metal acyls (**521**), and deprotonation at the β-position to form alkynylmetal complexes (**520**). Other common synthetic routes to metal vinylidenes included addition of electrophiles to metal acetylide complexes (e.g. the reverse of the reaction synthesizing **520**), and treatment of acylmetal complexes with dehydrating agents (i.e. the reverse of the reaction synthesizing **521**).

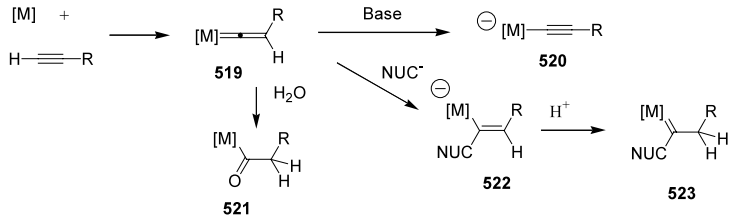
Specific reports which highlight the reaction pathways depicted in Scheme 84 include: (1) formation of ruthenium–vinylidene complexes from $TpRuCl(PR_3)_2$ derivatives (e.g. **524**) and a diverse array of terminal alkynes; these complexes catalyze the dimerization of terminal alkynes [430]; (2) formation of ruthenium–vinylidene complex **525** upon treatment of alkynylruthenium complexes with iodoacetonitrile; the resulting vinylidene complexes are converted to the corresponding cyclopropenylruthenium complexes upon treatment with base, and reconvert to a vinylidene complex upon treatment with mercuric chloride [431]; (3) formation of ruthenium vinylidene complexes from a cationic ruthenium–TMEDA complex (e.g. **526**) [432]; (4) synthesis and nonlinear optical studies of cationic β-azoruthenium–vinylidene complexes (e.g. **527**) [433]; (5) formation of a ruthenium vinylidene complex from methyl propiolate, which was transformed to the acetylide upon deprotonation [434]; and (6) formation of ruthenium–vinylidene complexes from $(t\text{-}Bu_2MeP)_2(NO)RuOTf$ and bis(trimethylsilyl)acetylene (e.g. **528**), which contrasts with an earlier report involving CO analogs of **528** where C–Si oxidative addition products were obtained [435].

It was reported the selenoalkynes (e.g. **529**, Scheme 85) couple with ruthenium complex **530** to afford selenovinylidene complexes (e.g. **531**) [436]. Reaction with phosphorus and nitrogen donor ligands results in a ligand substitution reaction, while reaction with π-acid ligands (CO and isonitriles) leads to expulsion of the selonacetylene (not confirmed by isolation) and all *trans*-$[RuCl_2L_2(PPh_3)_2]$. Imine–osmium–vinylidene complexes (e.g. **533**, Scheme 86) were prepared through internal hydride migration process of alkenylosmium–imido complexes (e.g. **532**) [437].

Treatment of ruthenium–vinylidene complexes (e.g. **534**, Scheme 87) with metal acetylides was reported [438]. Coupled products (e.g. **536**) were produced through initial reaction of the acetylide at ruthenium followed by coupling of the acetylide ligand with either



Scheme 83.



Scheme 84.

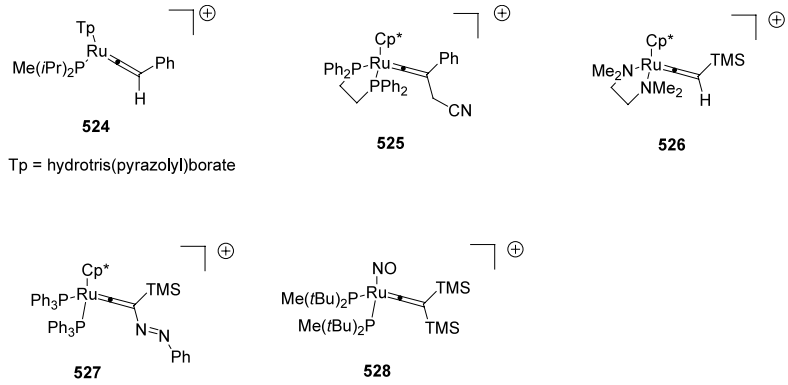


Fig. 12. Representative Group VIII metal–vinylidene complexes reported in 2000.

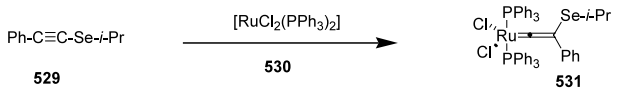
the vinylidene ligand, or the η^2-acetylene ligand arising from isomerization of the vinylidene ligand. Use of silver acetylide salts led to monocoupling products, while sodium and lithium acetylides led to products incorporating more than one alkyne unit.

Treatment of ruthenium complex **537** (Scheme 88) with 1-ethynylcyclohexanol led to cyclohexenylvinylidene complex **539** [439]. Treatment of this complex with water led to methylenecyclohexane (**541**); analogous treatment with D_2O led to a tridueterated analog. A mechanism involving addition of water to the carbene carbon and formation of a metal acyl complex **540**, followed by H–D exchange of the metal acyl, followed by decarbonylation and protonation (deuteration) of the resulting allylruthenium complex was proposed.

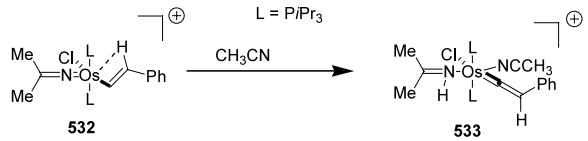
Numerous processes suggest Group VIII metal vinylidene complexes as intermediates (Scheme 89), including: (1) formation of Fischer carbene complexes (e.g. **543**) from alkynols and a cationic ruthenium complex; a phosphine–vinylidene coupling was observed when vinylphosphine complexes were employed [440]; (2) ruthenium-catalyzed conversion of propargyl alcohols to propargyl ethers [441]; (3) ruthenium-catalyzed alkyne dimerization [442]; (4) formation of mono- and bis-carbene complexes from *p*-bis(propargyl alcohol)benzene derivatives and a ruthenium halide complex or $(THF)W(CO)_5$ [443]; (5) ruthenium-catalyzed addition of carboxylic acids to terminal alkynes [444]; and (6) direct formation of ruthenium acetylides from ruthenium chlorides and terminal alkynes by sequential treatment with sodium hexafluorophosphate then triethylamine [445].

A Density Functional Theory study of the barrier to rotation in osmium– and ruthenium–vinylidene complexes was reported [446]. It was noted that donor ligands lead to a higher barrier to rotation. Rationalization of Raman properties for ruthenium vinylidene complexes using Density Functional Theory was also reported [447].

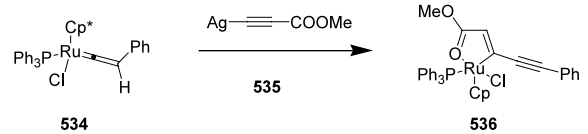
2.3.5.5. Group VIII metal complexes of higher cumulenes. Metal-higher cumulene complexes (**545**, **549**, Scheme 90) are produced from the coupling of coordinatively unsaturated Group VIII metal complexes with



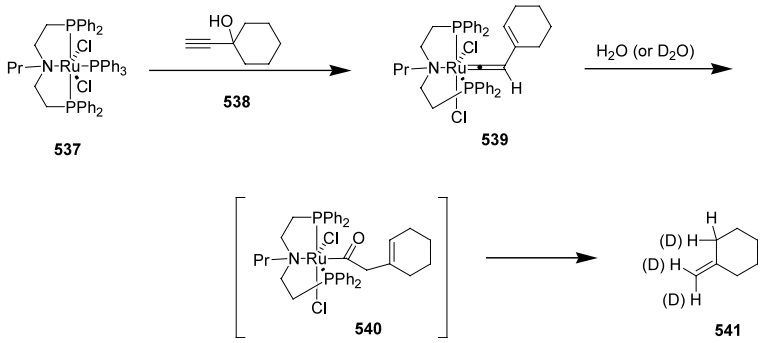
Scheme 85.



Scheme 86.



Scheme 87.



Scheme 88.

propargyl alcohols that contain no hydrogens β- to the OH group, or by addition of electrophiles to the δ-carbon of alkynylethynyl–metal complexes (**549**). A variety of reaction processes of Group VIII metal–cumulene complexes were reported in 2000. Common reaction pathways for these complexes include reaction with nucleophiles at the γ-position, resulting in alkynylmetal complexes (**546**), or attack at the γ-position, resulting in allenylmetal complexes (**547**). Representative examples of this class of compounds are depicted in Fig. 13.

Specific reports which highlight the reaction pathways depicted in Scheme 90 are depicted in Fig. 13, and include: (1) synthesis of carbene–alkynylruthenium complexes (e.g. **550**) through addition of Fischer carbene complex derived carbanions with cationic ruthenium–allenylidenes, which occurs exclusively at the γ-position [448]; and (2) synthesis of chelating Cp–phosphine–ruthenium–allenylidene (e.g. **551**) and –vinylidene complexes [449].

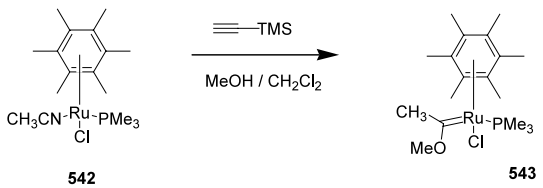
Additional reactions of butatrienylidene complexes (e.g. **552**, Scheme 91) were reported. Reaction of cationic allenylidene–ruthenium complexes (e.g. **552**) with propargyl alcohol led to propargyloxycarbene complexes (e.g. **553**), which undergo cycloaddition processes upon treatment with bases of varying strengths [450]. In all cases, a mechanism involving base-induced conversion of the propargyl group to an allene followed by intramolecular Diels–Alder reaction was proposed. Use of sodium carbonate as a base resulted in the cyclic Fischer carbene complex **554**, which undergoes reduction to afford the benzylruthenium complex **555**. Cycloaddition processes were also observed in the coupling of ruthenium allenylidene complexes with 2-aminopyridine derivatives and thioamides [451].

Numerous studies report on the generation of cumulenylidine systems (e.g. **561**, Scheme 92) from oxidation of alkynyl complexes [452–454]. The cumulenylidene resonance form was more important for more highly oxidized derivatives (e.g. **563**).

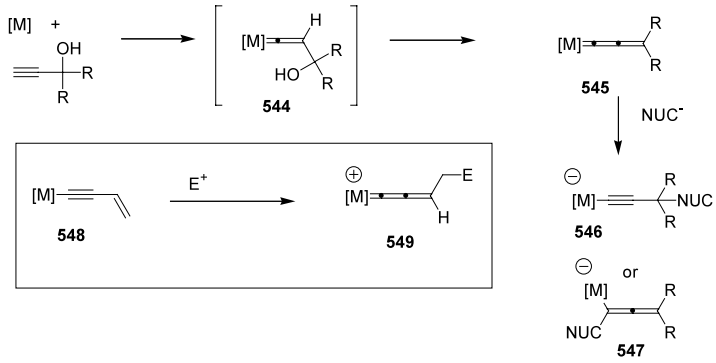
2.3.6. Group IX metal–carbene complexes

2.3.6.1. Simple carbene complexes. Reaction of rhodium–dinitrogen complexes (e.g. **564**, **566**, Scheme 93) with diazo compounds led to rhodium–carbene complexes [455]. An unusual C–H activation process occurred in the synthesis of the carbene complex from the complex featuring a saturated ligand (**566**), which was attributed to a β-hydride elimination process of carbene intermediate **567**, followed by formation of the benzyl complex, oxidative addition into the vinylic C–H bond, and reductive elimination of toluene; addition of a second mole of diazo compound results in the carbene complex (**573**) and the unsaturated dinitrogen complex (**572**).

A series of ligand exchange and coupling reactions were reported for diarylcarbene–rhodium derivatives (e.g. **574**, **575**, Scheme 94) [456]. Reaction of complex **575** with ethylene led to alkene complex **578** and the coupled product **579**; a mechanism involving formation of a rhodacyclobutane followed by β-hydride elimination and reductive elimination was proposed for the formation of **579**. Coupling of the phosphine complex of **575** with CO, isonitriles, or diazo compounds led to ketene (e.g. **577**) and related derivatives, while simple ligand exchange processes were observed for antimony complexes of **575**. Coupling with phenyl azide led to the unusual compound **580**. Treatment with sulfur or selenium led to the η^2-thioketone complexes. Thermolysis of the rhodium–carbene complex **574** ($L = Sb{i}Pr_3$) led to a carbene-bridged dirhodium complex, which provided complex **574** ($L = P{i}Pr_3$) upon treatment with triisopropylphosphine [457]. The synthesis and reactiv-



Scheme 89.



Scheme 90.

ity of indenyl-ligated analogs of carbene complex **575** (e.g. **581**, Scheme 95) was also reported [458]. Treatment of complex **581** with HCl or CO led to the substituted indenyl rhodium complexes (**582** or **583**). Iridium–carbene complex **585** (Scheme 96) was prepared from the treatment of chloroiridium complex **584** with silver hexafluorophosphate [459]. The process could be reversed by treatment of the carbene complex with chloride ion.

Synthesis of Fischer carbene–iridium complexes (e.g. **587**, Scheme 97) from ethers and tertiary amines using iridium complex **586** has been reported [460]. The hydride ligand arises from the α-hydrogen of the ether as noted through deuterium labeling studies. Isoprene is converted to 2-methyl-2-butene during the reaction process. Carbene complexes were successfully generated from anisole, THF, diethyl ether, and *N*,*N*-dimethylaniline. Boryloxycarbene–rhodium complexes (e.g. **589**) were generated from the coupling of complex **588** with iodomethane [461]. A mechanism involving oxidative addition followed by intramolecular hydride delivery and CO insertion was proposed. At 0 °C, hydride migration to the carbene carbon was observed, resulting in alkylrhodium complex **590**. A heterobimetallic iridium–thiocarbene complex was formed in low yield in the reaction of an iridium–rhodium bimetallic compound with carbon disulfide [462].

Thermolysis of iridabenzvalene derivative **591** (Scheme 98) resulted in isomerization to iridabenzene derivative **592** [463]. A similar rearrangement could also be promoted by silver ion, resulting in an oxidized iradabenzene derivative.

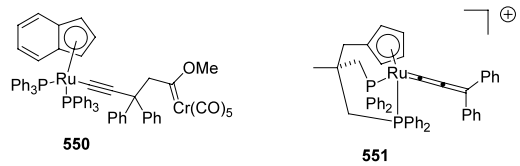
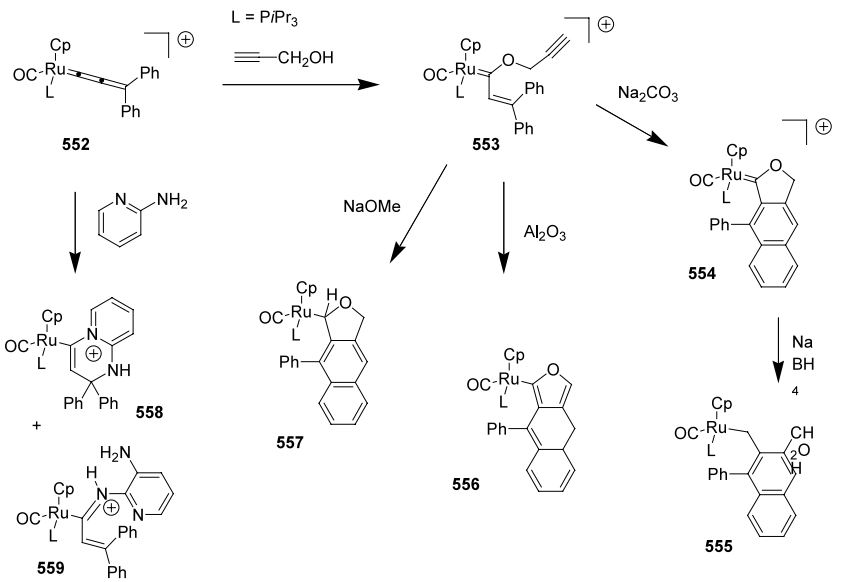
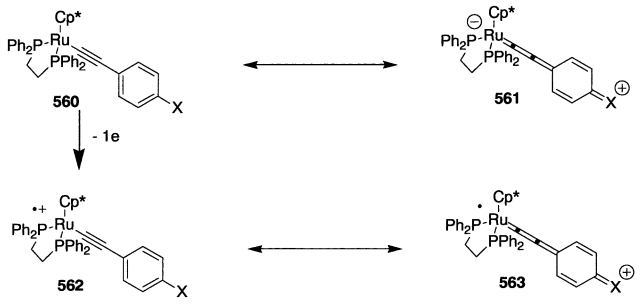


Fig. 13. Representative Group VIII metal–cumulenylidene complexes reported in 2000.



Scheme 91.

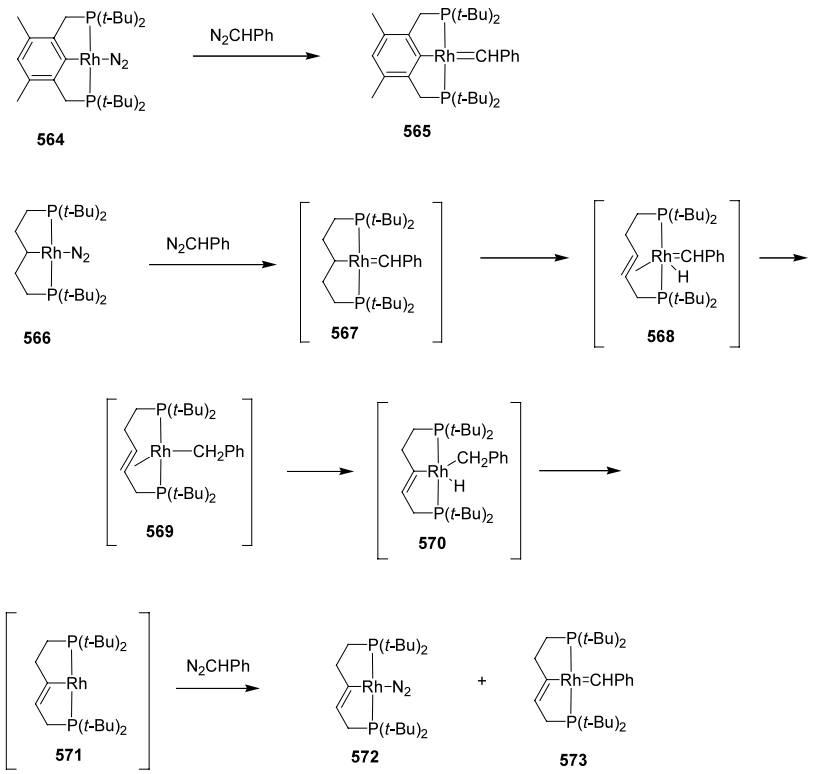


Scheme 92.

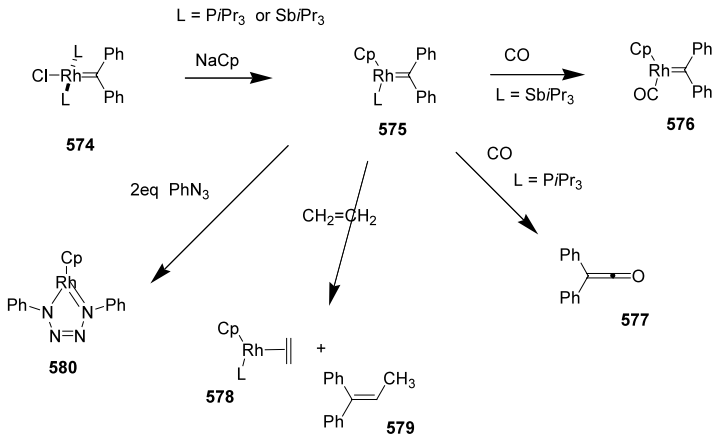
Several papers report on processes that propose Group IX metal carbene complexes as intermediates. Only processes that do not involve diazo compounds as the carbene precursor are included unless there is some effort to isolate the carbene complex. Rhodium–carbene complexes were proposed as intermediates in the cyclopropanation of alkenes by various rhodium(I) complexes [464]. Although the diazo complex could be isolated, the carbene complex could not. Iridium–carbene complexes (e.g. **595**, Scheme 99) were proposed as intermediates in the iridium-promoted ring expansion of vinylcyclopropenes (e.g. **593**) [465]. A cobalt carbene complex (e.g. **601**) was proposed as an intermediate in the cobalt-induced transformation of alkyne **598** into the fluorene derivative **602** [466].

A series of simple metal–carbene complexes and the analogous carbenoid structures were studied by Density Functional Theory [467]; a comparison between ruthenium, rhodium, palladium, and zinc species was the focus. The greatest π-bond energy was noted for ruthenium carbene complexes, and this decreases toward the right side of the periodic table.

2.3.6.2. Cumulene complexes. Similar synthetic procedures and reactivity patterns were generally observed for Groups IX and VIII (Schemes 84 and 90) metal–cumulene complexes. Coupling of rhodium–vinylidene complexes (e.g. **604**, Scheme 100) with 1,4-bis(triphenylstannyl)butadiyne (**603**) led to the carbon-bridged dimeric rhodium vinylidene species **605** [468]. Reaction with CO or isonitriles led to the alkynyl-migration product **606**. Various ligand exchange processes were reported for chloro-iridium analogs of vinylidene complex **604** [469]. Rhodium cumulenylidene complex **607**, featuring a *trans*-alkynyl ligand underwent a [2 + 1 + 1]-cycloaddition process resulting in rhodium–alkylidenecyclobutenone complex **608** [470]. A mechanism involving alkyne migration, followed by 1,3-shift of the metal, followed by CO insertion, followed by 1,3-shift of the metal and electrocyclic ring closure was proposed. Neutral iridium–butatrienylidene complex **611** was prepared from the iridium–dihydride complex **609** with enyne-triflate **610** [471]. Reaction with tri-



Scheme 93.



Scheme 94.

fluoroacetic acid led to alkenylvinylidene complex **612**. Group IX metal–vinylidene complexes were proposed as intermediates in iridium-catalyzed alkyne dimerization reactions [472].

Coupling of a series of terminal alkynes with diiridium complex **613** (Scheme 101) was reported [473]. Reaction with alkynols led to the expected cyclic carbene complexes (e.g. **615**) via the vinylidene intermediates (e.g. **614**). Reaction with simple terminal alkynes led to 1-thioalkylvinyliridium complexes (e.g. **617**) through intramolecular coupling of the thiolate ligand with the vinylidene complexes. Reaction with diphenylpropargyl alcohol led to α,β-unsaturated hydroxycarbene complex **616**.

2.3.7. Group X metal–carbene complexes

The coupling of nickel–acylate complexes (e.g. **618**, Scheme 102), formulated as carbene complexes, with acetylenes was studied [474]. The reaction led to mixtures of compounds **623**–**625**, however in all cases cyclopentenone **625** was the major product of the reaction. The complex mechanistic sequence depicted in Scheme 102 was proposed to account for formation of the observed products. A net alkyne insertion affords complex **619**, which undergoes coupling with a second acylnickel species (via Michael addition) to afford **620** or **621**. A net reductive elimination and protonation from **620** affords diketone **624**, while internal proton transfer, followed by an aldol process and reductive elimination affords cyclopentenone **625**. Butyrolactone **623** forms via CO insertion from intermediate vinylnickel species **619**.

Alkoxycarbene–platinum complexes (e.g. **627**, Scheme 103) were prepared from the coupling of platinum complex **626** with terminal alkynes in ethanol-containing solvent, presumably via the vinylidene complexes [475]. The crystal structure of an aminomethylene–palladium complex was reported [476]. A theoretical study of palladium- and rhodium-catalyzed cyclopropanation was reported [477], which supports the involvement of metal–carbene complexes.

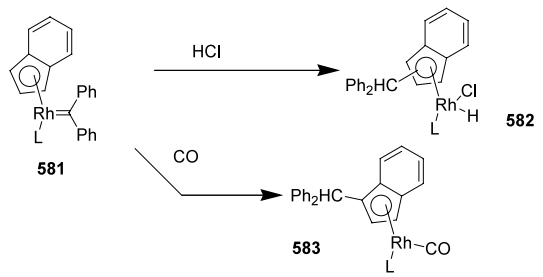
2.3.8. Lanthanide carbene complexes

The first report of a double bond between a transition metal and a lanthanide element was reported in 2000 [478]. Treatment of phosphimine complex **628** (Scheme 104) with samarium(III) complex **629** led to the carbene complex **630**.

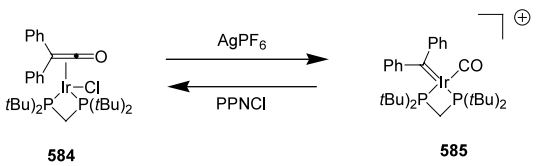
3. Metal–carbyne or metal–alkylidyne complexes

3.1. Review articles

Review articles featuring metal carbyne complexes which appeared in 2000 include: (1) synthesis of polymeric 1,6-heptadiyne derivatives by metathesis polymerization [479]; (2) synthesis of poly(aryleneethylene)s by



Scheme 95.

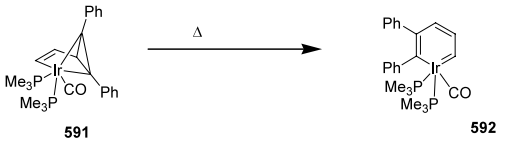


Scheme 96.

metathesis and other routes [480]; and (3) alkyne metathesis [481].

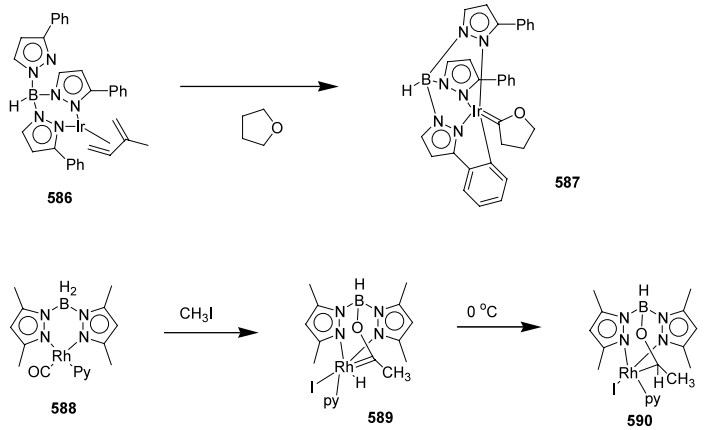
3.2. Synthesis and/or generation

A study of the photolytic coupling of tungsten hydride complex **631** (Scheme 105) with various alkynes

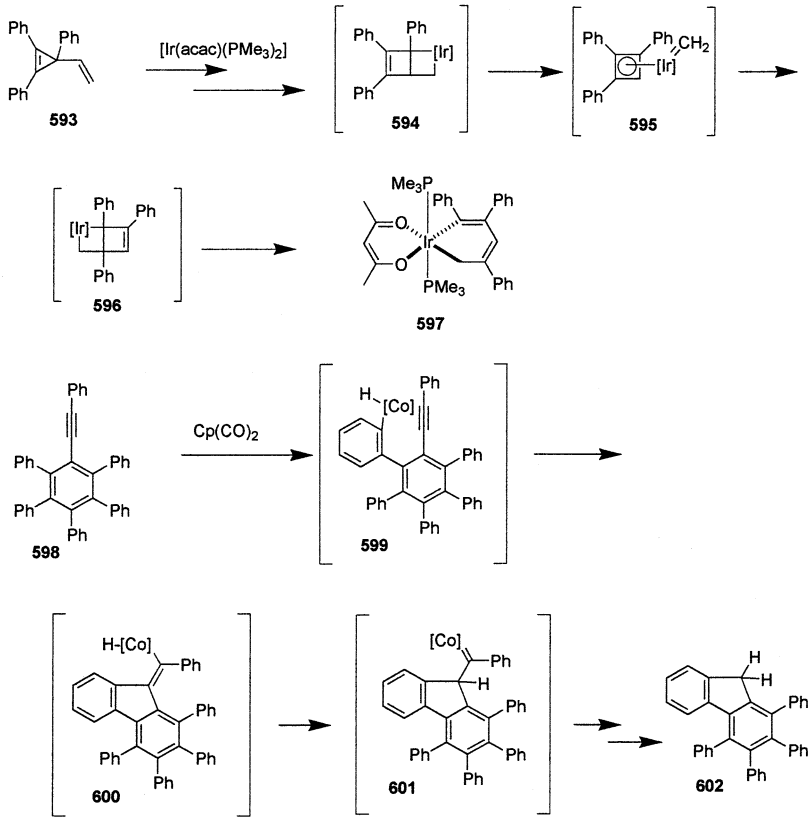


591 592

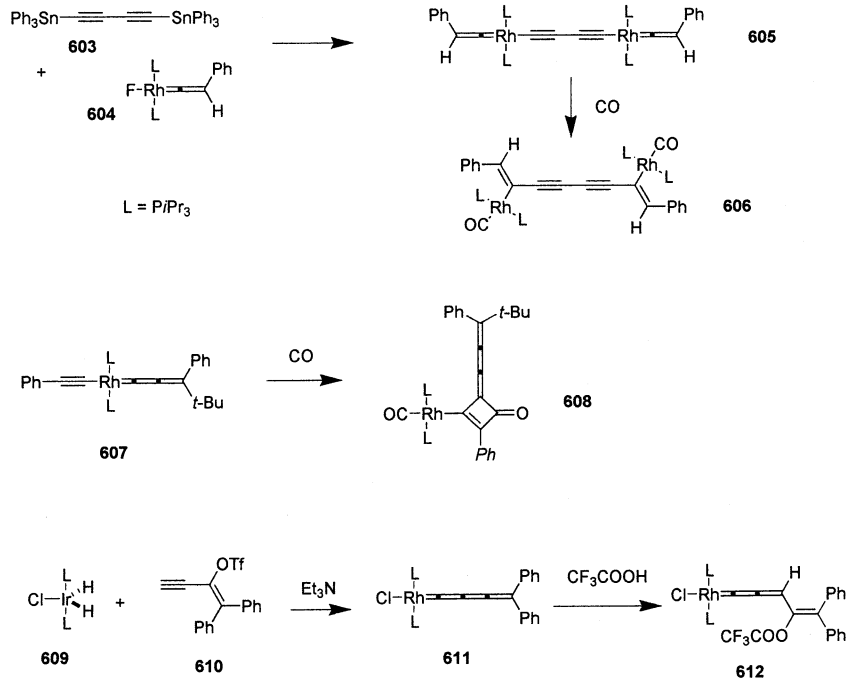
Scheme 98.



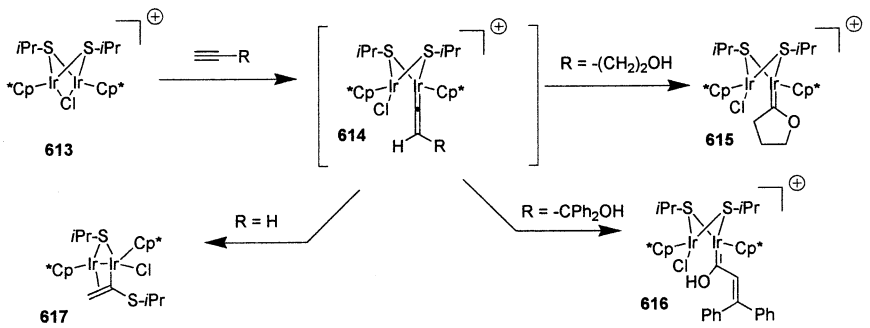
Scheme 97.



Scheme 99.



Scheme 100.

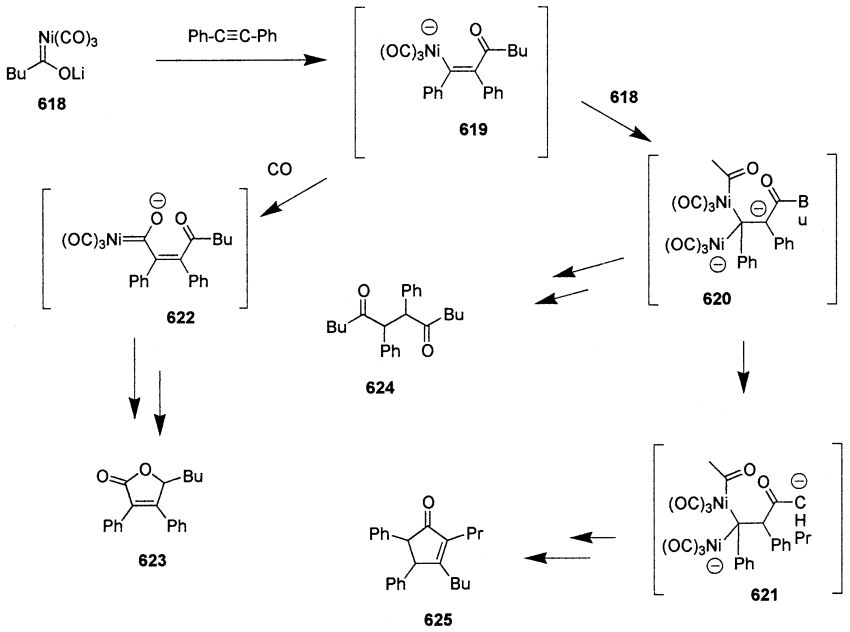


Scheme 101.

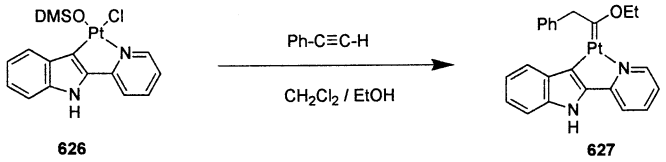
was conducted [482]. Phenylacetylene derivatives led to η^2-vinyltungsten complexes (e.g. **632**), while the analogous reaction with acetylene or trimethylsilylacetylene led to carbyne complexes (e.g. **634**) and η^2-vinyl complexes (e.g. **633**), which convert to carbyne complexes upon thermolysis. Reaction of complex **631** with *t*-butylacetylene leads to mixtures of η^2-acyl complex **637**, η^2-vinylcomplex **635**, and carbyne complex **636**. Reaction with 1-trimethylsilylpropyne led to a π-allyl complex, which rearranges to a carbyne complex upon thermolysis.

The reaction of cationic osmium hydride complex **638** (Scheme 106) with various propargyl alcohols has been studied [483]. Coupling with diphenylpropargyl alcohol (**639**) afforded the η^2-alkenyl complex **640**. Coupling with propargyl alcohol **642** afforded a mixture of compound **643** and the carbyne complex **644**, which converts to the alkenylvinylidene complex **645** upon treatment with sodium methoxide. Coupling with dimethylpropargyl alcohol also afforded a mixture of the η^2-alkenyl and carbyne complexes. In a related study, carbyne– and vinylidene–osmium complexes were also reported [484]. Allenylidene complex **646** was obtained from diphenylpropargyl alcohol, and was transformed into dicationic carbyne complex **647** upon protonation. Addition of methyllithium afforded neutral alkynyl complex **648**.

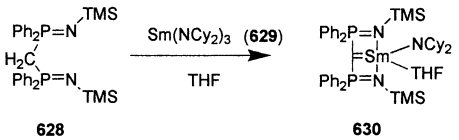
Coupling of osmium complex **649** (Scheme 107) with *t*-butylacetylene led to a mixture of carbyne complex **650** and vinylidene complex **651** [485]. A mechanism involving addition of HCl to an initially-formed vinylidene complex was proposed for the formation of the carbyne complex. Formation of the enynyl ligand in complex **651** was proposed to arise through migration



Scheme 102.



Scheme 103.

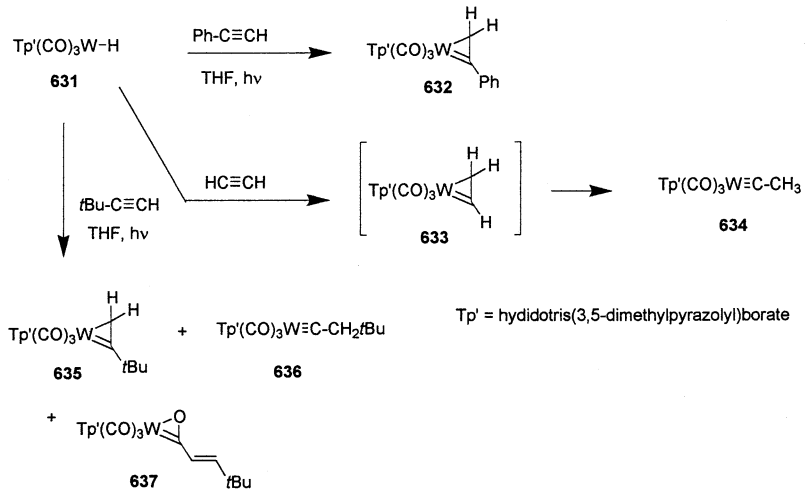


Scheme 104.

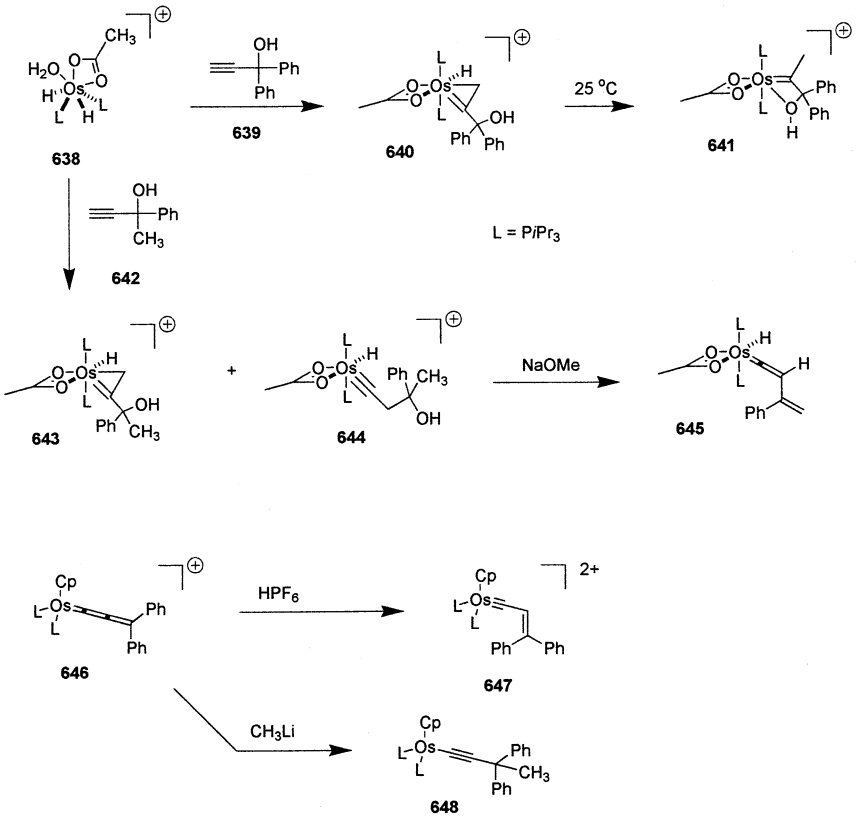
of an alkynyl ligand to a vinylidene ligand in an intermediate (e.g. **652**) featuring both types of ligands. Related osmium–carbyne complexes were prepared through the addition of HCl to osmium–vinylidene complexes [486].

Reaction of chlororuthenium hydride complex **653** (Scheme 108) with phenoxide ion led to phenoxide-ligated vinylidene derivatives (e.g. **654**) [487]. In the simple unsubstituted vinylidene complex **654**, rearrangement to the more stable carbyne complex **655** was reported.

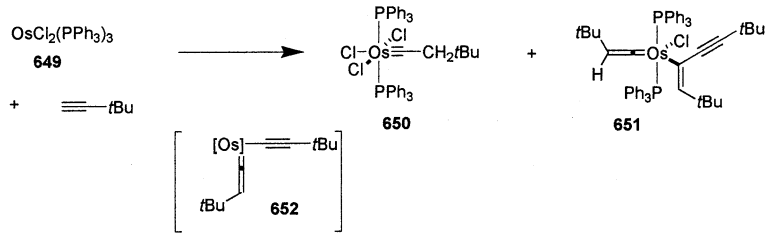
Cationic iron–aminocarbyne complex **656** (Scheme 109) was prepared in low yield through treatment of iron acylate complex **658** with trifluoroacetic anhydride and triphenylphosphine [488]. Alternatively, iodine oxi-



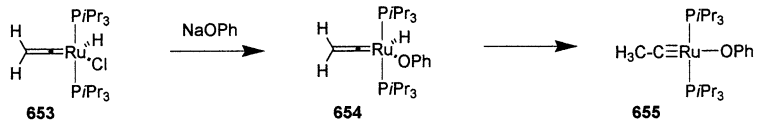
Scheme 105.



Scheme 106.



Scheme 107.



Scheme 108.

dation of acylate complex **657** afforded aminocarbyne complex **656** in higher yield. Cationic aminocarbyne complexes (e.g. **660**) were produced from treatment of molybdenum isonitrile complexes (e.g. **659**) with acid or methylating agents [489]. In the case of alkylisonitrile complexes, aminocarbene complexes featuring an agostic interaction were obtained. Similarly, protonation of rhenium–isonitrile complexes led to aminocarbyne complexes, which could be transformed back into isonitrile complexes by treatment with base [490]. Protonation of ruthenium–vinylidene complex **661** ($R = CF_3$) leads to an equilibrium mixture of carbyne complex **663** and acyloxycarbene complex **662** [491]. This behavior was unique to the trifluoroacetyl system; the acetyl complex (**662**, $R = CH_3$) exists completely as the acyloxycarbene complex.

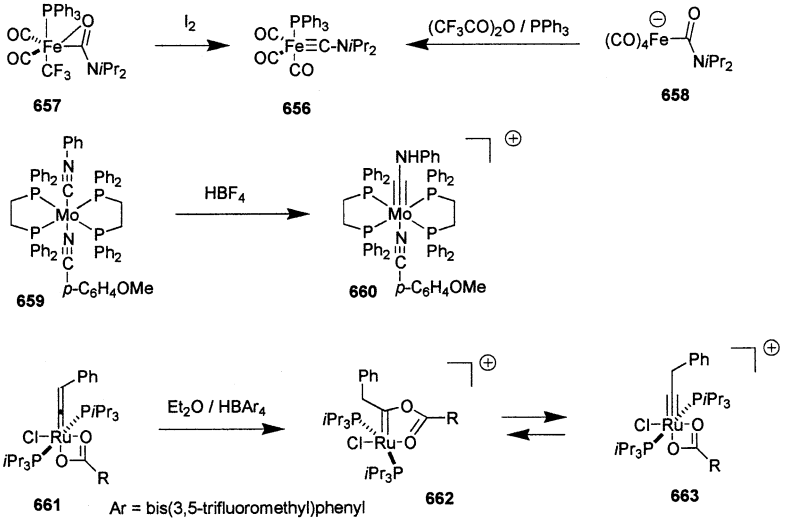
3.3. Reactivity

3.3.1. Addition reactions of metal–carbyne complexes

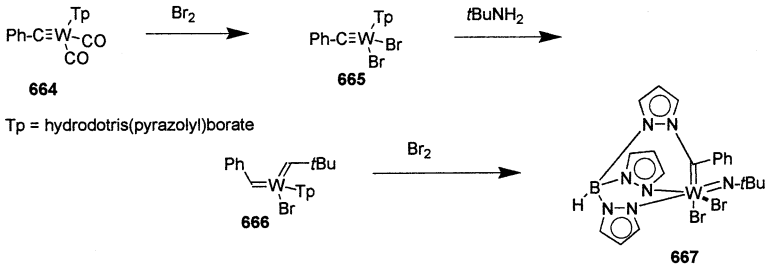
Oxidation of carbyne complex **664** (Scheme 110) with bromine afforded dibromotungsten–carbyne complex

665 [492]. Reaction with primary amines led to carbene–imido complex **666**, which transformed to the corresponding oxo complex upon exposure to air. Coupling of the carbene with the Tp ligand occurred during reaction of complex **666** with bromine, leading to chelating aminocarbene complex **667**.

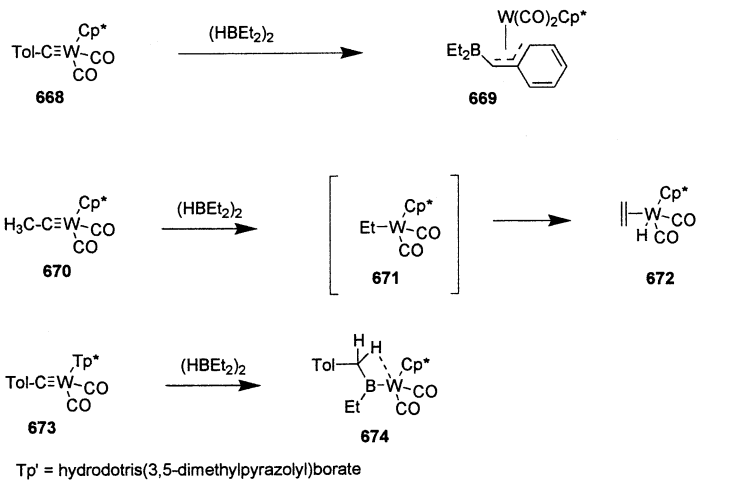
The reaction of tungsten–carbyne complexes with boron hydrides was reported (Scheme 111) [493]. Reaction of the arylcarbyne complex **668** with diethylborane dimmer led to the η^3-benzyl complex **669**. A mechanism involving regiochemically undefined addition of borohydride across the triple bond followed by



Scheme 109.



Scheme 110.



Scheme 111.

migration to afford the borane **669** was proposed. Reaction of the alkylcarbyne complex **670** with diethylborane afforded the ethylene complex **672** through reduction to the ethyltungsten complex followed by β-hydride elimination. Tungsten borane complexes (e.g. **674**) were obtained from Tp′ analogs (e.g. **673**).

Several examples of the addition of metal carbonyl anions (e.g. **676**, Scheme 112) to manganese– and rhenium–carbyne complexes (e.g. **675**) were reported in 2000 [494]. Addition of a methylpalladium complex across the metal–carbon triple bond was also reported [495].

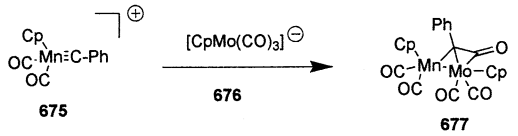
3.3.2. Ligand exchange and other processes that do not involve the carbyne ligand

Extensive ligand exchange/insertion processes were reported for tungsten carbyne–hydride complex **679** (Scheme 113), which was itself prepared from ligand exchange processes on tungsten–carbyne complex **678** [496]. Reaction with CO_2 or dimethyl acetylenedicarboxylate led to insertion products (e.g. **680**, **682**). A reversible hydride migration to give the agostic carbene complex was noted when carbyne complex **679** was treated with phosphine ligands. A series of vinylcarbyne–tungsten complexes and bridged bimetallic analogs (e.g. **685**) were prepared through ligand exchange processes [497,498]. The electrochemical and oxidation properties of these complexes were studied.

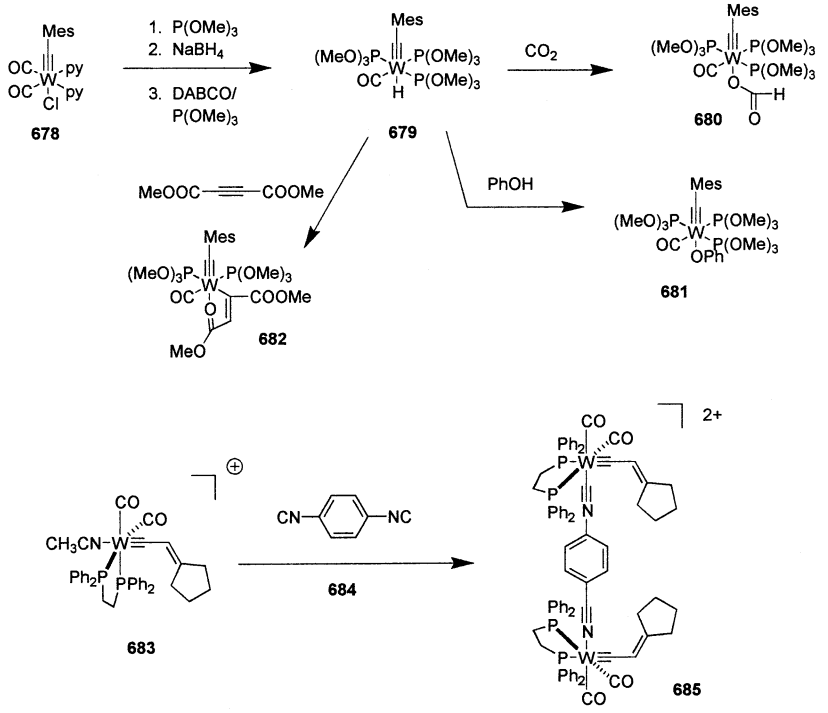
3.3.3. Alkyne metathesis

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 2000.

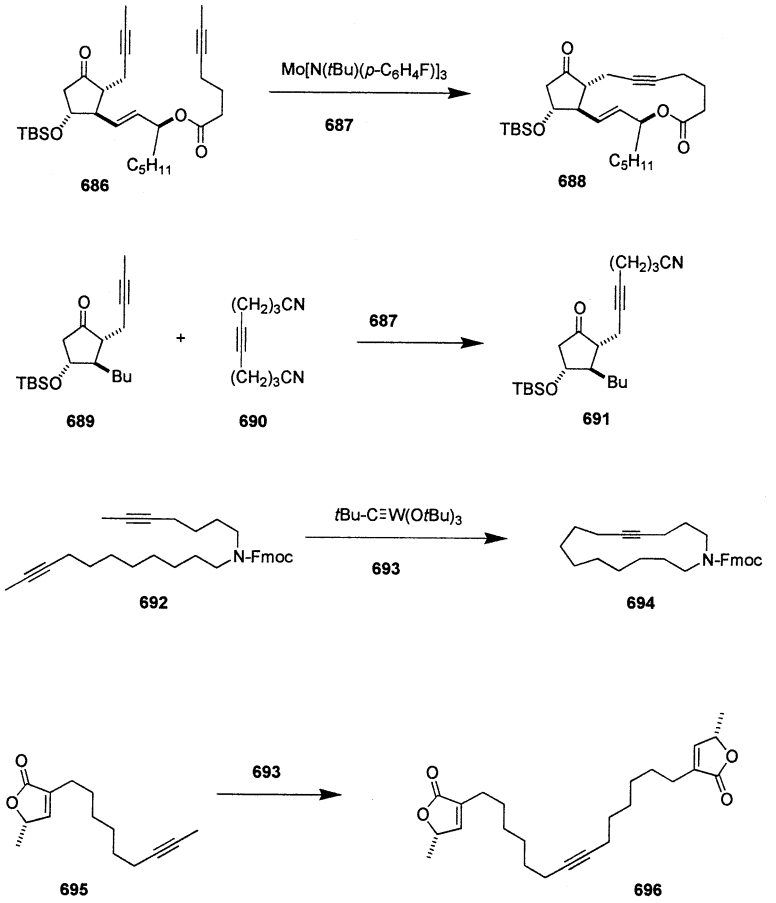
Both ring closing alkyne metathesis and cross metathesis initiated by molybdenum complex **687** (Scheme 114) were utilized as the key step in the synthesis of prostaglandin derivatives (e.g. **688**, **691**) [499,500]. For production of the *E*-macrocyclic ring system, alkyne metathesis followed by triple bond reduction was superior to alkene metathesis, which usually gives *E*–*Z* mixtures in similar ring systems. Other examples where ring closing alkyne metathesis was used as a key step in the synthesis of nonpolymeric compounds include: (1) synthesis of macrocyclic amines (e.g. **694**) for preparation of motuporamine C [501]; (2) synthesis of macrocyclic ketones [502]; (3) synthesis of macrocycle-bridged disaccharide derivatives [503]; and (4) synthesis of dehydrohomoancepsenolide via a



Scheme 112.



Scheme 113.

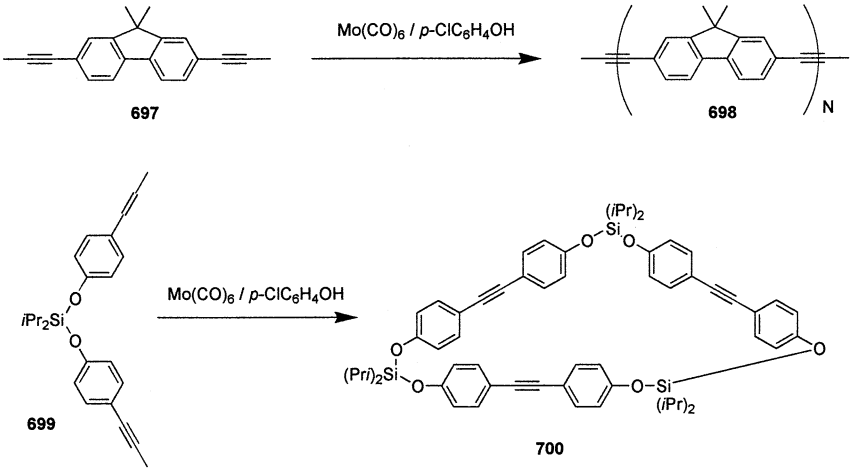


Scheme 114.

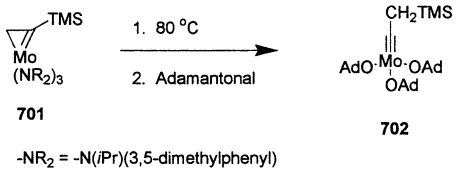
metathesis dimerization process (conversion of **695**–**696**) [504].

High molecular weight alkyne-containing polymers (e.g. **698**, Scheme 115) were prepared through metathesis polymerization (ADIMET) of acyclic diynes (e.g. **697**) using molybdenum hexacarbonyl and *p*-chlorophenol [505–507]. This process was effective for monomers that contain alkenyl substituents. This same catalyst system effected cyclic oligomerization using bis(*p*-alkynylphenyloxy)silane derivatives (e.g. **699**) [508]. A similar catalyst system using tungsten hexacarbonyl was also reported [509].

Thermolysis of η^2-alkenyl–molybdenum complex **701** (Scheme 116) followed by treatment with adaman-



Scheme 115.



Scheme 116.

tanol led to carbyne complex **702** [510]. Complex **702** was effective as a room temperature alkyne metathesis catalyst.

3.3.4. Other processes involving metal–carbyne complexes

Coupling of cationic carbyne complexes (e.g. **703**, Scheme 117) with alkynes has been examined [511]. Coupling with acetylene led to complex **704**, which was transformed to the alkenylcarbene complex **705** upon treatment with CO. Reaction with KOH led to the corresponding vinylidene complex **706**, which was converted to the dienylosmium complex **707** upon treatment with CO.

Oxycarbyne complex **709** (Scheme 118) was prepared through reaction of niobium–calixarene dimers **708** with CO [512]. The complex could be further reduced to carbide-bridged dimers (**711** and **712**) in various oxidation states by treatment with sodium metal.

3.4. Mechanistic/structural studies

Mechanistically-oriented studies of the reactions of metal–carbyne complexes include: (1) theoretical studies of iron carbonyls featuring a terminal carbide ligand [513]; (2) comparison of germylyne– and carbyne–tungsten complexes by density functional theory [514]; and (3) examination of Raman and Infrared spectra of tungsten–carbon triply bonded species [515].

Acknowledgements

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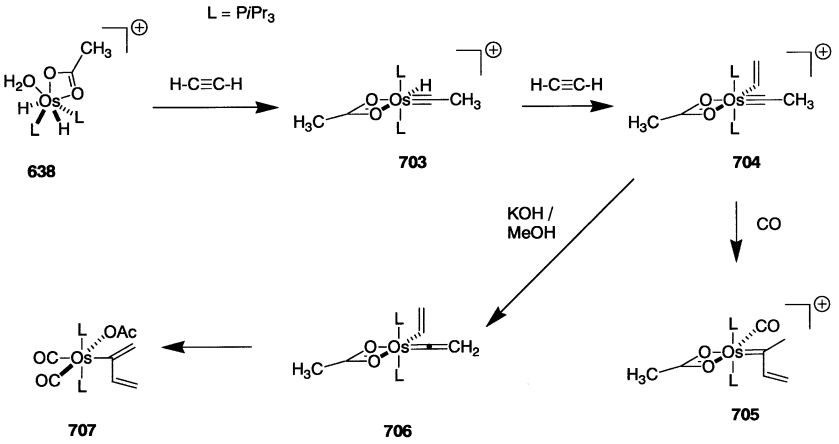
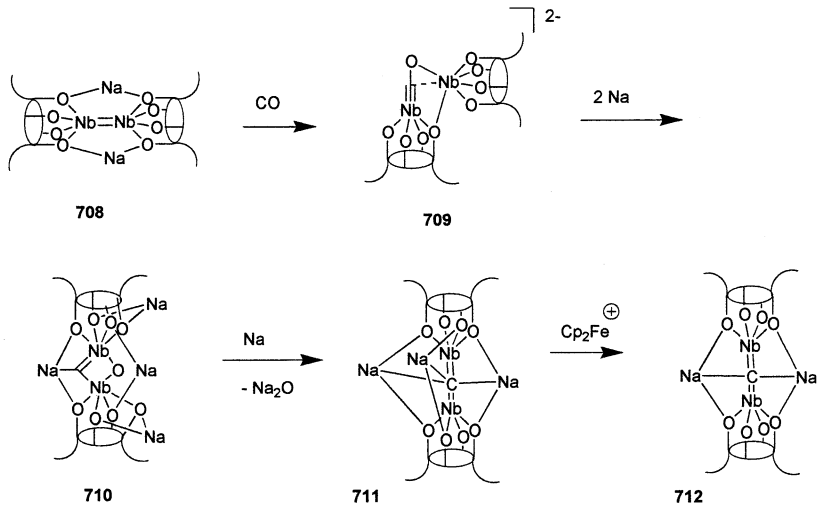


Scheme 117.



Scheme 118.

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