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The chemistry of the carbon-transition metal double and triple bond: annual survey covering the year 1997[☆]

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Contents

[☆] This is the first annual survey devoted to this subject material.

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Abstract

This survey is intended to be a comprehensive coverage of articles which report on the synthesis, reactivity, or properties of compounds which feature a multiple bond between carbon and a transition metal. Reactions which employ metal carbene complexes as transient intermediates generated through well-established routes are not covered unless there is some effort to characterize the carbene complex intermediate. 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 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 (J.C. Green, R.G.; Scurr, P.R. Arnold, F.G.N., Cloke, J. Chem. Soc. Chem. Commun. (1997) 1963; A.A. Danopoulos, D.M. Hankin, G. Wilkinson, S.M. Cafferkey, T.K.N. Sweet, M.B., Hursthouse, Polyhedron 16 (1997) 3879). 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. 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.

Keywords: Carbon–metal multiple bond; Metal carbene and carbyne complexes; Metathesis

Abbreviations

ROMP	ring opening metathesis polymerization
ADMETA	cyclic diene metathesis polymerization
RCM	ring closing metathesis
Grubbs catalyst I	structure **1** (Fig. 1)
Grubbs catalyst II	structure **2** (Fig. 1)
Schrock catalyst	structure **3** (Fig. 1)

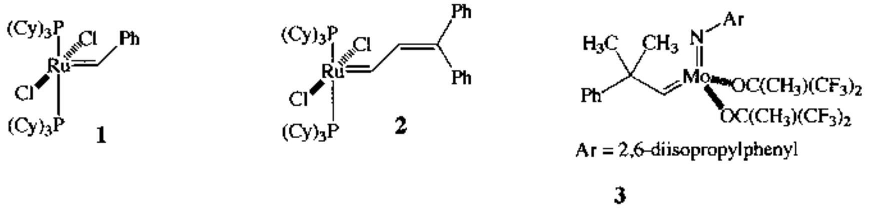


Fig. 1. Structures of alkene metathesis catalysts **1**–**3**.

1. Metal–carbene or metal–alkylidene complexes

1.1. Review articles

Several reviews covering aspects of metal–carbene complex chemistry have appeared in 1997. These reviews include the following subjects: (1) generation of titanium carbene complex intermediates from dialkyltitanium derivatives and subsequent reactions [1]; (2) generation of titanium vinylidene complexes from vinyltitanium species [2,3]; (3) the olefin metathesis reaction in organic synthesis [4,5]; (4)

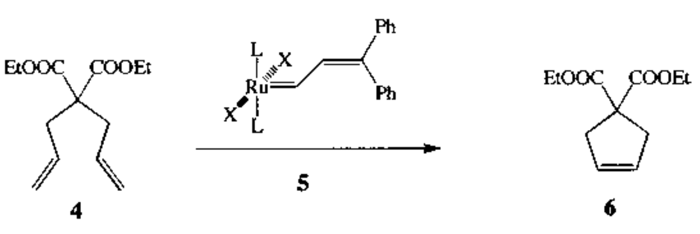
the use of the ring closing metathesis reaction for organic synthesis [6]; (5) the synthesis and reactivity of ortho carborane-substituted Fischer carbene complexes [7]; (6) the chemistry of alkynylcarbene complexes, which focuses on Fischer-type carbene complexes [8]; (7) the synthesis and reactivity of carbohydrate-modified Fischer carbene complexes [9]; (8) development of the physical organic chemistry of Fischer carbene complexes [10]; and (9) photolytic reaction processes of Fischer carbene–chromium complexes [11]. 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) theoretical studies of chemical bonds to transition metals [12]; (2) metal complexes of all-carbon ligands [13], (3) metal-assisted cycloaddition reactions [14], (4) carbonyl group alkenylation using metal alkyls and molybdenum or tungsten halides, which might involve metal alkylidene intermediates [15]; (5) the reactions of heterocyclic carbenes, which included several examples of the synthesis of metal–carbene complexes [16]; (6) reactions of alkynes with ruthenium complexes [17]; and (7) the synthesis and reactivity of triamidoamine–complexes [18].

1.2. Alkene metathesis

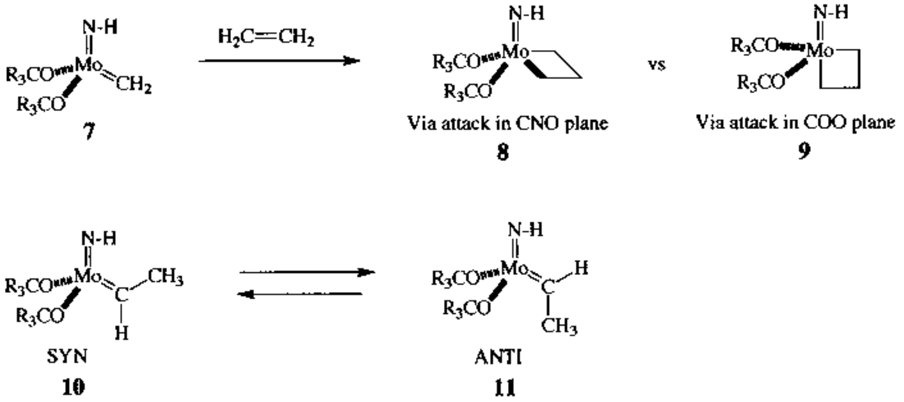
Alkene metathesis was the major reaction process reported for metal–carbene complexes in 1997, and this special section is devoted to papers which focus on this process. Many examples of both polymerization (ring opening metathesis polymerization (ROMP) and acyclic diene metathesis polymerization (ADMET)) reactions and small-molecule syntheses appeared. Only metathesis reactions initiated by a discrete transition metal–carbene complex, or metathesis reactions which discuss the carbene complex intermediates of this reaction have been included here.

1.2.1. General studies of alkene metathesis catalysts

A detailed study of the effect of structure on the alkene metathesis activity of a series of ruthenium carbene complexes of general structure **5** and mechanistic studies of olefin metathesis were undertaken [19] (Scheme 1); the reaction under study was ring-closing metathesis (RCM) of the diene **4**. A comparison of complexes differing only in the phosphine ligands revealed that more bulky phosphine ligands (i.e. those with larger cone angles) and more electron-donating phosphine ligands result in a more reactive olefin metathesis catalyst. A similar comparison of



Scheme 1.



Scheme 2.

halide ligands showed that the catalyst reactivity decreases in the order Cl > Br ≫ I. Steric and electronic effects of the halide and phosphine ligands appear to work in opposite directions. Theoretical studies of ligand and substituent effects in ruthenium alkylidenes were also reported [20]. Synthesis of additional modified ruthenium catalysts for alkene metathesis were reported [21,22].

Other studies correlating metal–carbene complex structure and alkene metathesis reactivity were conducted also. A comparison of the stability, metathesis activity, and selectivity of a variety of Schrock-type carbene complexes was reported [23]. Theoretical studies of the structure of molybdenum alkylidene complexes of general structure **7** (Scheme 2) and the reaction of these complexes with ethylene was conducted using ab initio calculations and density functional theory [24]. Formation of the metallacyclobutane ($R = H$) in the CNO plane (**8**) was found to be more favorable than attack in the COO plane (**9**) by 12.3 kcal mol^{-1}, and this energy difference was 18.8 kcal mol^{-1} for the complex where $R = F$. For the corresponding molybdenum–ethylidene complex, the SYN complex (**10**) was found to be more stable than the ANTI complex (**11**) by 2 kcal mol^{-1}.

1.2.2. ROMP

ROMP reactions remain a very active area of investigation. The strained alkene norbornene, norbornene derivatives, and copolymerizations involving a norbornene derivative and another alkene accounted for a large fraction of all reports of the ROMP reaction in 1997 (Fig. 2).

The ruthenium-catalyzed ROMP of thymine-linked norbornene derivative **12** afforded a polymer having characteristics reminiscent of DNA [25]. A similar ROMP reaction was performed on penicillin-linked norbornene derivative **13** [26]. Polymers displaying liquid crystal properties were prepared by ROMP reactions of norbornene diesters of general structure **14** using various molybdenum alkylidene complexes as catalysts [27]. The double-ROMP of quadricyclic compound **15** was accomplished successfully using the Schrock catalyst [28]. The polymer obtained

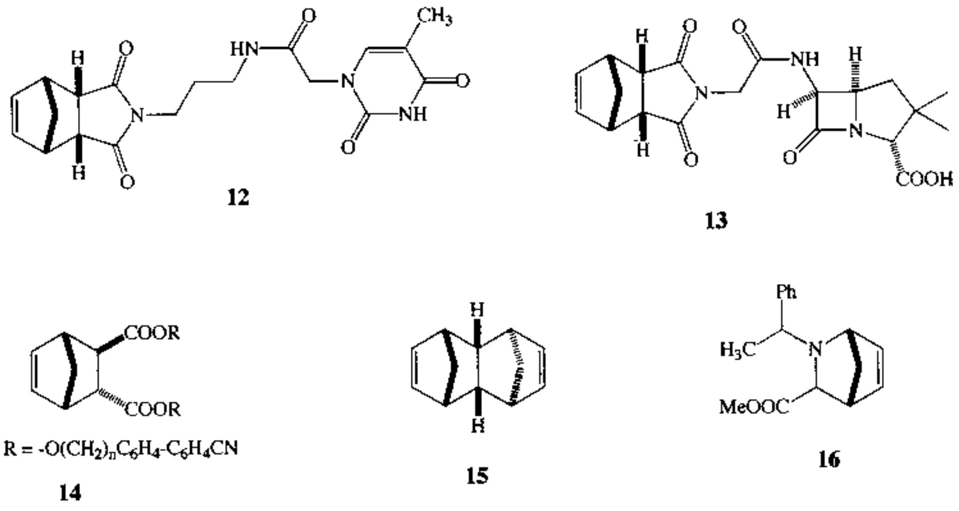
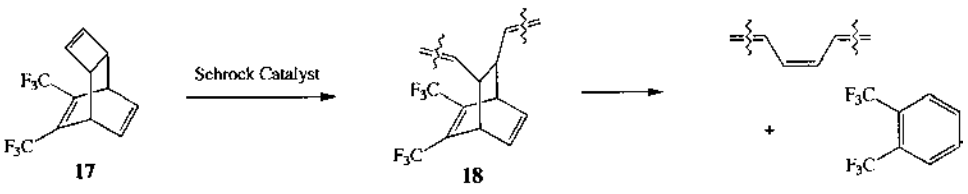


Fig. 2. Substrates for the ROMP reaction.

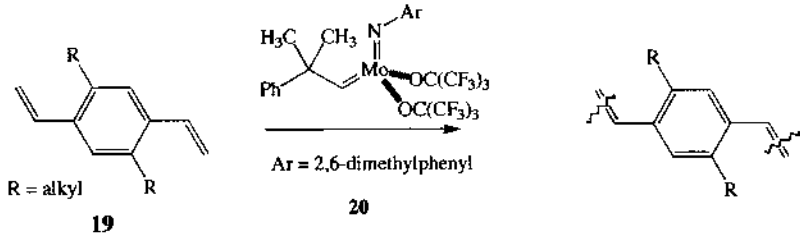
from this ROMP reaction underwent further metathesis copolymerization reactions with simple norbornene derivatives, resulting in crosslinked polymers. The ROMP of azanorbornene derivative **16** was accomplished using the Schrock catalyst [29].

Various copolymerizations involving norbornene derivatives were also reported . The ROMP copolymerization of norbornene and cyclopentene was studied [30]. Additional comparisons of benzonorbornadiene with 7-oxabenzonorbornadiene suggests that the oxygen atom facilitates the [2 + 2]-cycloaddition process. A variety of ROMP catalysts were examined in these studies, including molybdenum- and tungsten-chelating dienes and catalysts prepared from the coupling of phenylacetylene with ruthenium trichloride or osmium trichloride. The ROMP reaction of norbornene and cyclooctene was tested in supercritcal CO_2 using either the Grubbs catalysts or the Schrock catalyst [31].

The ROMP of other strained alkene systems was also examined. The ROMP of tricyclo[6.2.2.$0^{2,5}$]deca-3,7,9-triene (**17**) using the Schrock catalyst afforded the expected polymer **18** (Scheme 3), which serves as a polyacetylene precursor via the retro-Diels Alder reaction [32]. Precursors to polyphenylenevinylene were prepared through the ROMP of barrelene (bicyclo[2.2.2]octa-2,4,6-triene) and barrelene derivatives [33].



Scheme 3.



Scheme 4.

Numerous patents have been issued for polymers obtained through ROMP procedures involving metal carbenes [34,35] or for new carbene complexes which serve as ROMP and/or alkene metathesis catalysts [36–40]. A tantalum–alkylidene ROMP catalyst [41] and a metal–carbene catalyst generated photolytically from tungsten hexacarbonyl [42] were also reported.

1.2.3. ADMET polymerization

A series of molybdenum complexes bearing structural similarity to the Schrock catalyst were tested in their ability to catalyze the ADMET oligomerization reaction of *p*-divinylbenzene derivatives of general structure **19** [43,44] (Scheme 4). Good molecular weight control was observed since the oligomers precipitated from the solution. The solubility, and thus the molecular weight were controlled by the size of the R groups in the monomer. Catalysts containing the 2,6-dimethylphenylimido ligand (**20**) were the most active. The molybdenum-carbene complexes were efficient catalysts for the ADMET polymerization of tin-containing dienes [45].

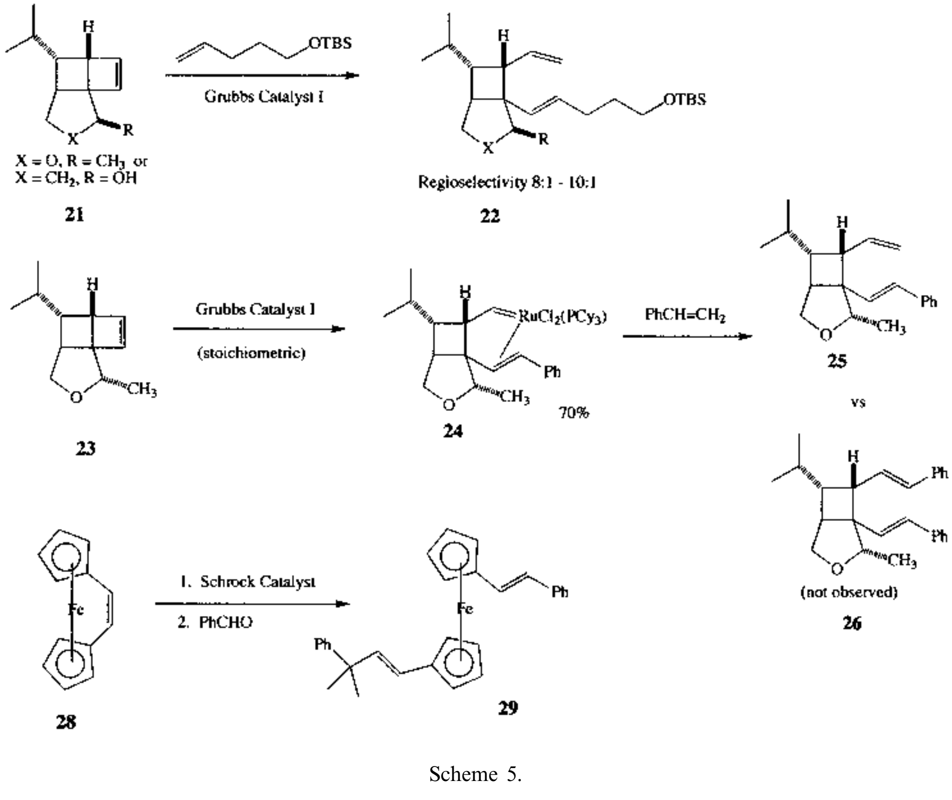
1.2.4. Nonpolymer-forming ring opening metathesis reactions

The cross metathesis of various bicyclo[2.2.0]hexene derivatives with monosubstituted alkenes using the Grubbs ruthenium catalyst was investigated [46,47] (Scheme 5). The regioselectivity of the process was controlled through steric effects. Only compounds of general structure **21** would undergo a regioselective cross-metathesis reaction with the silyl ether of 4-penten-1-ol. If the R group was replaced by a hydrogen, or if the R group was on the other side of the ring (**23**) little or no regiocontrol was noted in the cross-metathesis reaction. Stoichiometric coupling of **23** with Grubbs catalyst I afforded the unusual carbene complex **24** [48]. Complex **24** was effective as an olefin metathesis catalyst, and successfully catalyzed the cross metathesis of cyclobutene **23**. Treatment of complex **24** with styrene afforded ethenyl compound **25** and not phenylethenyl compound **26**, which suggests that benzylidene–ruthenium complexes and not the methylene–ruthenium complexes are the catalytic species in the cross metathesis reactions involving styrene. High yields of nonpolymeric metathesis products were observed in the co-metathesis reaction of various strained alkenes with monosubstituted alkenes using either ruthenium carbene or molybdenum carbene catalysts [49]. The reaction of the polymer-bound norbornene derivative with *p*-methoxystyrene and the Grubbs catalyst I afforded polymer-bound cross-metathesis products [50].

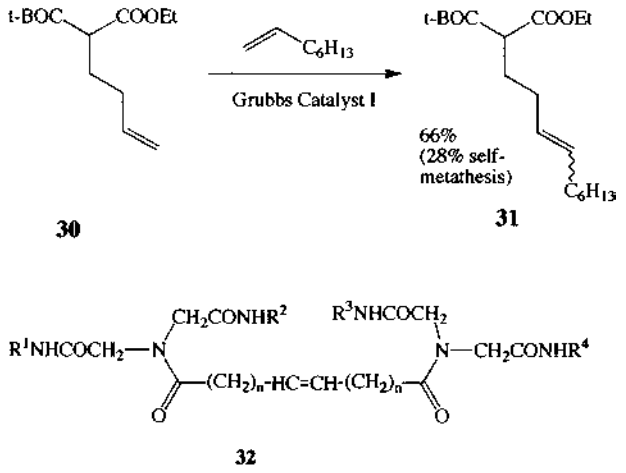
Alkene metathesis reactions of vinyl-bridged ferrocene derivative **28** have been studied [51] (Scheme 5). The stoichiometric reaction with the Schrock catalyst followed by benzaldehyde afforded the ferrocenylenevinylene derivative **29**. A block copolymer containing a polyferrocenylenevinylene substructure was formed from **29** and norbornene using the Schrock catalyst.

1.2.5. Simple cross metathesis reactions

The cross metathesis reaction of various monosubstituted alkenes and alkene-containing protected α-amino acid derivatives (**30**, Scheme 6) using Grubbs catalyst I was investigated [52]. A mixture of cross metathesis and self-metathesis products was observed using styrene, 1-hexene, or 1-octene and the alkene partner. A diverse array of polyamides of general structure **32** (i.e. a combinatorial library) were prepared by olefin metathesis of mixed derivatives of **32**, using Grubbs catalyst I [53].



Scheme 5.

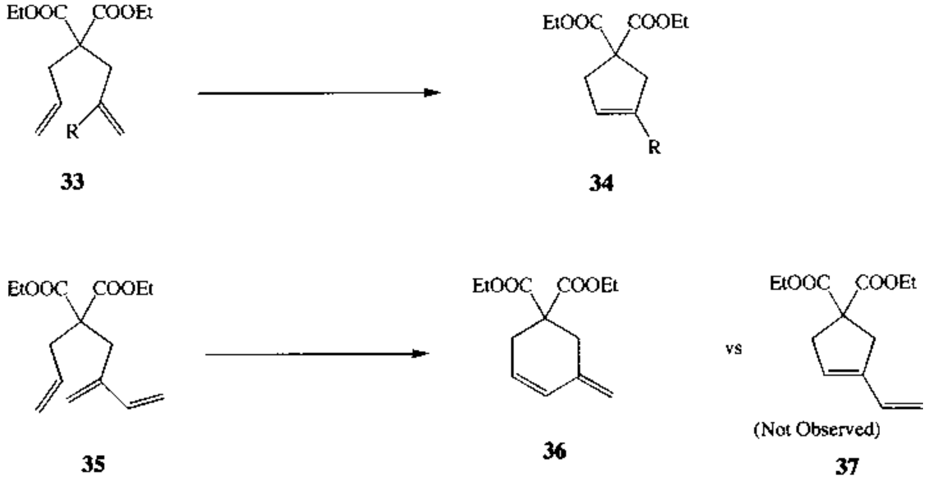


Scheme 6.

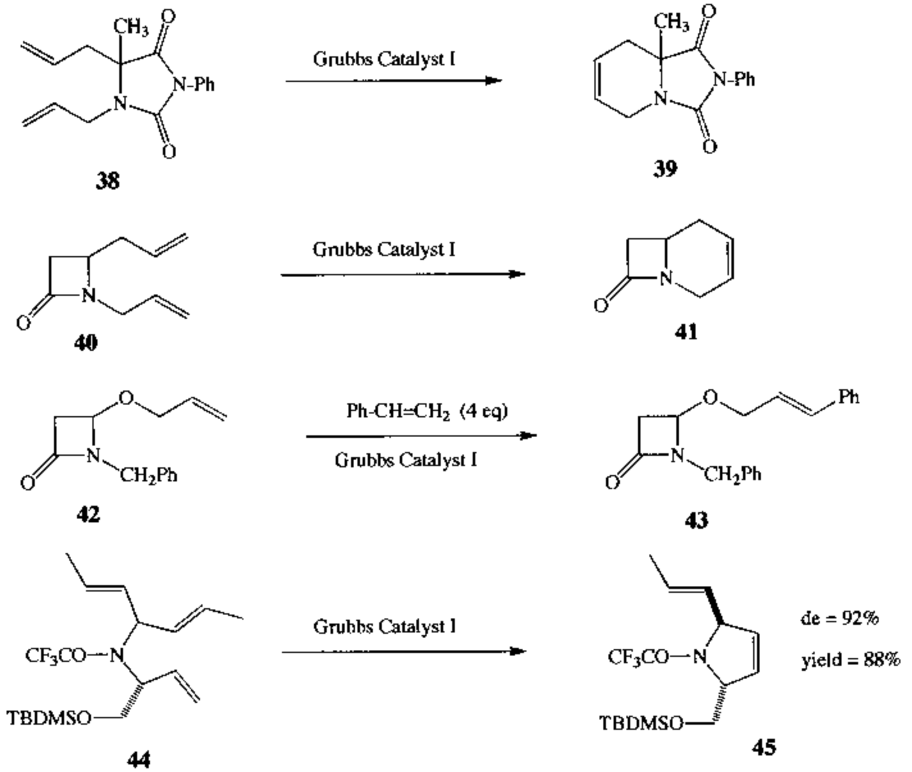
1.2.6. Ring closing metathesis

The RCM reaction 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 effect of alkene substitution patterns on the efficiency of the RCM reaction was investigated [54]. For diene **33** ($R = CH_3$) (Scheme 7), the RCM reaction was efficient for five-, six-, and seven-membered ring formation using either Grubbs catalyst I or the Schrock catalyst. For triene **35**, the RCM reaction using Grubbs



Scheme 7.



Scheme 8.

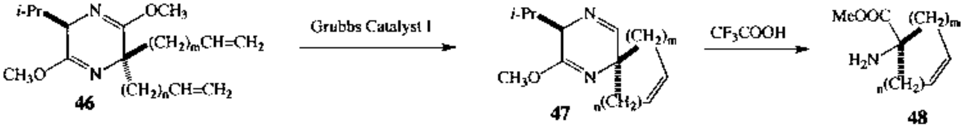
catalyst I led exclusively to six-membered ring derivatives. Examples of the RCM reaction of other substrates featuring additional substitution and/or functionality were also reported.

Numerous examples of the formation of nitrogen heterocycles using the RCM reaction were reported in 1997 (Scheme 8). Nitrogen tethered dienes of general structure **38**, readily available from amino acids and ureas, undergo the RCM reaction using Grubbs catalyst I [55]. The RCM reaction has been employed for the synthesis of β-lactam derivatives [56]. Dienes tethered by β-lactams (**40**) undergo the RCM reaction upon exposure to Grubbs catalyst I; this reaction was efficient for the formation of six- and seven-membered ring fused β-lactam derivatives. The simple cross metathesis of styrene derivatives and β-lactam containing alkenes (**42**) was also investigated. Using a four-fold excess of styrene derivative and Grubbs catalyst I, the cross-metathesis product was produced in yields of 42–70%. The formation of dihydropyrrole derivatives via the RCM reaction of bis(allylamides) was reported [57]. Excellent diastereoselectivity was observed in the RCM reaction of triene-amide **44** using Grubbs catalyst I at room temperature.

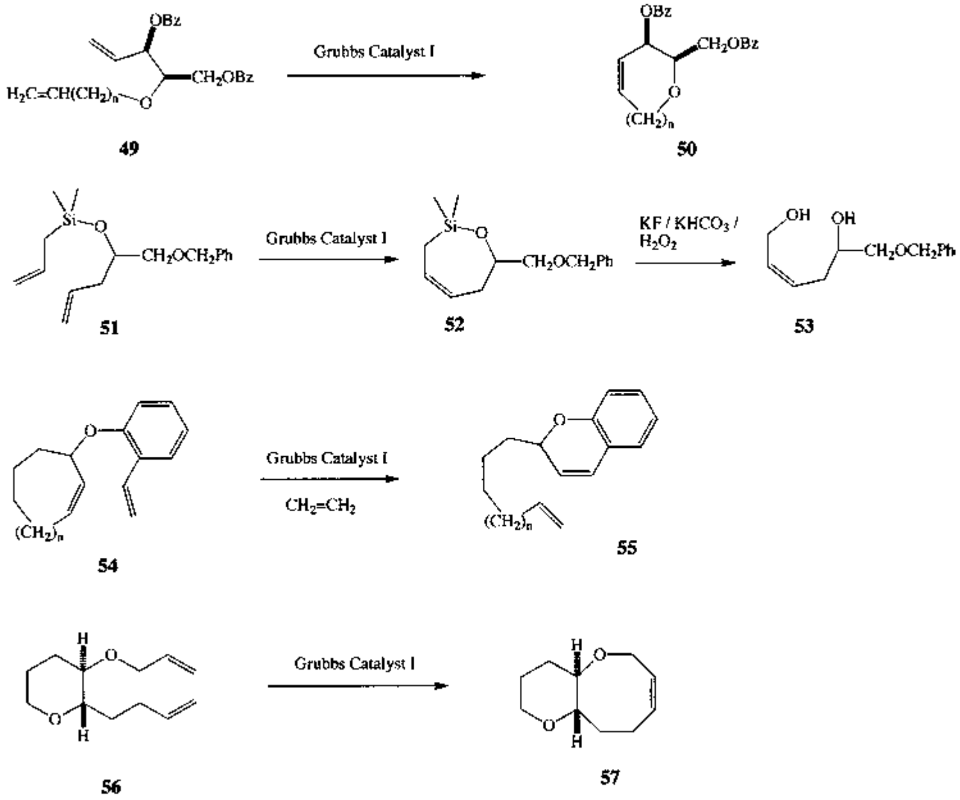
The RCM reaction has been employed in the enantioselective synthesis of carbocyclic α-amino acids (Scheme 9). Diene derivatives of general structure **46** undergo the RCM reaction using Grubbs catalyst I, resulting in a spirocyclic compound **47** [58], which afforded the α-amino ester upon treatment with trifluoroacetic acid. The RCM reaction was efficient if a six- or seven-membered ring was formed, however, severe reactivity differences were sometimes noted for stereoisomeric dienes. Five-membered ring-containing amino acids could be produced in high yield if the RCM reaction was conducted after conversion of the heterocyclic compound **46** to the α-amino ester. A similar study of analogs containing a chiral alcohol functionality in the diene tether was examined [59]. The RCM reaction has also been used for the synthesis of amino acid derivatives where the nitrogen and the α-carbon are part of a six- or seven-membered ring [60].

Many examples of oxygen heterocycle synthesis using the RCM reaction were reported in 1997 (Scheme 10). Diene-ethers of general structure **49** readily afforded six- to nine-membered ring cyclic ethers upon treatment with Grubbs catalyst I [61]. During the formation of nine-membered rings, dimeric compounds were observed as minor byproducts. The use of the RCM reaction for the synthesis of C-aryl glycosides was investigated [62]. Silyloxy-containing heterocycles (**52**) were prepared using the RCM reaction of siloxy-tethered dienes (**51**) [63], which afford *cis* alkenes (**53**) after oxidative cleavage of the carbon–silicon bond. A similar study using allylsilane derivatives was also reported [64]. A hybrid RCM-ring opening metathesis reaction was examined for various allyl *o*-styryl ethers of general structure **54** [65]. When the reaction was conducted under an ethylene atmosphere using the Grubbs catalyst, the RCM product was produced in high yield for the cycloheptene and cyclooctene derivatives. A low yield of RCM product was observed for the cyclohexene derivative, while no RCM product was observed for the cyclopentene derivative. In the absence of ethylene, a substantial amount of dimeric compounds were produced. The RCM reaction has been employed for the synthesis the six-, seven-, eight-, and nine-membered oxygen heterocycles present in the natural product brevitoxin and related systems (**57**) [66–69]. Resin-bond α,ω-dienes undergo simultaneous ring closure and resin release to form the heterocyclic derivatives [70]. Dihydropyrans, pipecolic acids, and Freidinger lactams have been prepared using this method. Formation of eight-membered ring ethers using the RCM reaction was found to be an often unreliable process, however, predictable success could be achieved when conformational effects are favorable [71]. The RCM reaction has been employed for the synthesis of sulfur-containing heterocycles using either sulfide- or disulfide-tethered dienes [72].

The RCM reaction was a key step in the total synthesis of the anticancer drug Epothilone A (**60**, Scheme 11) [73–78]. The RCM reaction of diene **58** and similar structures afforded Z–E mixtures of the macrocyclic product **59**.

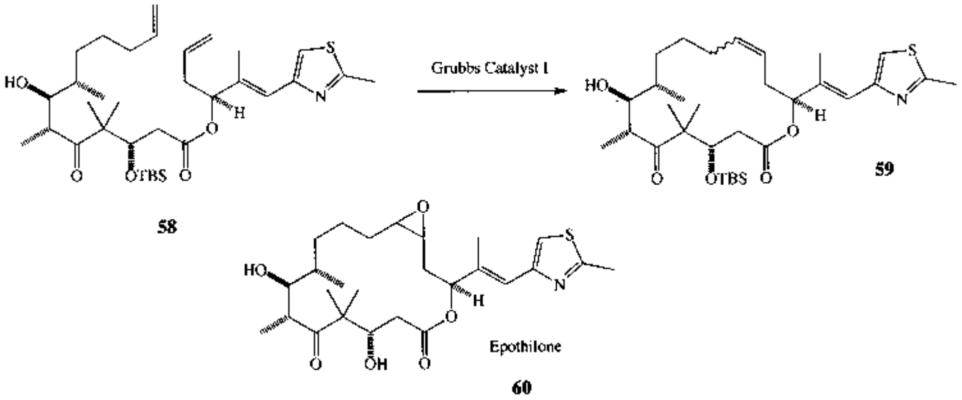


Scheme 9.



Scheme 10.

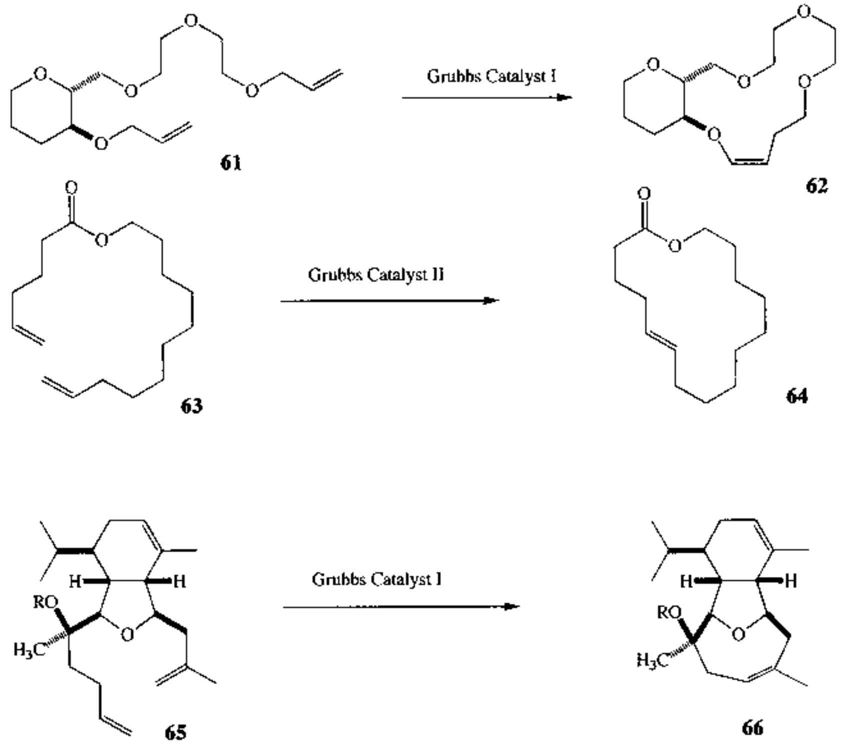
Numerous other examples of successful macrocyclic ring closure using the RCM reaction have appeared (Scheme 12). Examples include crown ether derivatives (**62**) [79,80], catenanes [81], trefoil knot compounds [82], macrocylces related to roseophilin [83], macrocyclic lactones (**64**) [84–87], macrocyclic lactams [88], and macrocyclic peptide derivatives [89]. The RCM reaction of diene **65** afforded the macrocyclic compound **66**, which is missing a carbon atom [90]; the proposed loss of a carbon atom was attributed to 1,3-isomerization of the alkene prior to metathesis. In most of these cases, ADMET polymerization and oligomerization processes were competitive with RCM reactions, however, the RCM pathway could usually be maximized using high dilution conditions. In the RCM-based synthesis of macrocyclic lactones, the relative position of the carbonyl groups and alkenes was very critical to the success of the RCM reaction. Stable chelates suppress the metathesis reaction, however addition of titanium isopropoxide as a chelation blocker overcame this effect. In the macrocyclic peptide synthesis, presence of a proline residue was critical to the success of the RCM reaction.



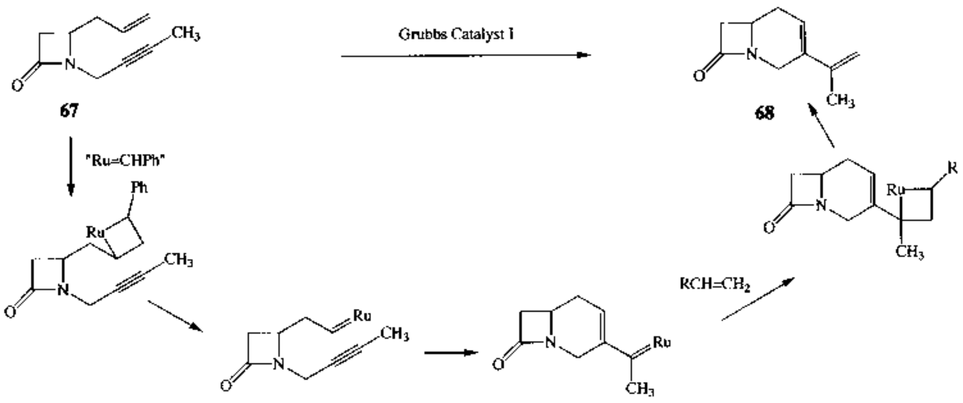
Scheme 11.

1.2.7. Alkene metathesis involving alkyne components

The RCM reaction of enynes tethered via a β-lactam ring (**67**, Scheme 13) [91] and via the heterocyclic ring system depicted in Scheme 9 [92] were reported in



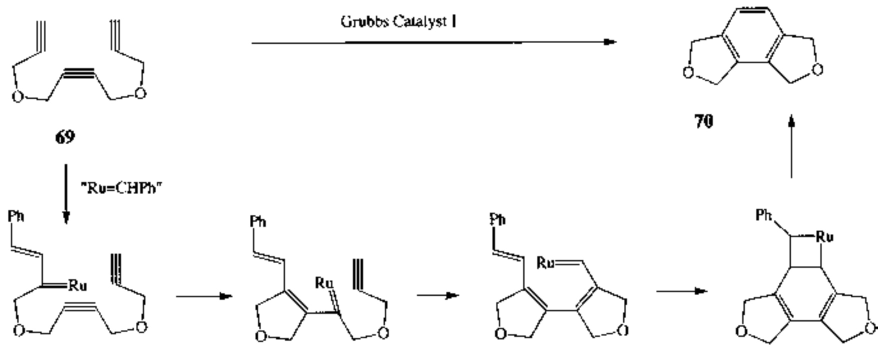
Scheme 12.



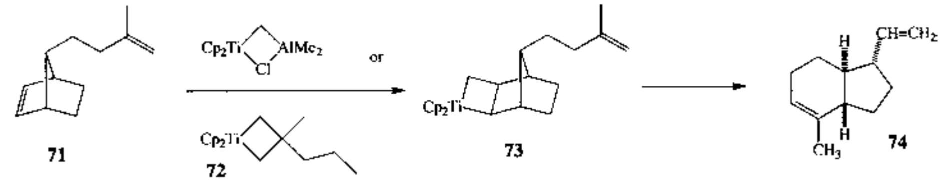
Scheme 13.

1997. Closure to six-membered ring derivative **68** proceeded very readily using 10 mol% of Grubbs catalyst I; a mechanistic description of this reaction is depicted in Scheme 13. An intermolecular cross metathesis of ethylene and acetylene was also reported [93].

The use of Grubbs catalyst I as an alkyne trimerization catalyst has been reported (Scheme 14) [94]. A variety of triynes of various tethers were effectively isomerized to the corresponding aromatic derivative using this catalyst. A mechanism involving one intermolecular alkyne insertion followed by two successive intramolecular alkyne insertions, followed by a ring-closing alkene metathesis step was proposed. Polymerization of 1-ethynyl-1-methoxycyclohexane was effected using a tungsten–carbene catalyst in the presence of aluminum trichloride [95].



Scheme 14.



Scheme 15.

1.2.8. Other metathesis reactions

The noncatalytic RCM-rearrangement reaction of norbornene derivative **71** (Scheme 15) using titanium reagents was examined [96]. Reaction of norbornene **71** with the Tebbe reagent led to the stable metallacycle **73**, however reaction with titanacyclobutane **72** induced transformation to the desired compound **74**. An attempt to induce this conversion enantioselectively using chiral titanium carbene complex precursors failed.

1.2.9. Alkene polymerization by metal–carbene complexes which do not involve an alkene metathesis mechanism

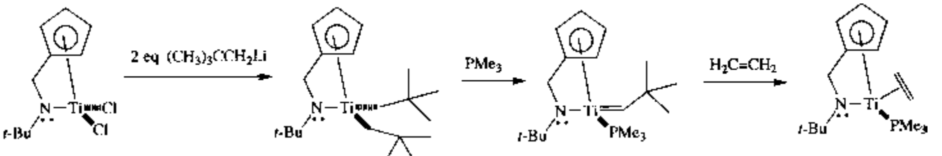
The polymerization of alkenes using alkylidene–transition metal complexes has resulted in numerous patents. Group IV–alkylidene complexes, which are generated in situ from the reaction of Group IV metallocene dihalides with alkylaluminum reagents, serve as efficient olefin polymerization catalysts [97–100]. A study of ethylene polymerization using chloro(methyl)methyltitanocene/methylaluminoxane catalysts revealed that titanium alkyls and not titanium–carbene complexes are involved in the polymerization process [101].

1.3. Individual carbene or alkylidene complexes classified according to metal

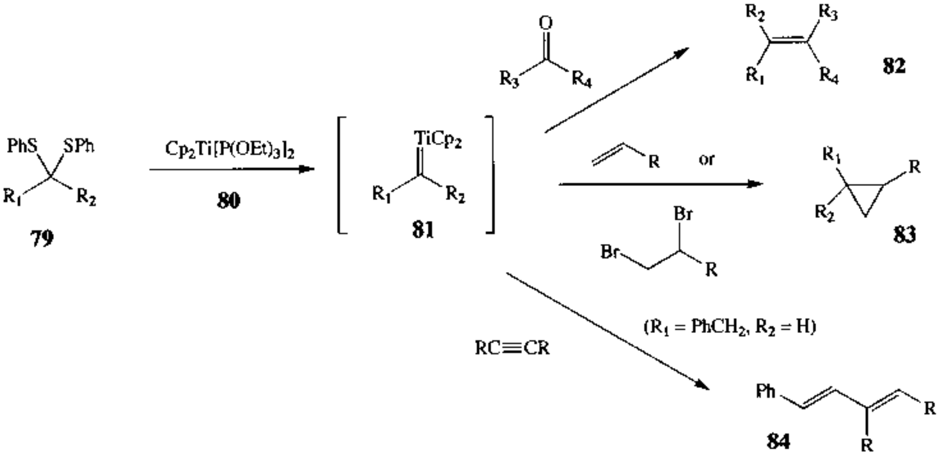
1.3.1. Group IV metal–carbene complexes

Both isolable titanium–carbene complexes and reactions which involve titanium alkylidene complexes are covered in this section. Routine uses of the Tebbe and related reagents for carbonyl methylenation reactions are not covered in this survey.

The synthesis and reactivity of chelated titanium alkylidene complexes (**75**, Scheme 16) was investigated [102]. The unusual net ligand exchange reaction (**77** → **78**) was observed upon treatment of alkylidene complex **77** with ethylene.



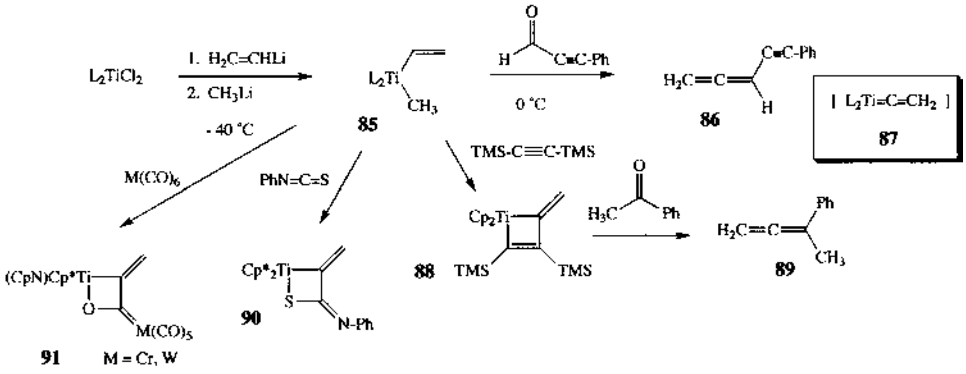
Scheme 16.



Scheme 17.

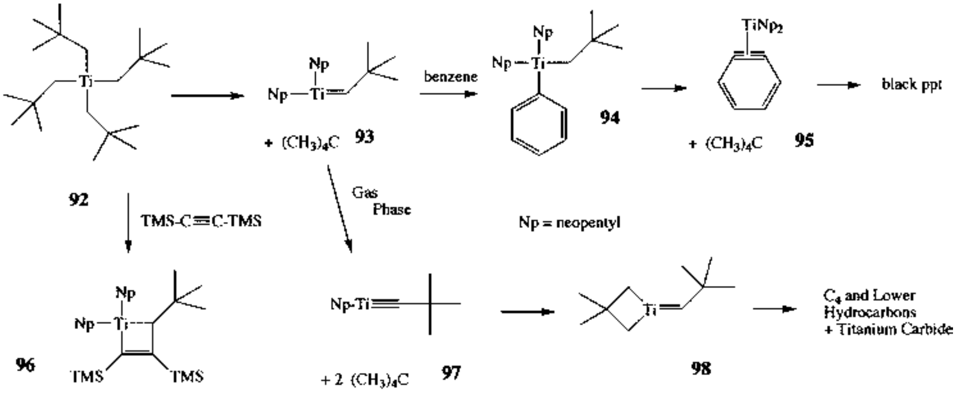
The heterocoupling of dithioacetals **79** and carbonyl compounds induced by titanium complex **80** was recently reported (Scheme 17) [103]. The reaction mechanism proposed involved conversion of the dithioacetal to the corresponding titanium–alkylidene complex **81**, followed by olefination of the carbonyl compound. The reaction is tolerant of a variety of R groups, and also allows for the formation of enol ethers from esters. Coupling of these in situ-generated complexes with a variety of organic compounds was reported. The analogous vinylcarbene intermediate (**79**, R_1 or R_2 = alkenyl) was prepared from allylic dithioacetals [104], and this compound provided cyclopropane derivatives (**83**) upon coupling with alkenes or 1,2-dibromo compounds. Coupling of in situ-generated titanium–alkylidene complexes with alkynes afforded 1,3-dienes (**84**) [105]. A detailed mechanistic study of the McMurry carbonyl reductive dimerization reaction has provided evidence that alkylidene complexes similar to **81** are important intermediates in this process [106].

Titanium vinylidene complexes (**87**, Scheme 18), generated in situ from decomposition of divinyltitanium species or alkyl–vinyltitanium species, have been studied. The application of titanium vinylidene complexes to the synthesis of allene derivatives was investigated [107]. If the decomposition of alkyl–vinyltitanium complex **85** (L = Cp) was conducted in the presence of organic carbonyl compounds, allene derivatives (**86**) were produced. If the decomposition reaction was conducted in the presence of bis(trimethylsilyl)acetylene, the corresponding metallacyclobutene (**88**) could be isolated, which converts to the allene upon heating in the presence of a carbonyl compound. The coupling of isothiocyanates with in situ-generated complex **85** (L = Cp*) afforded thiometallacyclobutane derivatives (**90**) [108]. The synthesis and reactivity of (*N*,*N*-dimethylaminomethyl)tetramethylcyclopentadienyl (Cp*N) analogs of complexes **85** and **87** were also studied [109]. Decomposition of complex **85** (L = Cp*N and Cp*) in the presence of group VI metal carbonyls afforded bimetallic Fischer carbene complexes (**91**).



Scheme 18.

The decomposition of tetraneopentyltitanium (**92**), which involves titanium alkylidenes as intermediates, was studied in both the solution phase [110] and in the gas phase [111]. The mechanism in Scheme 19 was proposed for the conversion of complex **92** to titanium carbide in benzene solution. First α-hydride elimination and reductive elimination (forming neopentane leads to alkylidene complex **93**. Next, oxidative addition into the C–H bond of benzene and carbene insertion affords (phenyl)trineopentyltitanium complex **94**. β-Hydride elimination and reductive elimination affords benzyne complex **95**, which then decomposes to a black precipitate. This reaction pathway was supported by several observations: (1) if the thermolysis was conducted in the presence of bis(trimethylsilyl)acetylene, the metallacyclobutene **96** was isolated, (2) 2 mol of neopentane were produced in the thermolysis reaction, and (3) when the thermolysis was conducted in benzene-d_6, one mole of neopentane d_0 and one mole of a mixture of neopentane d_1 and d_2 was produced. A similar first step was proposed for the gas phase decomposition of tetraneopentyltitanium. Further decomposition of the initially-formed titanium



Scheme 19.

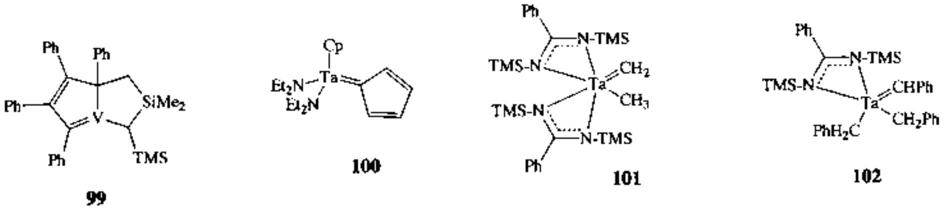


Fig. 3. New Group V metal–carbene complexes.

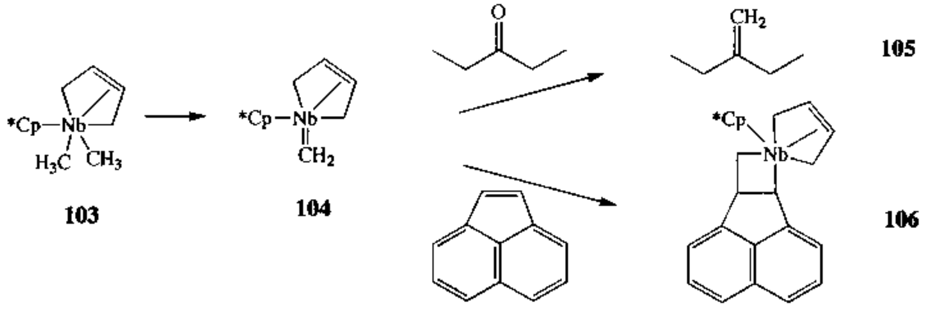
alkylidene occurs by α-hydride elimination (forming carbyne **97**) and γ-C-H activation (forming metallacyclobutane **98**) to eventually produce titanium carbide and a mixture of C_4 and lower hydrocarbons. Similar decomposition of tetrakis(trimethylsilylmethyl)titanium proceeded also through titanium alkylidene complex intermediates [112].

1.3.2. Group V metal–carbene complexes

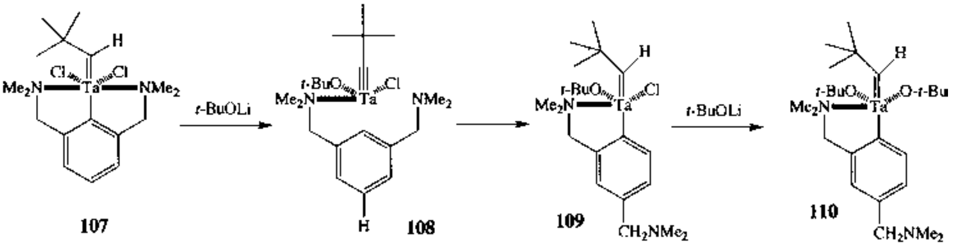
Numerous papers emphasizing the synthesis of Group V metal–carbene complexes appeared in 1997 (Fig. 3), including synthesis of vanadium alkylidene complex **99** from a vanadium–borane complex and diphenylacetylene [113], synthesis of cyclopentadienylidene–tantalum complex **100** in low yield from a monocyclopentadienyl–tantalum complex and methyllithium [114], and synthesis of tantalum–alkylidene complexes **101** and **102** by deprotonation or dehydrohalogenation processes, respectively [115].

The niobium–butadiene complex **103** (Scheme 20) was found to serve as a synthetic equivalent to a niobium methylene complex (**104**, a possible intermediate in the reaction) [116]. Treatment of complex **103** with organic carbonyl compounds afforded the corresponding methylenation product **105**. Treatment of complex **103** with strained alkenes led to the corresponding niobacyclobutanes (**106**). Niobium–alkylidene complexes were also implicated as intermediates in alkyl migrations involving alkylniobium–acetylene complexes [117].

Several studies emphasizing the reactivity of tantalum–alkylidene complexes appeared in 1997 (Scheme 21). The unusual compound **110** was observed from the



Scheme 20.

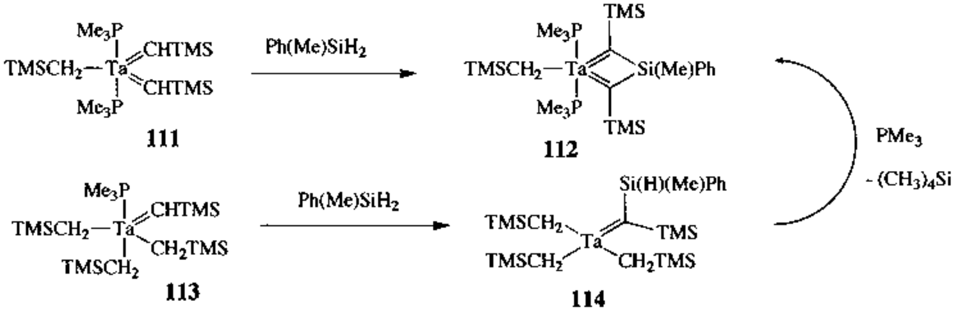


Scheme 21.

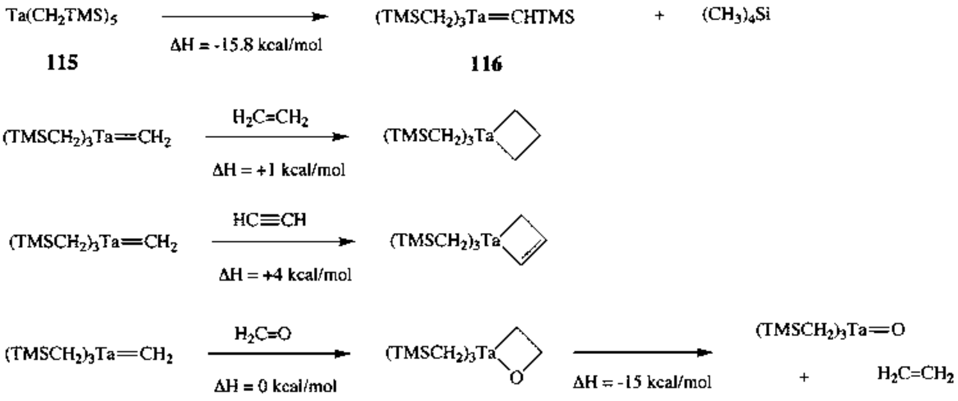
reaction of complex **107** with lithium *t*-butoxide, which involves a net change in the substitution pattern of the aromatic ring [118]. Based on deuterium labeling studies, a mechanism involving α-hydrogen abstraction and reductive elimination, forming the alkylidyne complex **108**, followed by C–H activation and reductive elimination was proposed. Synthesis and reactivity studies were conducted on tantalum alkylidene complexes featuring an isomeric tridentate diaminoaryl ligand [119], and upon tantalum–alkylidene complexes featuring aryloxy ligands [120].

The reaction of tantalum–alkylidene and bis-alkylidene complexes with silicon hydrides was investigated (Scheme 22) [121]. Replacement of the α-hydride by silicon accompanied by loss of hydrogen was the general process observed in these reactions. Reaction of the bis alkylidene complex **111** with methyl(phenyl)silane afforded the cyclic bis-alkylidene complex **112**. A similar reaction of alkylidene complex **113** with methy(phenyl)silane afforded the alkylidene complex **114** accompanied by bis alkylidene complex **112**; complex **114** converted to complex **112** under the reaction conditions. Detailed mechanistic studies of these reaction processes using kinetics and deuterium labeling were presented.

The thermodynamic parameters for the synthesis of tantalum–alkylidene complex **116** (Scheme 23) from pentaalkyl complex **115** and for reactions of complex **116** with various unsaturated organic compounds were determined experimentally [122]. Conversion of the pentaalkyltantalum complex **115** to the alkylidene complex **116** and tetramethylsilane was exothermic by 15.8 kcal mol^{-1}. The thermodynam-



Scheme 22.



Scheme 23.

ics for iodinolysis of pentaalkyltitanium complex **115** were determined also; iodinolysis of one of the titanium alkyl bonds was exothermic by 38 kcal mol^{-1}, while iodinolysis of all five bonds was exothermic by 75.1 kcal mol^{-1}. Based upon this data, the following bond dissociation energies were determined: Ta=C = 126 kcal mol^{-1}; Ta–C = 67 kcal mol^{-1} (based on the cleavage of one Ta–C bond). The calculation of ΔH for a variety of reactions of tantalum alkylidene complexes were based upon the experimentally-determined bond dissociation energies above and some previously known quantities; the results are depicted in Scheme 23.

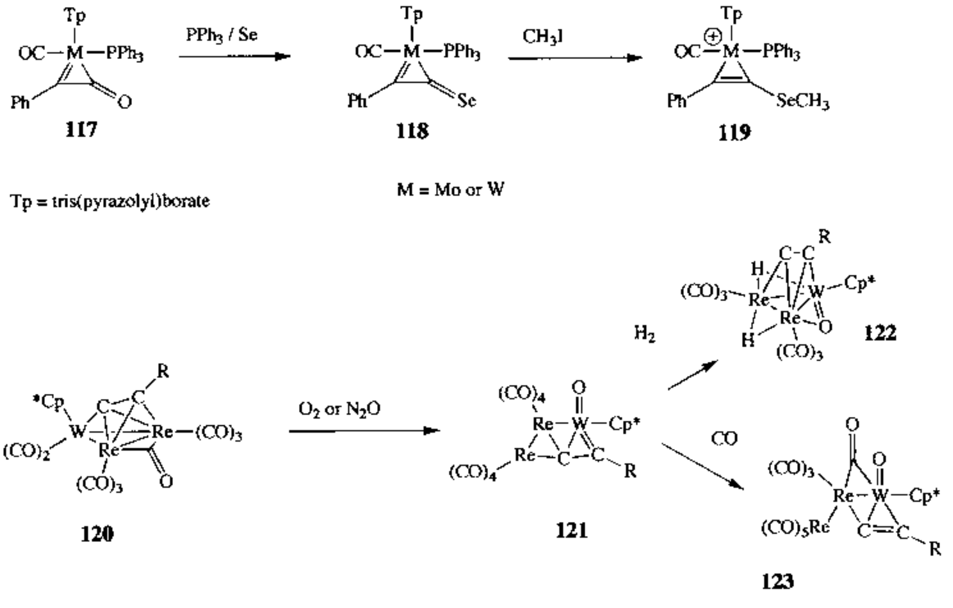
1.3.3. Group VI metal–carbene complexes (further classified according to structure and reaction type)

1.3.3.1. Schrock-type carbene complexes. A significant portion of this subject material has already been presented in the alkene metathesis section.

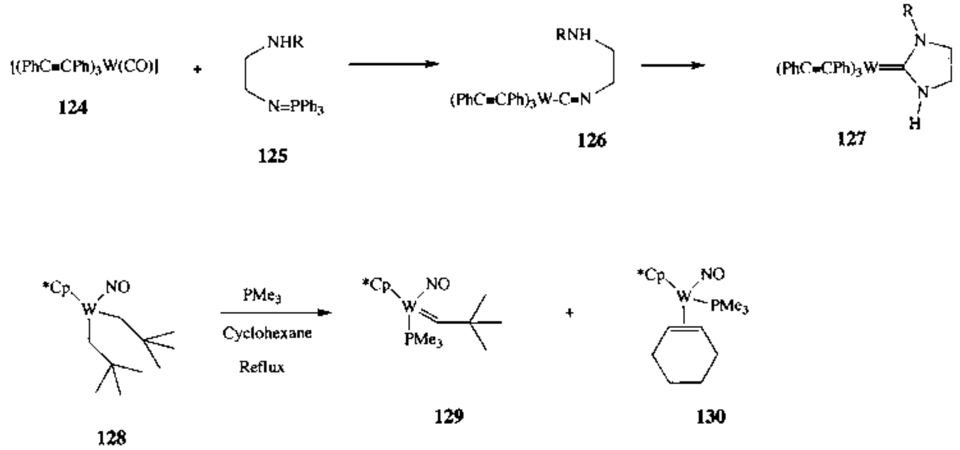
The chalcogen exchange reaction of molybdenum and tungsten ketenylidene complexes (**117**, Scheme 24) was studied [123]. The conversion of the carbonyl compound to the selenocarbonyl compound **118** was effected by treatment with triphenylphosphine and selenium. Selenoketenylidene complex **118** was converted to the cationic alkyne complex **119** by treatment with iodomethane. Tungsten–alkylidene complexes were prepared by reaction of the tungsten–rhenium cluster compound **120** with oxygen or nitrous oxide [124]. Reaction with CO and dihydrogen were reported; the major products of these reactions are depicted in Scheme 24. A tungsten carbene linkage was formed during the hydrogenation of ruthenium–tungsten cluster **121** [125].

1.3.3.2. Publications focusing on synthesis of Fischer carbene complexes of Group VI metals. The most common procedure used for the synthesis of Group VI metal–carbene complexes was the Fischer synthesis, which involves coupling of an organolithium reagent with a Group VI metal carbonyl derivative, followed by alkylation of the resulting acylate. New carbene complexes which were synthesized in 1997 by this route include bis(diphenylphosphino)carborane-ligated carbene complexes [126], and bimetallic carbene complexes synthesized from chromium-complexed lithiothiophene [127]. Numerous other carbene complexes were prepared using this synthetic route, however they are discussed in subsequent sections, where the focus of the manuscripts is reactivity and not synthesis.

Other less common procedures for the synthesis of Group VI metal–carbene complexes were reported. The synthesis of carbene complexes employing the coupling of anionic metal–carbonyl derivatives with 1,3-dihalopropane derivatives [128] or thioacyl halides [129] was reported. The diaminocarbene–tungsten complex **127** was prepared from the diphenylacetylene–tungsten complex **124** using phosphinimine **125** (Scheme 25) [130]. This reaction probably involves a Staudinger-type reaction between the phosphimine group and the carbonyl ligand to produce an isocyanide complex (**126**), followed by intramolecular nucleophilic attack by the amine. When the less nucleophilic arylamine was employed, the reaction stopped at the isocyanide complex stage. The diaminocarbene complex **127** was an effective catalyst for the polymerization of diphenylacetylene. Thermolysis of dineopentyltungsten **128** in the presence of trimethylphosphine afforded alkylidene complex **129** and cyclohexene complex **130**, which results activation of a C–H bond of the solvent cyclohexane [131]. Alkylidene complex **129** did not convert to cyclohexene complex **130** upon exposure to refluxing cyclohexane.



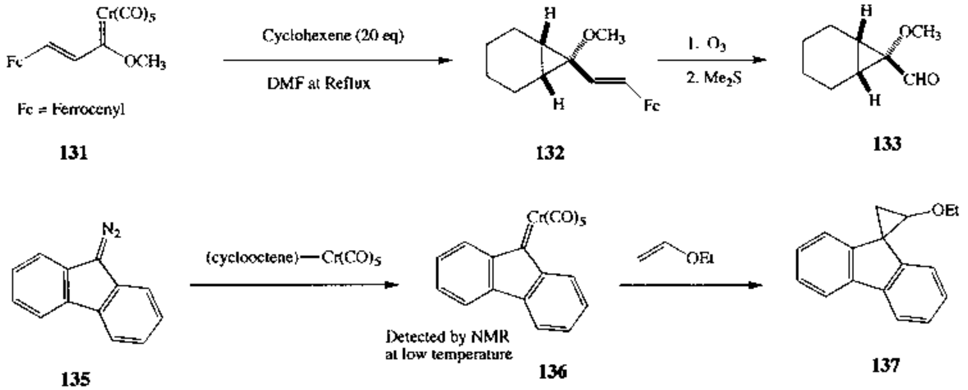
Scheme 24.



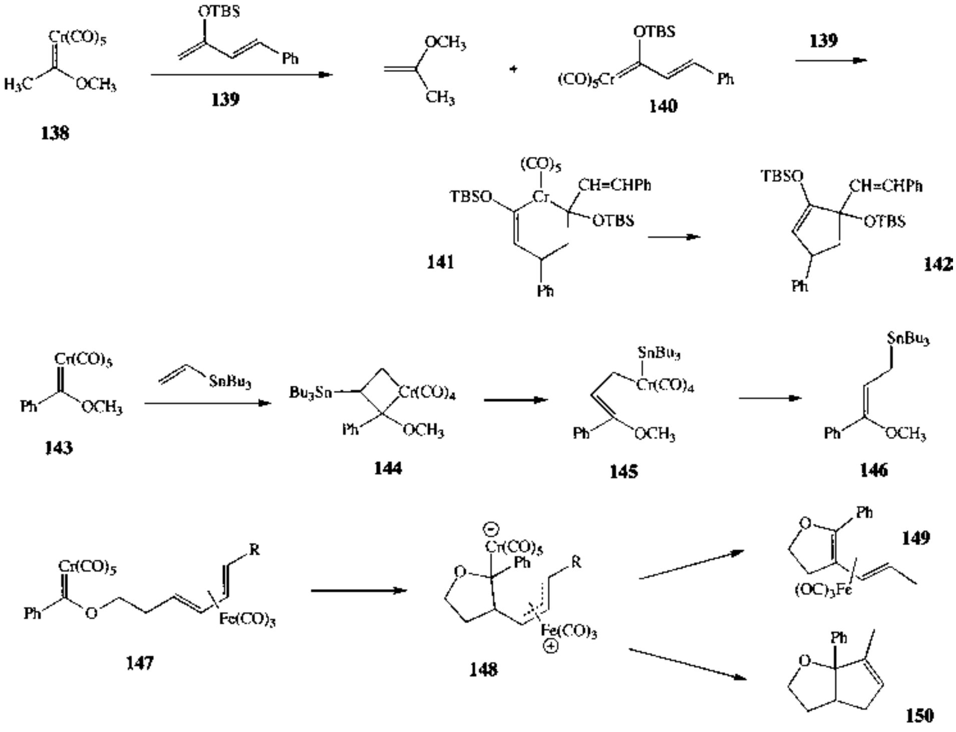
Scheme 25.

1.3.3.3. Reaction of Group VI metal–carbene complexes with alkenes and dienes. This section focuses on reactions of Group VI metal–carbene complexes which involvd coupling at the carbene-carbon. Other examples of the coupling of carbene complexes with alkenes where the reactive site is elsewhere can be found under the heading: cycloaddition reactions occurring at the C–C π-bond of α,β-unsaturated metal–carbene complexes.

Cyclopropanation is a common reaction pathway for the coupling of Fischer carbene complexes with polarized alkenes. Successful cyclopropanation of unactivated alkenes was achieved using the ferrocenylvinylcarbene–chromium complex **131** (Scheme 26) [132]. The cyclopropanation of cyclohexene required a 20-fold molar excess of cyclohexene; the reaction was conducted in refluxing DMF. In cases involving monosubstituted alkenes or *cis* 1,2-disubstituted alkenes, the cyclopropane stereoisomer where the methoxy group and the original alkene substituents



Scheme 26.



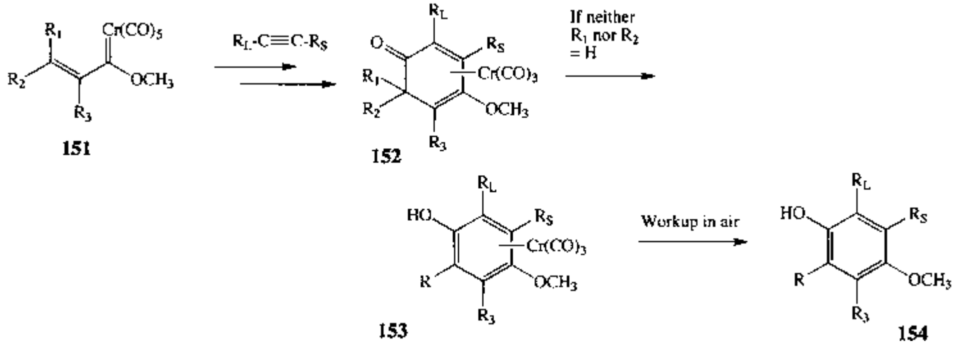
Scheme 27.

are cis was produced with a high degree of stereoselectivity. Ozonolysis readily converted the ferrocenylvinyl group into an aldehyde (**134**). Chromium–carbene complex intermediates can be generated from the reaction of organic diazo compounds with pentacarbonylchromium–alkene complexes [133]. The ^{13}C-NMR spectrum revealed evidence for the carbene complex **136**; a peak at δ 360 was observed upon mixing the chromium–alkene complex and diazo compound at low temperature. When generated in the presence of electron-rich alkenes, these carbene complexes afforded cyclopropanation products (**137**). Reaction of acetoxycarbene complexes with silyloxydienes afforded products resulting from selective cyclopropanation of the enol ether functionality [134].

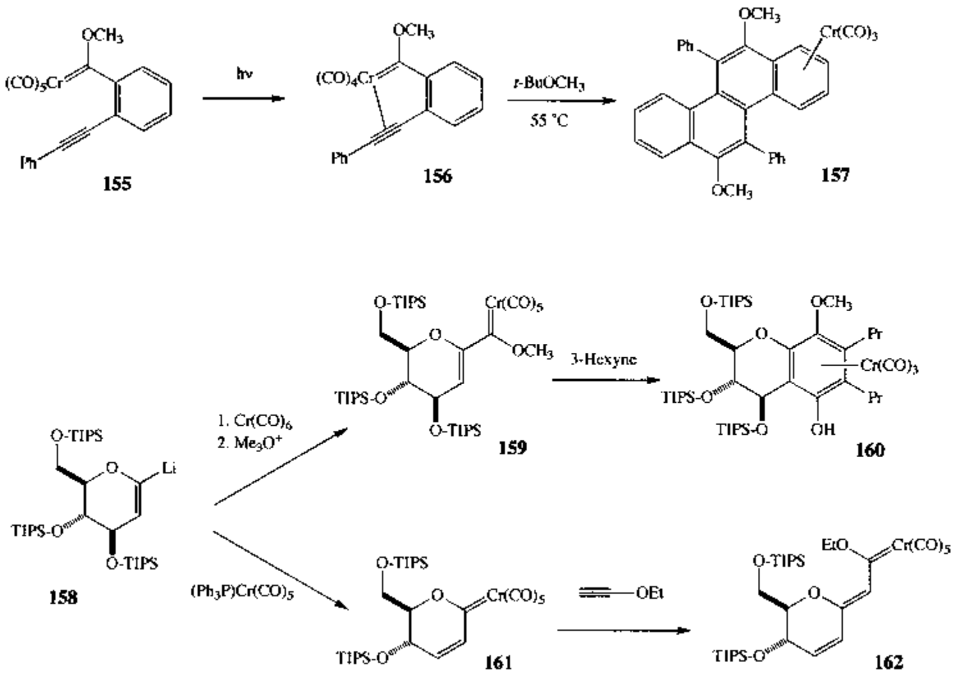
More complex reaction pathways were commonly observed for the coupling of Fischer carbene complexes with alkenes (Scheme 27). A novel five-membered ring-forming dimerization reaction (resulting in cyclopentenone **142**) was observed in the coupling of Fischer carbene complexes with siloxydiene derivatives [135]. A mechanism was proposed involving formation of alkenylcarbene complex **140** through alkene metathesis, followed by formation of metallacyclohexene **140** via [4 + 2]-cycloaddition involving the chromadiene as the four carbon component and the enol ether double bond of the diene as the two carbon component, followed by reductive elimination. The reaction of Fischer carbene complexes with vinylstannanes and vinylgermanes afforded enol ether–allylstannanes (or germanes) (**146**) in moderate-good yield [136]. Based on deuterium-labeling studies, a mechanism involving [2 + 2]-cycloaddition, followed by β-metal elimination, followed by reductive elimination, was proposed. The intramolecular reaction of chromium carbene complexes with diene–iron tricarbonyl complexes was studied [137]. Five-membered ring oxygen heterocycles were produced in this reaction. A mechanism involving electrophilic attack at the coordinated diene, followed by either β-hydride elimination (if R = H) or ring closure (if $R = CH_3$) was proposed.

1.3.3.4. Reaction of Group VI metal–carbene complexes with alkynes-benzannulation. Many examples of benzannulation using α,β-unsaturated chromium–carbene complexes and alkynes (commonly known as the Dötz reaction) were reported in 1997. The general reaction equation is depicted in Scheme 28. Examples include: (1) stereoselective benzannulations using chiral auxiliary-containing phenyl- and alkenylcarbene complexes [138], (2) stereoselective cyclohexadienone annulations using alkenylcarbene–chromium complexes and propargylic alcohol derivatives [139], (3) stereoselective benzannulations involving atropoisomeric 2-indolylcarbene complexes [140], (4) synthesis of 5,8-quinolinedione derivatives using benzannulation reactions of dihydropyridylcarbene complexes [141], and (5) synthesis of the insecticide parvaquone using the benzannulation reaction between an arylcarbene complex and ethynylcyclohexane [142].

Additional detailed studies of the of the chromium carbene–benzannulation reaction were also reported (Scheme 29). Photolysis of *ortho*-alkynylcarbene complex **155** afforded the alkyne–carbene complex **156**, which was stable enough for spectroscopic characterization [143]. Thermolysis of **156** in refluxing methyl *t*-butyl ether led to the chrysene derivative **157** (a single diastereomer), which results from an unusual benzannulative dimerization reaction. Direct thermolysis of the nonchelated carbene complex afforded predominantly carbene dimerization products [144]. Benzannulation of carbohydrate-templated chromium carbene complexes was also investigated [145]. A normal benzannulation reaction was observed when cyclohexenylcarbene derivative **159** was treated with 3-hexyne. Carbene complex **161**, which is frozen in the s-trans conformation, was prepared by a novel synthetic route utilizing from alkenyllithium reagent **158** and the triphenylphosphine(pen-



Scheme 28.

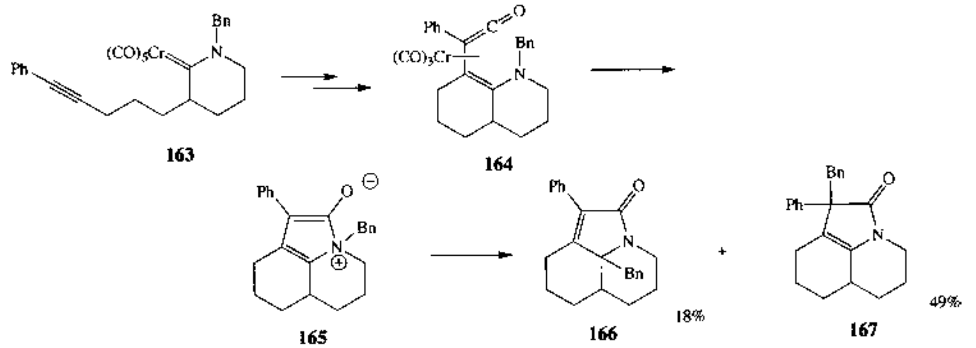


Scheme 29.

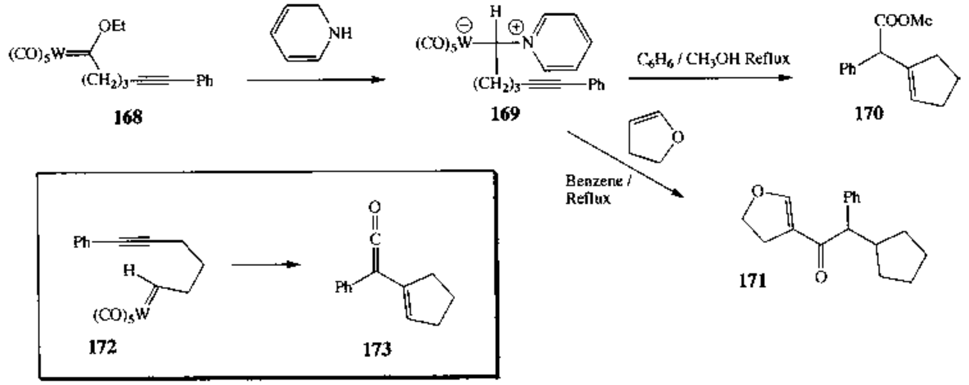
tacarbonyl)–chromium (0) complex. The reaction of the carbene complex **161** with ethoxyacetylene afforded the stable carbene complex **162**, which represents a net chain extension of the carbohydrate derivative.

1.3.3.5. Nonbenzannulation reactions of Group VI metal–carbene complexes with alkynes. A common reaction pathway in the coupling of carbene complexes with alkynes is the formation of a vinylketene intermediate (**164**, Scheme 30), followed by the trapping of the ketene with a nucleophile [146]. Several examples of this general class of reactions were reported in 1997 including: (1) intramolecular alkyne-amiocarbene complex (**163**) coupling, resulting in pyrrolidone derivatives (**165** and **166**) after alkyl shift processes, (2) coupling of propargyl alcohols with carbene complexes, resulting in β-lactone derivatives [147], and intramolecular trapping by enol derivatives, resulting in cyclopentanone derivatives [148].

The intramolecular coupling of dihydropyridine–carbene complex adducts (**169**, Scheme 31) and alkynes was investigated [149]. These adducts, which serve as a source of nonheteroatom-stabilized Fischer carbenes (**172**), upon thermolysis produced predominantly ester **170** (and the conjugated double bond isomer), which is the methanol-trapping product of ketene **173**. Thermolysis in the presence of dihydrofuran afforded unsaturated ketone **171** as the major product. The authors proposed a mechanism involving tungsten-induced oxidative ligand coupling of dihydrofuran and ketene **173**, followed by a β-hydride elimination–reductive elimination sequence.

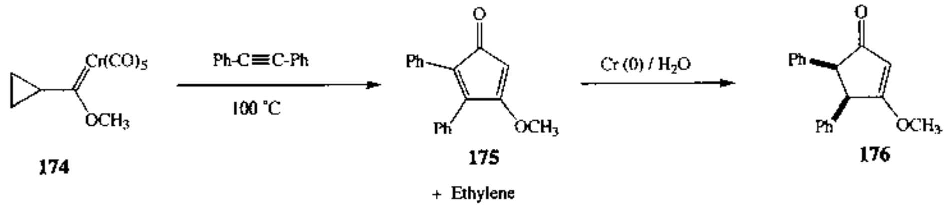


Scheme 30.



Scheme 31.

The cyclopentannulation reaction of the cyclopropylcarbene–chromium complex **174** (Scheme 32) and diphenylacetylene was investigated further using solvents of extreme polarity difference [150]. When the reaction was conducted in hexane, cyclopentadienone **175** was the exclusive product of the reaction species. When the reaction was conducted in a 1:1 dioxane:water mixture, the reduction product, cyclopentenone **176**, was obtained. An electron-transfer mechanism was proposed for the reduction, which is suppressed is the less polar solvent hexane.

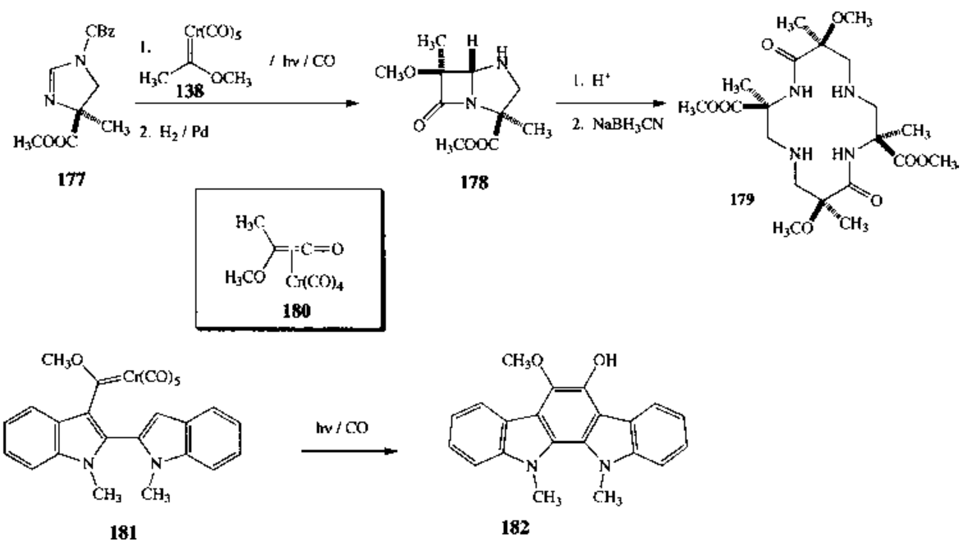


Scheme 32.

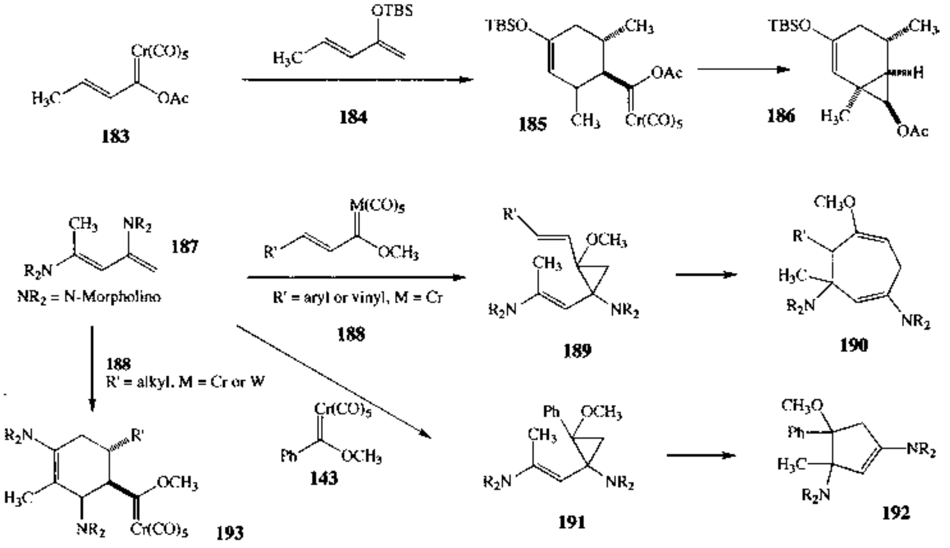
1.3.3.6. Photolysis reactions of Group VI metal–carbene complexes. Several publications concerning the formation of chromium ketene complexes (**180**, Scheme 33) through photolysis of Fischer carbene–chromium complexes appeared in 1997. Photolytic coupling of imine **177** with methylcarbene complex **138** afforded the β-lactam derivative **178** with a very high degree of stereoselectivity, which was converted to cyclam **179** by treatment with camphorsulfonic acid and sodium cyanoborohydride [151]. The formation of optically active activated ester derivatives through the photochemically-induced coupling of optically active chromium carbene complexes and chlorinated phenol derivatives was described [152]. The synthesis and photolytic reactions of α-alkoxycarbene–chromium complexes was described [153]. The requisite carbene complexes could only be synthesized via the chromium pentacarbonyl dianion route; the Fischer route using alkoxymethyllithium derivatives failed. Successful cycloaddition with enamide derivatives was achieved using a DMF + carbazole solution as a filter. Indolocarbazoles (**182**) were produced in the photolysis of biindolecarbene derivative **181** [154].

A detailed mechanistic study of photolytic reactions of Fischer carbene complexes was reported [155]. The study suggests that conversion of the carbene complex to the coordinated ketene (**138** → **180**) could not occur by excitation into the metal–ligand charge transfer band, as was proposed previously. Excitation into the low energy ligand field excited state band was suggested as the primary source of the ketene intermediate.

1.3.3.7. Reactions occurring at the conjugated C–C π-bond of α,β-unsaturated Group VI metal–carbene complexes. Numerous reaction processes where a carbene complex activates a π-bond for nucleophilic addition or cycloaddition reactions (i.e. the



Scheme 33.



Scheme 34.

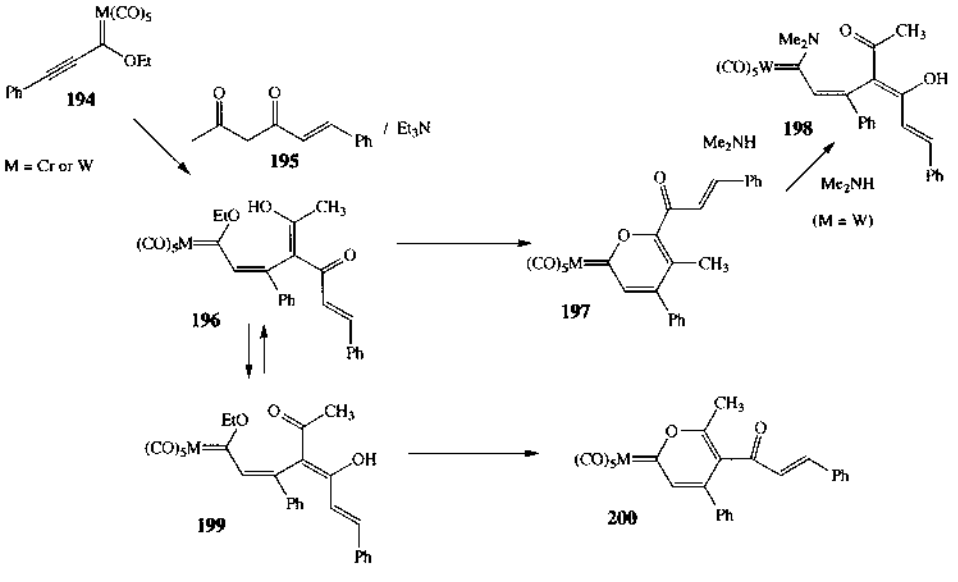
carbene complex is a surrogate for an activated ester) were reported in 1997. The following reaction processes, in which the carbene complex functionality survives the reaction, were reported for α,β-unsaturated Group VI metal–carbene complexes: (1) synthesis of chiral cyclopropylcarbene complexes through Michael addition of iodomethyllithium to chiral and enantiomerically-pure α,β-unsaturated carbene complexes [156], (2) formation of cyclic and open-chain phosphine derivatives through Michael addition of vinylphosphide anions to alkenylcarbene–tungsten complexes [157], (3) the Diels–Alder reaction involving alkenylcarbene–tungsten complexes and 2-amino-1,3-dienes [158,159], (4) the exo-selective Diels–Alder reaction involving chiral alkenylcarbene complexes [160], (5) the Diels–Alder reaction of 2-azadienes with alkenylcarbene–tungsten complexes [161], (6) the stereoselective 1,3-dipolar addition reaction involving diazo compounds and chiral and enantiomerically pure α,β-unsaturated Fischer carbene complexes [162], and (7) the Pauson–Khand reaction of enynes tethered through carbene complexes [163,164].

In many cases, the reaction of 1,3-dienes and alkenylcarbene complexes produced other compounds in addition to simple Diels–Alder adducts (Scheme 34). The reaction of acetoxycarbene **183** and 2-silyloxydienes afforded bicyclo[4.1.0]heptane derivatives (**186**) [165]. A mechanism involving the Diels–Alder reaction followed by intramolecular C–H insertion was proposed. The competition between direct the Diels–Alder reaction and reactions occurring at the carbene carbon was a feature of cycloaddition reactions involving dienamine **187** and various α,β-unsaturated

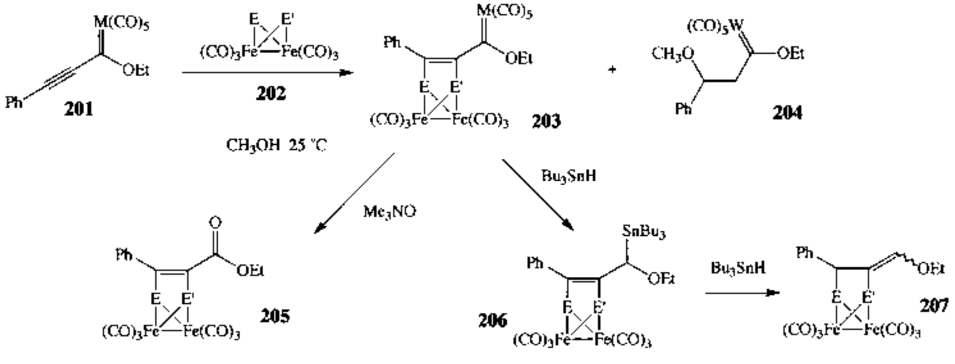
Fischer carbene complexes [166]. Arylvinylcarbene–chromium complexes afforded seven-membered rings (**190**) via a cyclopropanation–divinylcyclopropane rearrangement sequence. The reaction of the diene with the arylcarbene–chromium complex **143** afforded cyclopentane derivatives (**192**) via a cyclopropanation–vinylcyclopropane rearrangement sequence. Alkylvinylcarbene–chromium and tungsten carbene complexes afforded primarily Diels–Alder products (**193**). Other reactions involving the coupling of 1,3-dienes with α,β-unsaturated carbene complexes also feature competition between the Diels–Alder and carbene addition (or other) pathways, including: (1) the coupling of 2-azadienes with various types of α,β-unsaturated carbene complexes [167], and (2) the coupling of 1-azadienes with alkynylcarbene–chromium complexes [168,169].

Reaction of alkynylcarbene–chromium and tungsten complexes with 1,3-diketone enolates afforded pyranylidene complexes (**197** and **200**, Scheme 35) [170]. A mechanism involving Michael addition followed by heterocyclic ring closure was proposed. The major isomer was that where the oxygen of the alkenyl-substituted carbonyl group is attached to the carbene carbon. Aminolysis afforded ring-opened aminocarbene complex **198**. Similar studies involving Michael additions of enamines to alkynylcarbene complexes were reported also [171].

The unusual cycloaddition reaction between iron-bridging chalcogenide complexes (**202**, E, E′ = S, Se or Te, Scheme 36) and alkynylcarbene–chromium and



Scheme 35.



Scheme 36.

–tungsten complexes was studied [172,173]. Fischer carbene bridging-diiron complexes (**203**) were obtained from this reaction, accompanied by the β-methoxycarbene complex **204** formed from Michael addition of the solvent, methanol. The reaction was regioselective for formation of the product where the lower molecular weight chalcogen was in the β-position. Treatment of the complexes with trimethylamine-N-oxide afforded the corresponding ester **205**; no cleavage of the diiron unit occurred under these conditions. Reduction with tributyltin hydride in the presence of pyridine afforded enol ether derivatives (**207**) by way of the anticipated allylstannane derivative **206** [174]. The allylstannane could be isolated if only one equivalent of tributyltin hydride was used, however, only the enol ethers were observed when excess tributyltin hydride was used. Tributyltin hydride induced the conversion of the allylstannane to the enol ether.

1.3.3.8. Physical organic chemistry of Group VI Fischer carbene complexes. The thermodynamic and kinetic acidity of various Fischer carbene complexes was determined in 50:50 water:acetonitrile; the experimentally-determined pK_a values are listed in Fig. 4. Comparisons of cyclic vs noncyclic carbene complexes [175], the effect of alkyl substitution [176], and the effect of metal, phenyl substitution, and alkoxy group [177] were emphasized in these studies.

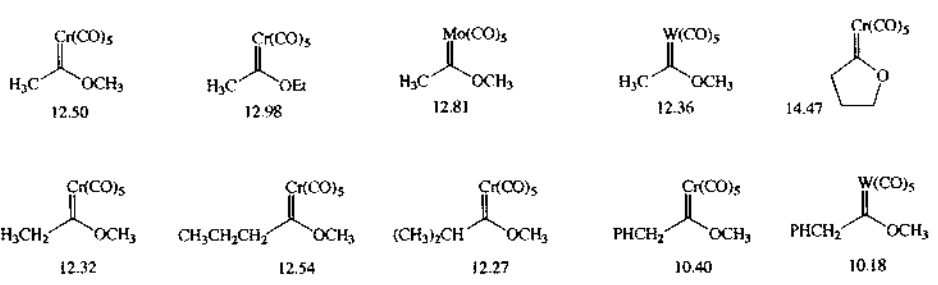
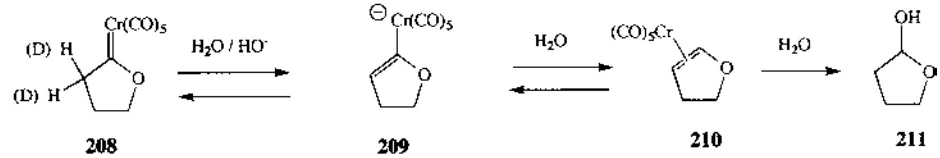


Fig. 4. Experimentally-determined pK_a values for Fischer carbene complexes.

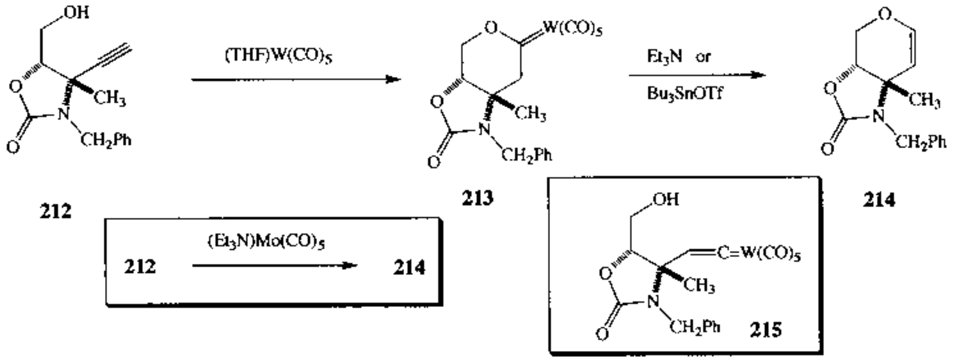


Scheme 37.

A detailed mechanistic study of the hydrolysis of Fischer carbene complexes, which produces aldehydes, was conducted [178,179]. The mechanism depicted in Scheme 37 was proposed for the hydrolysis of carbene complexes which contain α-hydrogens (**208**). The following observations supported this mechanism: (1) the reaction is base-catalyzed, and (2) there is a large deuterium isotope effect (deuterium in the α-position). A mechanism involving direct attack of hydroxide ion at the carbene carbon was proposed for carbene complexes which do not have α-hydrogens.

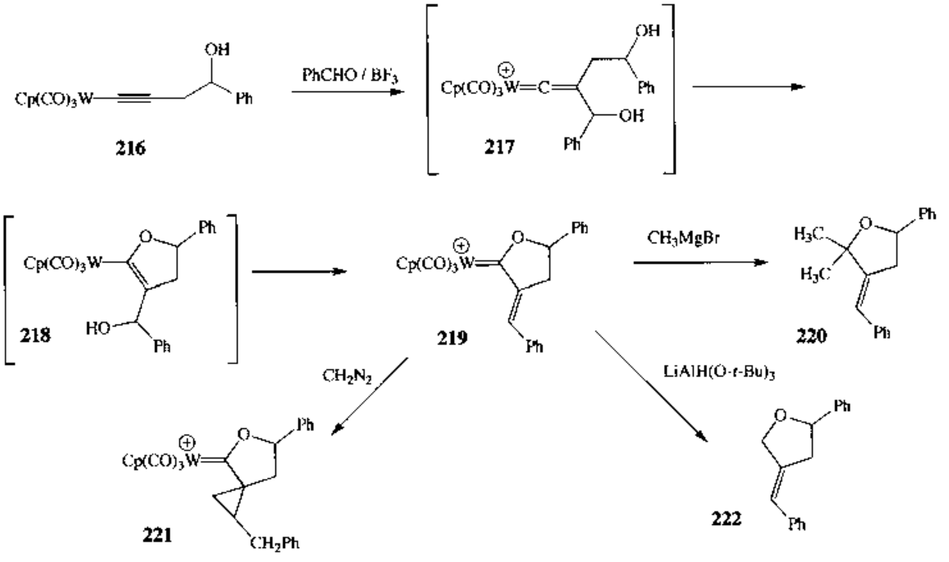
Other studies emphasizing structural aspects of Group VI metal–carbene complexes were reported in 1997. The synthesis and chiroptical properties of *m*-cyclophane-substituted carbene complexes [180] and binapthyl-substituted carbene and (bis)carbene complexes [181] were reported. A theoretical study comparing the electronic distribution of alkoxycarbene–chromium and aminocarbene–chromium complexes was conducted [182]. For alkoxycarbene complexes, the π-electrons of the Cr–C–O were described as a three-center, four-electron bond with most of the electron density at the d_{yz} orbital of chromium and the p_z orbital at O. For aminocarbene complexes, the π-bond character was delocalized towards the *trans*-carbonyl ligand.

1.3.3.9. Synthesis and reactivity of Group VI metal–vinylidene complexes, and reactions which involve vinylidene-metal complexes as intermediates. Many examples of the coupling of alkynols with Group VI metal pentacarbonyl sources were reported in 1997. The general reaction pathway followed in these couplings is conversion of the alkyne to a metal–vinylidene complex, followed by intramolecular nucleophilic attack of the alcohol at the carbene carbon to generate a Fischer carbene complex. The conversion of alkynol **212** (Scheme 38) to glycal derivative **214** could be accomplished by treatment of alkynol **212** with the pentacarbonylmolybdenum–THF complex [183]. Alternatively, a two-step sequence was deomnstrated, which involved conversion of alkynyl **212** to stable the tungsten–carbene complex **213**, followed by treatment of the carbene complex with either triethylamine or tributyltin triflate. Similar processes were employed for the construction of other heterocyclic rings, including pyrroles and tetrahydropyridines [184]. Cyclopentene rings were formed by a similar route using an intramolecular attack by malonate derivatives as the ring-forming step [185]. The reaction of bis(propargylic alcohol) derivatives with tungsten pentacarbonyl–THF and methanol led to the formation of the expected bis(alkenylcarbene)complexes [186]. Similar chromium–vinylidene intermediates could also be trapped via [2 + 2]-cycloaddition reactions with enamine derivatives [187].

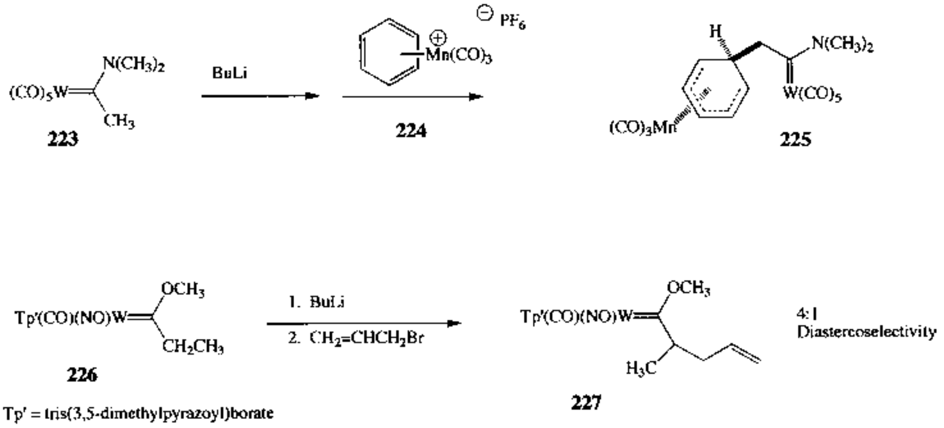


Scheme 38.

Group VI metal–vinylidene complexes were also generated via electrophilic attack on alkynyl-metal complexes at the β-position. A variety of bimetallic tungsten–vinylidene complexes were prepared from the reaction of anionic alkynyl–tungsten complexes with electrophilic alkene– and polyene–metal complexes [188]. Cyclic Fischer carbene complexes (**219**, Scheme 39) were prepared from the coupling of homopropargyl alcohol–tungsten complexes (**216**) with aldehydes and Lewis acids [189]. A mechanism involving electrophilic attack of the activated aldehyde at the β-carbon of the alkyne complex, forming the cationic vinylidene complex **217**, followed by nucleophilic attack of the alcohol at the carbene carbon and elimination was proposed. These carbene complexes underwent



Scheme 39.



Scheme 40.

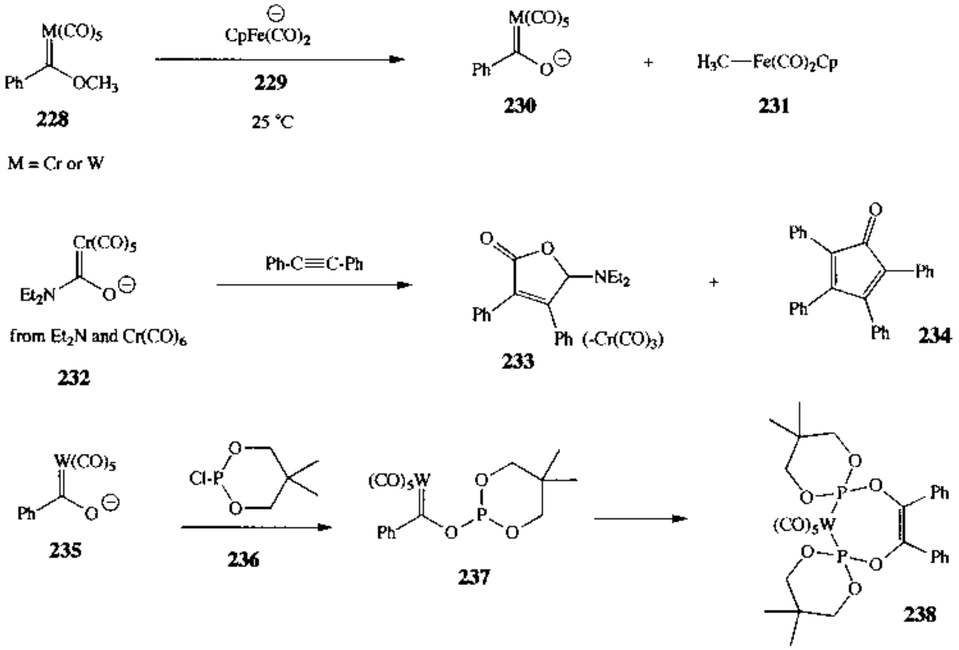
a variety of synthetically-useful transformations, including reduction by hydride reducing agents, alkylation by Grignard reagents, and cyclopropanation, sometimes accompanied by double-methylene insertion products (**221**). Tungsten–vinylidene complexes were proposed as intermediates in the reaction of anionic alkynyltungsten complexes and allylic halides [190].

1.3.3.10. Reaction involving carbanions derived from Group VI metal–carbene complexes. Several examples of reactions which involve deprotonation of a Group VI Fischer carbene complex at the α-position, followed by reaction with an electrophile were reported in 1997 (Scheme 40). Heterobimetallic compounds were prepared from the reaction of carbene complex anions with cationic polyene–metal complexes (**224**) [191]. Other electrophiles studied include phosphorus electrophiles[192], α-bromoglycine derivatives [193], fumaryl chloride [194], and pyrylium salts [195]. Generation and electrophilic trapping reactions for γ-carbanions of α,β-unsaturated carbene complexes were reported also [196]. The diastereoselectivity of the reaction of carbanions derived from chiral Fischer carbene complexes (**226**) and alkyl halides was examined [197]. Deprotonation of ethylcarbene complex **226** followed by allyl bromide afforded the anticipated allylated carbene complex **227** as a 4:1 mixture of diastereomers. The opposite diastereomeric ratio was obtained through deprotonation of the 3-butenylcarbene analog of complex **226** followed by methylation.

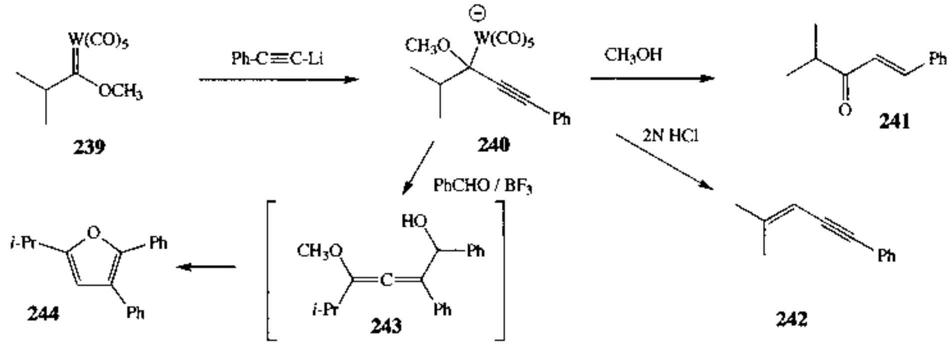
1.3.3.11. Reactions involving Group VI metal–acylate anions or iminoacyl anions. Treatment of Group VI Fischer carbene complexes with various anionic organometallics (**229**, Scheme 41) resulted in a dealkylation reaction, affording the acylate complex **230** [198]. Of the monoanions tested, anion **229** was the most reactive ($t_{1/2}$ = a few seconds at 25°C). The reaction of aminoacylate chromium complex **232** (generated in situ from the coupling of lithioamides and chromium hexacarbonyl) with diphenylacetylene afforded the arene-complexed and uncomplexed amino-furanone derivatives **233**, and minor amounts of tetraphenylcyclopentadienone (**234**) [199]. A mechanism involving alkyne insertion and carbonyl insertion, producing a vinylketene complex, was proposed. The reaction with phenylacetylene was considerably more complex.

The reaction of tungsten acylates (**235**) with phosphorus chlorides was investigated [200]. The anticipated phosphoroxycarbene complex **236** could not be isolated but was observed by NMR. The carbene dimerization product **238** was the exclusive product when aryl complexes were employed. Hydrogen shift processes were competitive with the formation of **238** when acylate complexes containing α-hydrogens were used. Stable *N*-phosphorus-substituted carbene complexes analogous to **237** were obtained by treatment of nitrogen analogs of complex **235** with phosphorus chlorides [201]. Reaction of molybdenum acylates with boron trifluoride etherate was also conducted; the major products in this case were also dimeric [202].

1.3.3.12. Other reactions of Group VI metal–carbene complexes. New reaction processes for anionic propargyl–tungsten complexes (**240**, Scheme 42), which were derived from the addition of alkynyl anions to Fischer carbene complexes (**239**), were investigated [203,204]. If the complex was simply allowed to warm to 25°C, the α,β-unsaturated ketone **241** was obtained via an allene intermediate. Treatment of propargyl compound **240** with 2 M HCl afforded the enyne derivative **242**.



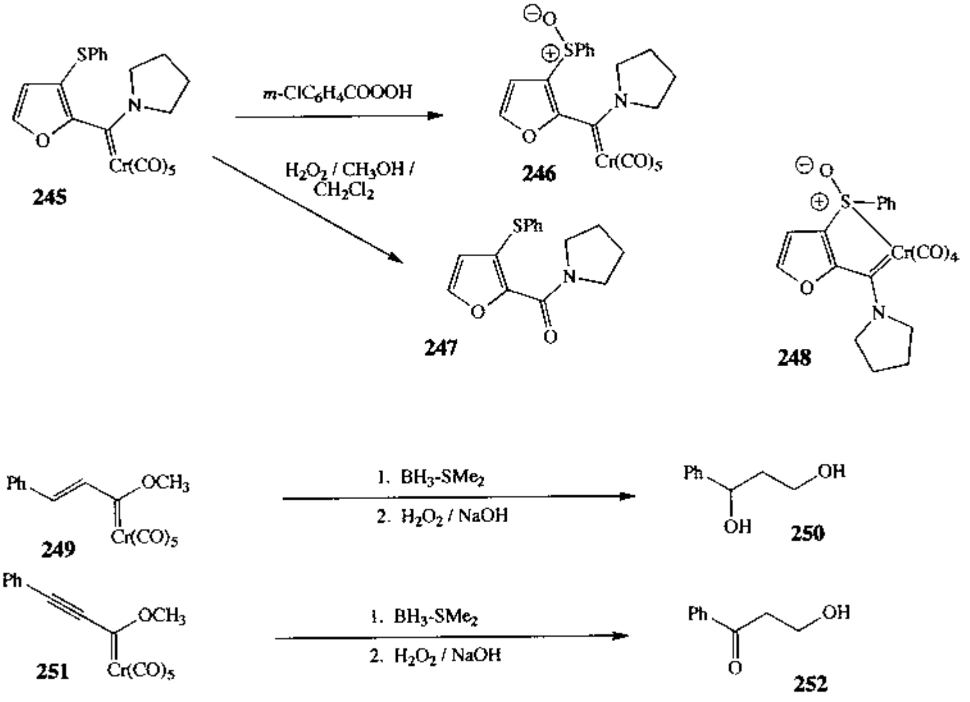
Scheme 41.



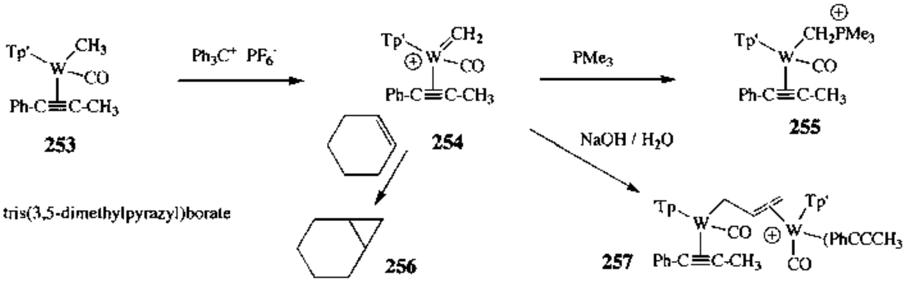
Scheme 42.

Reaction with aldehydes and Lewis acids afforded furan derivatives (**244**). A mechanism involving electrophilic attack at the γ-position, forming the allene **243** followed by acid-catalyzed ring-closure was proposed. This methodology was used as the cornerstone for the total synthesis of the antibiotic PI-091 [205].

Reactions of Group VI metal–carbene complexes with oxidizing or reducing agents were reported in 1997. Oxidation of sulfide-containing aminocarbene com-



Scheme 43.



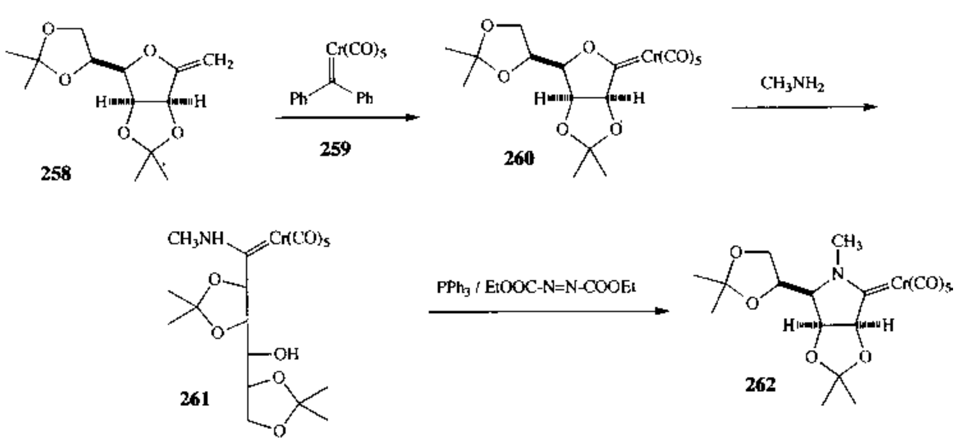
Scheme 44.

plex **245** (Scheme 43) with mCPBA led to the sulfoxide-substituted aminocarbene complex **246** in 100% yield [206]. Oxidation with hydrogen peroxide afforded a mixture of the corresponding amide **247** and the sulfur-coordinated carbene complex **248**. The iodine oxidation chemistry of diheteroatom-stabilized carbene complexes was also studied [207]. A series of bimetallic Group VI metal–carbene complexes were converted to the corresponding tellurone complexes upon treatment with tellurium metal [208]. Hydroboration-oxidation of alkenylcarbene of complexes (**249**) afforded 1,3-diols (**250**) [209]. The analogous reaction using alkynylcarbene complex **251** led to the β-ketoalcohol **252**.

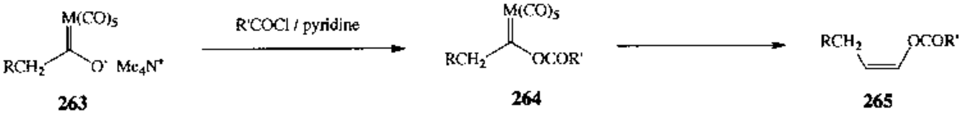
Several studies of the synthesis and reactivity of methylene–tungsten complex **254** (Scheme 44) were reported in 1997. Stable cationic carbene–alkyne complex **254** was produced via hydride abstraction from the alkyl–tungsten complex **253** [210,211]. The reaction with trimethylphosphine afforded the phosphonium salt **255**; a similar reaction process was observed with other nucleophiles. The carbene complex **254** was an effective reagent for the cyclopropanation of a variety of nonpolarized alkenes, including cyclohexene and various styrene derivatives, and was also an effective catalyst for aziridination reactions between imines and ethyl diazoacetate. The unusual dimerization product **257** was isolated in low yield upon treatment of complex **254** with base [212]. The extra carbon is thought to arise from an ethylene complex formed as a result of carbene dimerization.

Synthesis and aminolysis of a variety of carbohydrate-derived carbene complexes was reported in 1997. Carbene complex **260** (Scheme 45) was prepared from methylenetetrahydrofuran **258** by an alkene metathesis route [213]. A net conversion of the oxygen heterocycle **260** to the nitrogen heterocycle **262** was effected by the sequence of aminolysis-ring opening followed by a Mitsonobu-type ring closure process. Other examples utilizing carbene complexes for carbohydrate synthesis included a three-carbon chain extension process based on the conversion of homopropargyl alcohols to cyclic carbene complexes [214], and preparation and aminolysis of iron–, chromium–, molybdenum–, and tungsten–alkoxycarbene complexes derived from aldonic acid chloride derivatives and the corresponding metal carbonyl dianions [215].

Decomposition reactions of acyloxycarbene complex **264** (Scheme 46) were studied [216]. In most cases, enol ester **265** was the major organic product in good–moderate yield; optimal yields were obtained when pyridine was an additive. Primarily the *Z* isomer was obtained in this reaction.

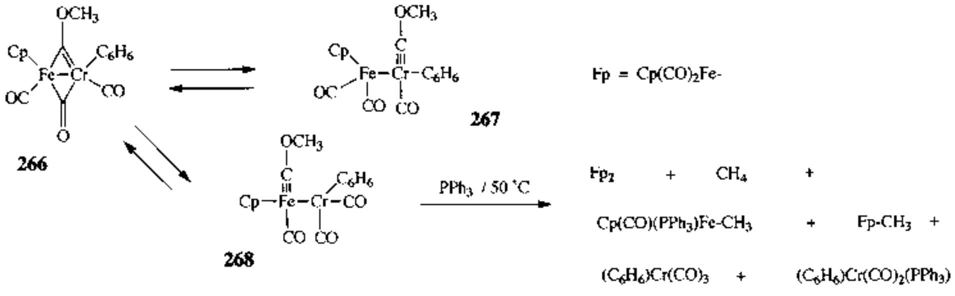


Scheme 45.



Scheme 46.

The mechanism for the decomposition of heterobimetallic-Fischer carbene complex **266** (Scheme 47) was studied [217]. The complex undergoes a *cis–trans* stereochemical isomerization in competition with a decomposition reaction. A mechanism involving reversible interconversion of the bridging carbene complex and nonbridging carbyne complexes was proposed for the isomerization and decomposition processes. The decomposition was proposed to arise from iron carbyne complex **268**, while the stereochemical isomerization was proposed to arise from the chromium carbyne complex **267**.



Scheme 47.

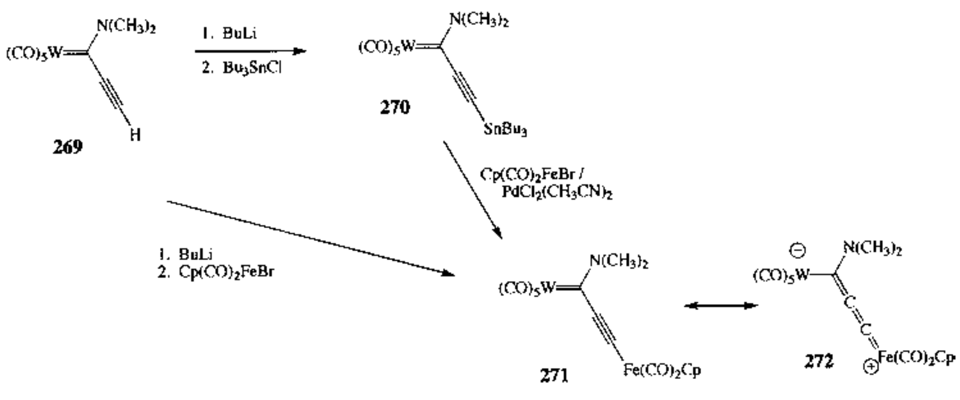
A series of bimetallic carbene complexes (**271**, Scheme 48) were prepared via the coupling of anions derived from alkynyl–aminocarbene complexes (**269**) [218]. Substantial contribution from the vinylidene resonance form **272** was noticed based upon the infrared and NMR spectra of the complexes. These carbene complexes could also be prepared by direct palladium-catalyzed reaction of the stannylakynylcarbene complex **270** with metal halides. The analogous compound containing an extra alkyne group were prepared in a similar manner [219].

1.3.4. Group VII metal–carbene complexes

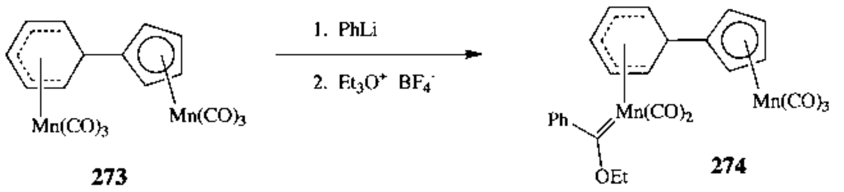
The new Group VII metal–carbene complexes were prepared according to the Fischer synthetic route (see Section 1.3.3.2) involving group VII metal carbonyl derivatives and organolithium reagents. A heterobimetallic rhenium–carbene complex was prepared from chromium–complexed lithiothiophene using this synthetic route [220]. Trimetallic alkynylcarbene–rhenium complexes were prepared from the reaction of ruthenium-substituted alkynyllithium reagent using various dimetal carbonyl derivatives [221]. The formation of a carbene complex from the dimanganese carbonyl complex **273** (Scheme 49) afforded only the monocarbene complex **274** regardless of the amount of organolithium reagent employed [222]. Exclusive reaction at the manganese carbonyl complexed to the open-chain pentadienyl ligand was observed. A manganese–carbene complex intermediate was postulated as an intermediate in a failed Fisher-type synthesis using a 2-(2-pyridylphenyl)manganese carbonyl complex [223].

The dicationic (π-allyl)carbene–rhenium complex **278** (Scheme 50) was prepared from the coupling of complex **275** with (2-vinylphenyl)diphenylphosphine in the presence of silver tetrafluoroborate [224]. A mechanism involving oxidative ligand coupling of the alkyne and alkene chelate, affording metallacyclopentene **277**, followed by deprotonation and σ–π allyl interconversion was proposed.

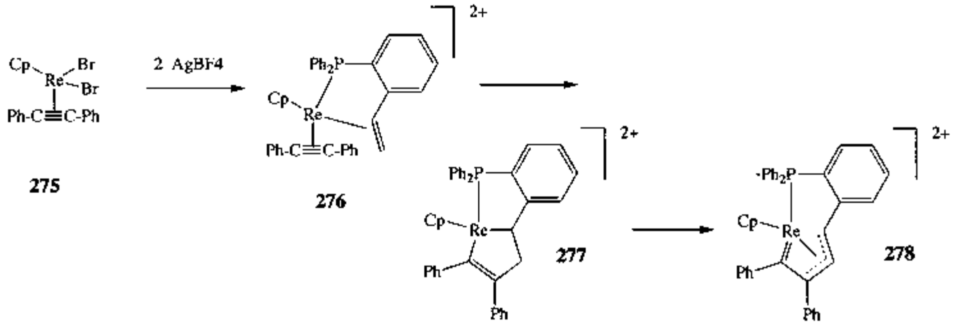
The synthesis and reactivity of cyclopentadienyl-tethered rhenium–carbene complexes was investigated (Scheme 51) [225]. Unlike untethered rhenium–hydroxycar-



Scheme 48.

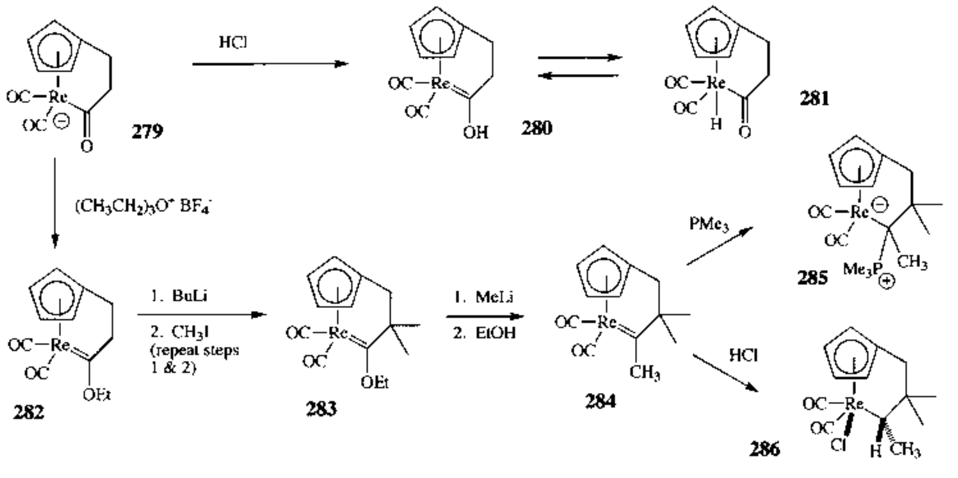


Scheme 49.



Scheme 50.

bene complexes, complex **280** was in equilibrium with the hydrido-acyl complex **281**. The position of equilibrium was solvent dependent; hydroxycarbene **280** was favored in THF or methanol, while the hydrido-acyl complex **281** was favored in acetone. If the tether was lengthened by one methylene unit, the hydroxycarbene complex was the only species at equilibrium, regardless of the solvent. The unusual



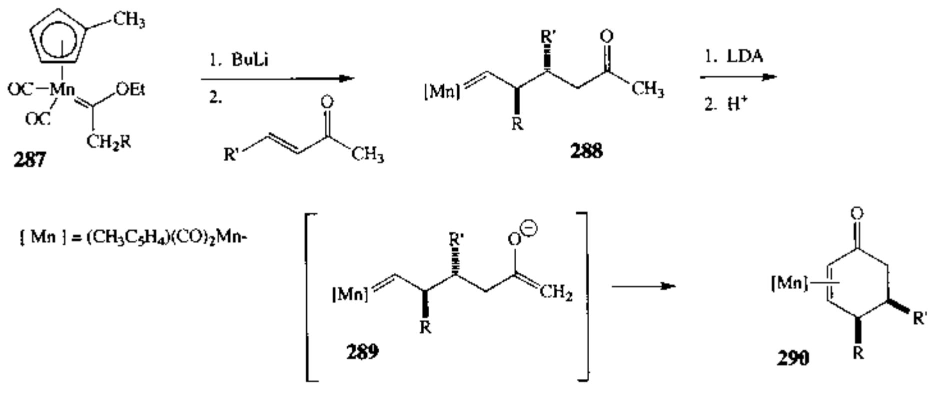
Scheme 51.

equilibrium effect noted for carbene complex **280** was attributed to deviation from the ideal 3-legged piano stool geometry due to the tether. Tethered carbene complex **282** was converted to the corresponding nonheteroatom-stabilized carbene complex **284**, which was reactive to both electrophiles and nucleophiles (amphiphilic) [226]. Reaction with trimethylphosphine afforded the phosphonium salt **285**. Reaction with HCl led to complex **286**, in which HCl added to the carbon–rhenium double bond in a *syn* fashion.

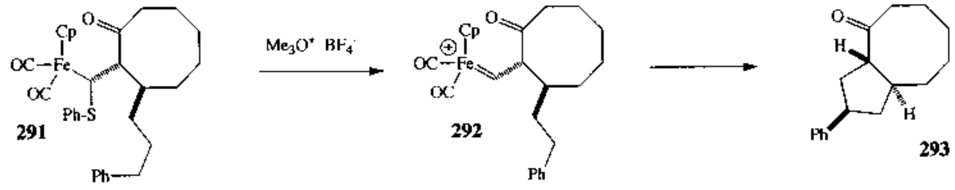
Michael addition reactions of carbanions derived from the manganese carbene complex **287** were investigated (Scheme 52) [227]. When the reaction was conducted at − 78°C, δ-oxocarbene complexes (**288**) were isolated in good yield after protonation; moderate selectivity favoring the ANTI diastereomer was observed in cases where neither R nor R′ is H. If the reaction was warmed to 25°C prior to protonation, the η^2-cyclohexenone complexes (**290**) were produced directly from **287**. Alternatively, treatment of complex **288** with LDA also resulted in the formation of the cyclohexenone complex **290**. A mechanism involving an intramolecular aldol-type reaction of enolate **289** was proposed for the formation of cyclohexenone complexes. Demetallation of the cyclohexenone complex **290** was effected by treatment with either triphenylphosphine or CO at high pressure.

1.3.5. Group VIII metal–carbene complexes

1.3.5.1. Cationic nonheteroatom-substituted metal–carbene complexes which are not cumulenes. A variety of metal–carbene complexes of this class were generated through protonation of alkenyl–metal complexes [228,229], hydride abstraction of alkyl–metal complexes [230], and through elimination reactions [231]. A highly regio- and stereoselective C–H insertion reaction was observed upon generation of the cationic iron–carbene complex **292** (Scheme 53) from the phenylthiomethyliron complex **291.**

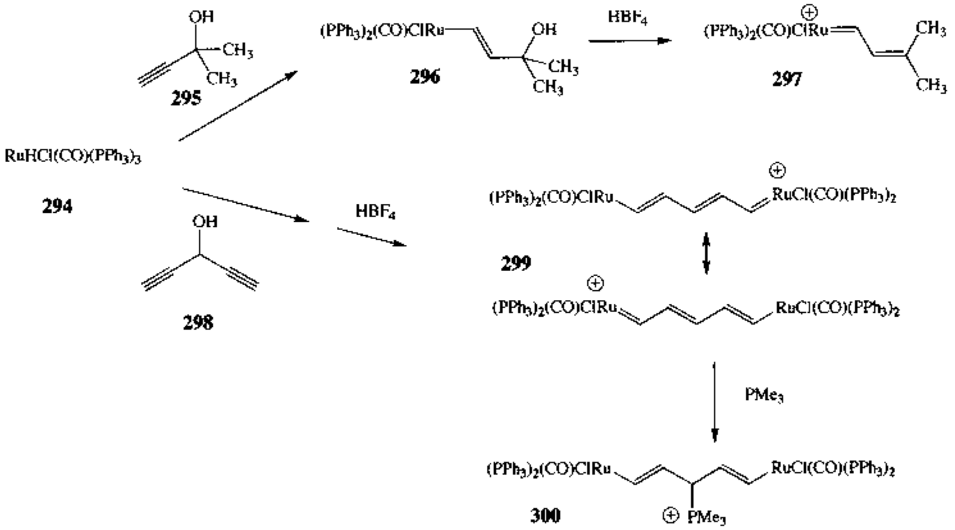


Scheme 52.

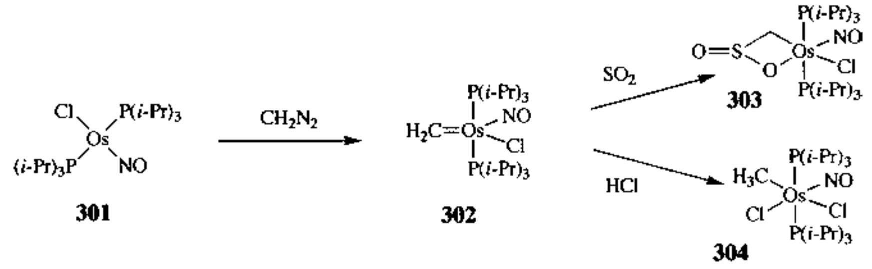


Scheme 53.

Carbene complexes of this class were also generated from propargyl alcohol derivatives using a tandem hydrometallation-elimination sequence (Scheme 54). Coupling of ruthenium hydride **294** with propargyl alcohols (**295**) afforded γ-hydroxy-vinylruthenium complex **296**, which was converted to cationic alkenylcarbene complex **297** by acid-induced elimination [232]. Analogous bimetallic ruthenium carbene complex **299** was prepared from the 2:1 coupling of ruthenium hydride **294** with 1,4-butadiyn-3-ol (**298**) [233]. The resulting alkylideneruthenium–alkenylruthenium complex was completely delocalized. Reaction with trimethylphosphine led to the dialkenyl–diruthenium complex **300**; only ligand exchange processes occurred upon reaction with bis(diphenylphosphino)ethane. A chiral analog of the bimetallic carbene complex **300** was accessed through a similar series of reactions using bis(diphenylphosphino)ethane as an additive in the vinylmetal synthesis [234].



Scheme 54.



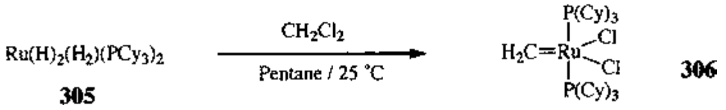
Scheme 55.

1.3.5.2. Neutral nonheteroatom-substituted metal–carbene complexes which are not cumulenes. Numerous additional examples of the synthesis and reactivity of this class of compounds has been presented in the alkene metathesis section.

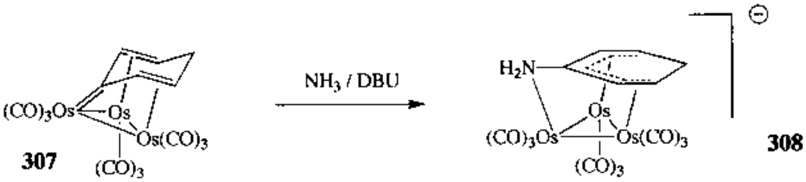
Complexes of this class were commonly synthesized from the reaction of neutral coordinatively-unsaturated (or weakly-ligated) metal complexes with diazo compounds or other carbene precursors (Scheme 55). The osmium–methylene complex **302** was obtained from the coupling osmium complex **301** with diazomethane [235]. Coupling of carbene complex **302** with sulfur dioxide afforded the metallacycle **303**, while reaction with HCl led to the corresponding osmium–methyl complex **304**. Similar carbene complexes prepared from this route include ruthenium carbene complexes prepared from the reaction of a ruthenium-chelating acetate complex with diphenyldiazomethane [236], an osmium hydride–carbene complex prepared from the coupling of a coordinatively-unsaturated osmium–hydride complex with various organic diazo compounds [237], an iron–calixarene–carbene complex obtained from the coupling of an iron–calixerene complex with diphenyldiazomethane [238], and an iron–porphyrin–carbene complex was prepared by the coupling of an iron–porphyrin with diphenyldiazomethane [239]. An iron–porphyrin–dichlorocarbene complex was also prepared form an iron–porphyrin and chloroform/base; this complex readily releases the dichlorocarbene unit upon photolysis [240]. A ruthenium–carbene complex was proposed as an intermediate in the diazomethane-induced transformation of a vinylruthenium complex into a π-allyl complex [241].

The unusual formation of the ruthenium–methylene complex **306** (Scheme 56) through the coupling of the ruthenium–hydride complex **305** with dichloromethane was reported [242]. The analogous dideuteromethylene complex was produced using dichloromethane-d_2. The reaction was inhibited by external hydrogen.

The reaction of osmium–carbene complex **307** (Scheme 57) with ammonia afforded the aminocyclohexadienyl complex **308** if DBU was added to the reaction



Scheme 56.



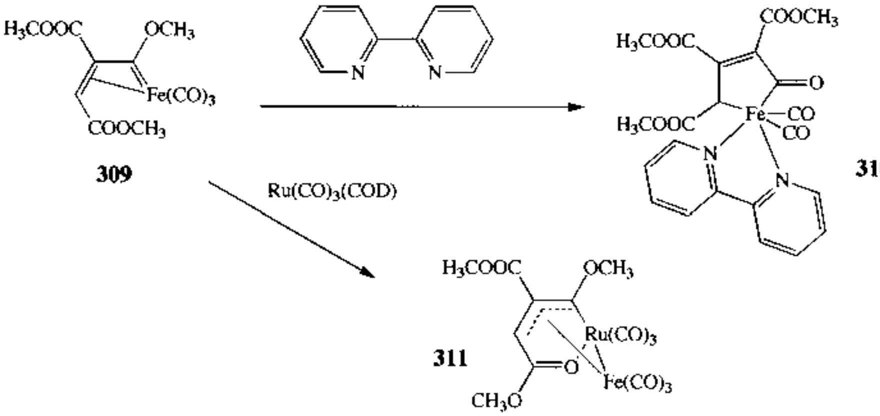
Scheme 57.

mixture [243]. In the absence of DBU, only reversible formation of the aminocyclohexadienyl complex was noted.

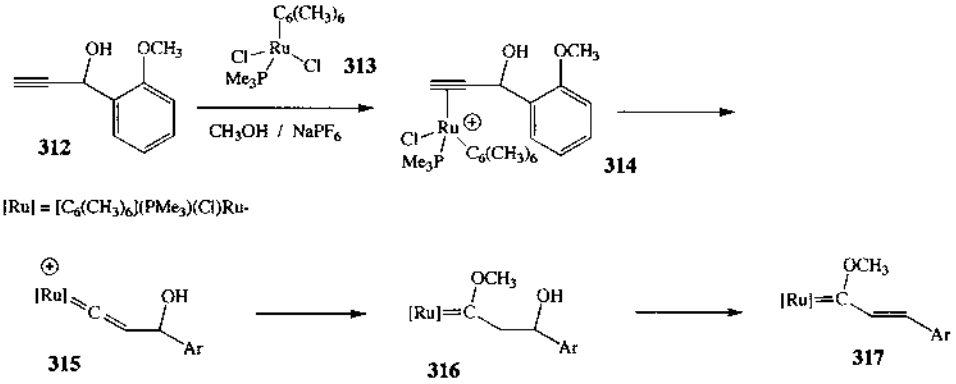
1.3.5.3. Heteroatom-substituted Group VIII–metal carbene complexes. Reaction of η^3-vinylcarbene–iron complex **309** (Scheme 58) with chelating pyridine ligands afforded the ferracyclopentenone derivative **310** via a vinylketene–iron complex intermediate [244]. The reaction of complex **309** with ruthenium–carbonyl complexes afforded the bimetallic complex **311** [245].

Fischer alkenylcarbene–ruthenium complexes (**317**, Scheme 59) were prepared from the reaction of propargylic alcohols with the permethylbenzene–ruthenium complex **312** in methanol [246]. Even through the reaction proceeds through a series of chiral complexes, no stereoselectivity was observed during the transformation to the carbene complex; regardless of the enantiomeric purity of the starting alcohol, only the racemic carbene complex was obtained. Other carbene complexes were prepared similarly [247].

The synthesis and reactivity of π-allyl ligated iron–carbene complexes (**319**, **322**, Scheme 60) was studied [248]. These complexes were synthesized by alkylation of the corresponding acylate complexes (**318**). The reaction of the oxygen analog of the carbene complex **319** with nucleophiles (enolates) led to the trimethylenemethane complex **321**. The reaction of the aminocarbene analog of the complex



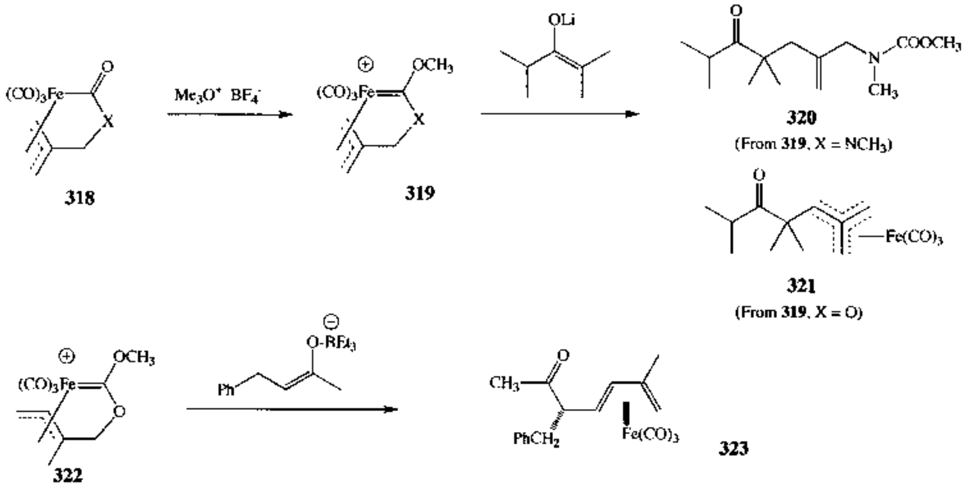
Scheme 58.



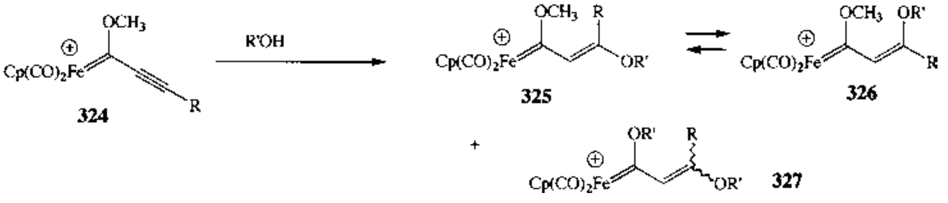
Scheme 59.

319 with enolates led to the amine–ketone derivative **320** after oxidative workup. The reaction of cationic π-allyl-dialkoxycarbene iron complex **322** with ketone enolates led to η^4-diene iron complexes (**323**) [249]. This reaction proceeded with a very high degree of diastereoselectivity.

The reaction of cationic alkynylcarbene–iron complexes with alcohols was investigated [250]. Predominant attack of the alcohol at the β-position was observed, resulting in the β-alkoxyalkenylcarbene complex (**325**–**327**). In the case where R = t-Bu, mixtures of products resulting from attack at the β-position and attack at the carbene carbon were obtained. Other studies of the synthesis of related cationic α,β-unsaturated iron carbene complexes [251] and their reactivity with ligands and nucleophiles were reported also [252] (Scheme 61).



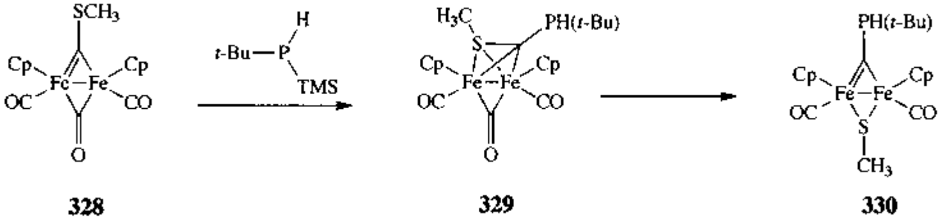
Scheme 60.



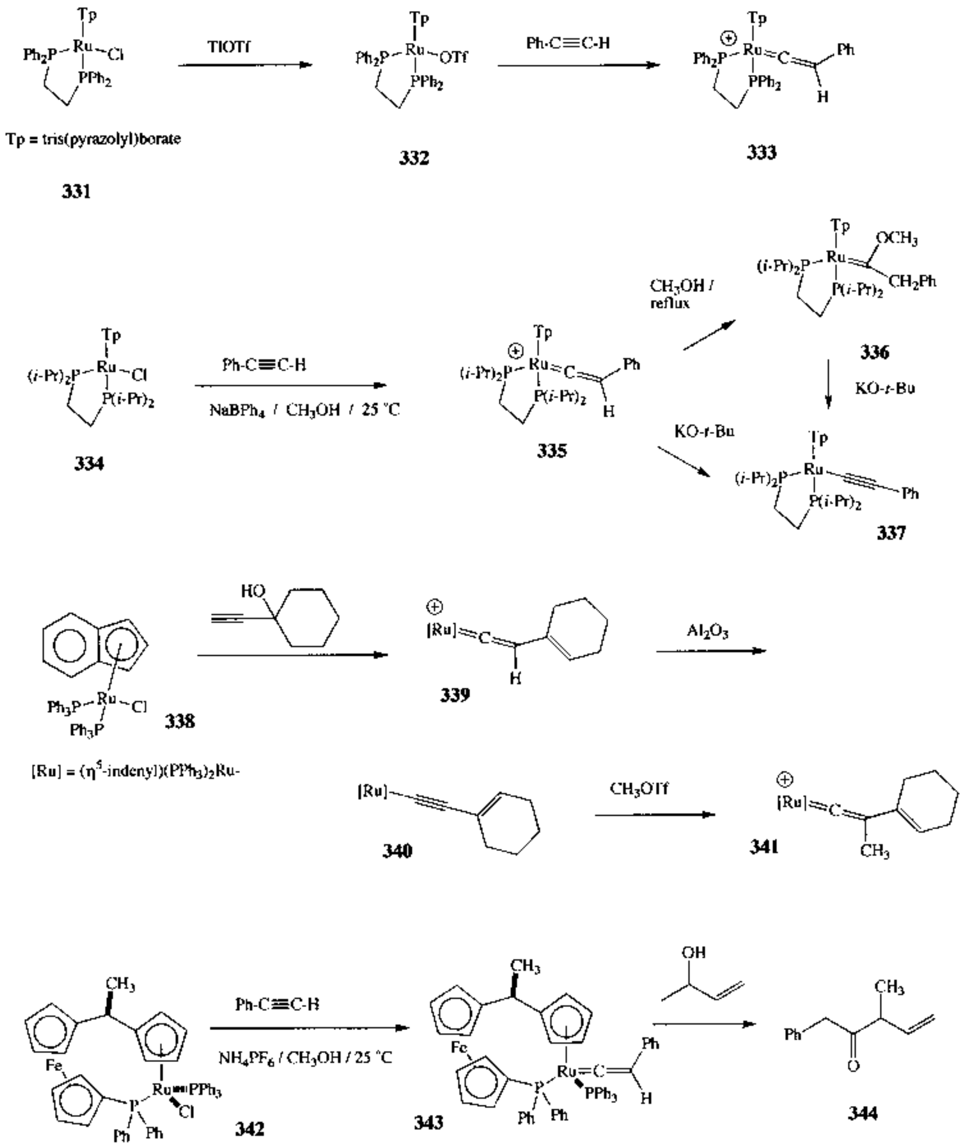
Scheme 61.

Bimetallic carbene complexes of this structural class were also reported in 1997 [253,254]. For example, bridging phosphinocarbyne–diiron complex **330** was obtained from the reaction of bridging thiocarbyne–diiron complex **328** with a phosphine. The bridging carbene–diiron complex **329** was the initial product, which converted to the bridging carbyne complex **330** at room temperature (Scheme 62).

1.3.5.4. Group VIII metal–vinylidene complexes. Many examples of the formation of metal vinylidene complexes via coupling of Group VIII metal halides with terminal or silylated alkynes were reported in 1997. Representative examples are depicted in Scheme 63. Common reaction pathways for these complexes include reaction with alcohols to form Fischer carbene complexes (or water to form metal acyls) and deprotonation at the *β*-position to form alkynylmetal complexes. Activation of ruthenium halide **331** with thallous triflate, followed by the reaction of the resulting triflate **332** with phenylacetylene led to the cationic ruthenium–vinylidene complex **333** [255]. Similarly, the ruthenium–vinylidene complex **335** was obtained from the reaction of ruthenium halide complex **334** with terminal alkynes [256]. The vinylidene complex was converted to Fischer carbene complex **336** upon treatment with refluxing methanol. Either the vinylidene complex **335** or Fischer carbene complex **336** could be converted to the corresponding alkynylruthenium complex **337** upon treatment with potassium *t*-butoxide. The alkenylvinylidene complex **339** was obtained from the reaction of the indenylruthenium chloride complex **338** with 1-ethynylcyclohexanol [257]. Dehydration occurs under the reaction conditions for the vinylidene complex formation. The reaction with alumina afforded the alkenylalkynylruthenium complex **340**, which afforded the *β*-substituted vinylidene complex **341** upon treatment with methyl triflate. Enantiomerically-pure heterobimetallic iron vinylidene–ruthenium complex **343** was prepared from the



Scheme 62.

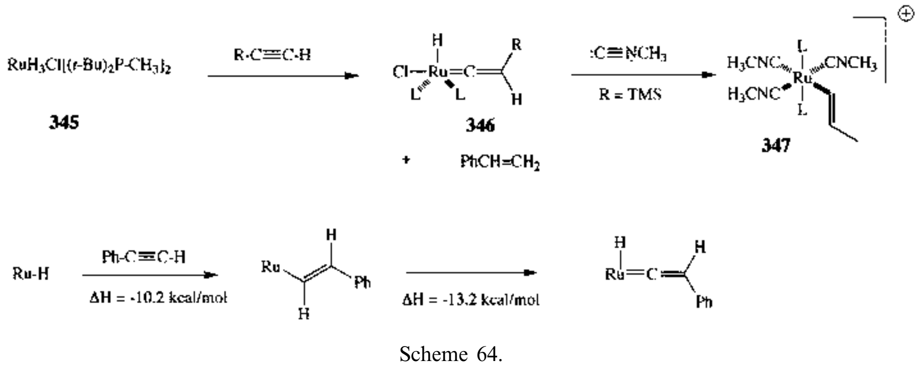


Scheme 63.

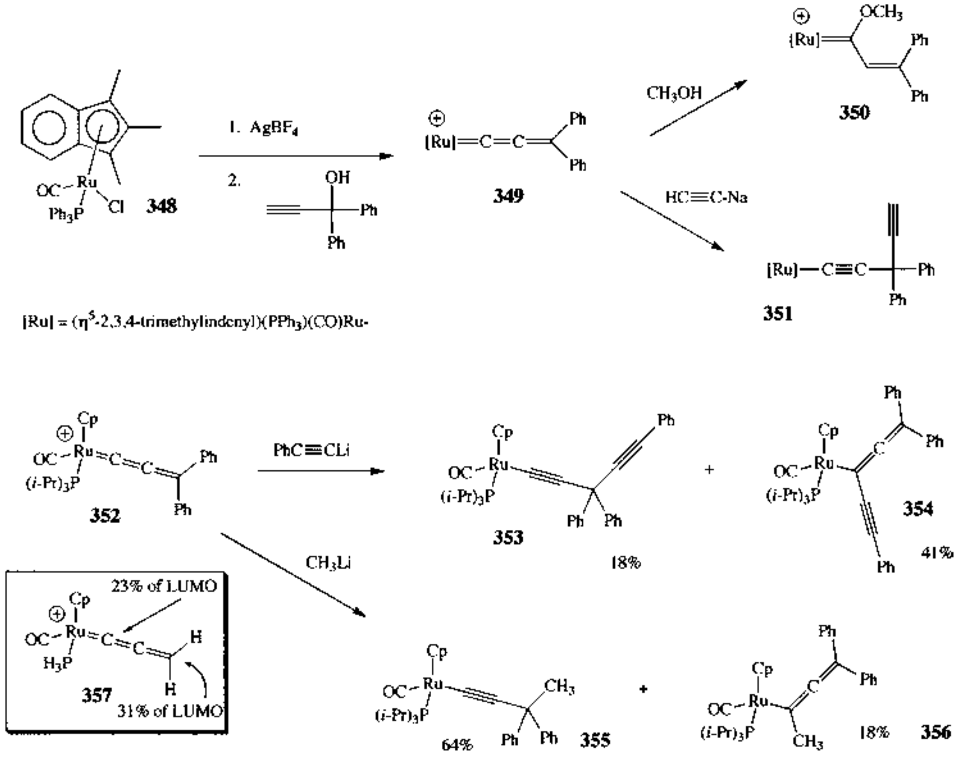
reaction of ruthenium halide derivative **342** with phenylacetylene [258]; a single diastereomer resulting from inversion at ruthenium was produced in this reaction. The vinylidene complex coupled with 3-butyn-2-ol to afford β,γ-unsaturated ketone **344** with a moderate degree of enantioselectivity.

Numerous other studies of the synthesis and reactivity of Group VIII metal–vinylidene complexes appeared in 1997. Examples include studies of: (1) synthesis of cationic ruthenium vinylidenes from alkynes and the interconversion of η^2-alkyne complexes, vinylidene complexes, and alkynyl complexes [259], (2) synthesis and nonlinear optical properties of cationic cycloheptatrienyl-substituted ruthenium–vinylidene complexes featuring resonance delocalization of the positive charge into a cycloheptatrienyl cation system [260], (3) synthesis of cationic iron–vinylidenes from acetylene, silylated acetylenes, and diacetylenes, and the interconversion of η^2-alkyne complexes, vinylidene complexes, and alkynyl complexes [261], (4) synthesis and the reactivity of neutral ruthenium–vinylidene complexes [262], (5) synthesis of neutral ruthenium vinylidene complexes and studies of their stability and vinylidene ligand displacement/exchange reactions [263], (6) synthesis of cationic ruthenium vinylidenes and mono- and double-deprotonation reactions [264], (7) synthesis and reactivity of cationic ruthenium vinylidene complexes featuring the vinyldiphenylphosphine ligand [265], (8) synthesis and reactivity of cationic ruthenium–vinylidene complexes featuring the *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane (Me_3tacn) ligand [266], (9) synthesis and reactivity of cationic ruthenium complexes featuring a cobalt-tethered tridentate phosphite (L_{OEt}) ligand [267], (10) synthesis of cationic ruthenium–vinylidene complexes featuring two bidentate phosphine ligands and their reactions with alkynes [268], (11) synthesis and reactivity of bimetallic ruthenium vinylidene complexes featuring a sulfide-bridged ruthenium dimer linkage [269], (12) reactions of indenyl-coordinated ruthenium–vinylidene complexes [270], and (13) synthesis and reactivity of neutral heterobimetallic ruthenium–hydride vinylidene complexes prepared from ferrocenylacetylene [271]. Ruthenium–vinylidene complexes have also been proposed as reactive intermediates in the coupling of arylruthenium chlorides with terminal alkynes [272].

Ruthenium–vinylidene complexes (**346**) were prepared from the reaction of the ruthenium–trihydride complex **345** with terminal alkynes [273]. Two alkynes are required for the synthesis of the vinylidene since one mole of alkyne is converted to the alkene during the reaction. A mechanism involving hydrometallation of the alkyne followed by α-hydride elimination was proposed for formation of the vinylidene complex; this mechanism was supported through deuterium labeling studies. Theoretical calculations suggest that both the hydrometallation and α-hydride elimination steps are exothermic (Scheme 64).



Scheme 64.



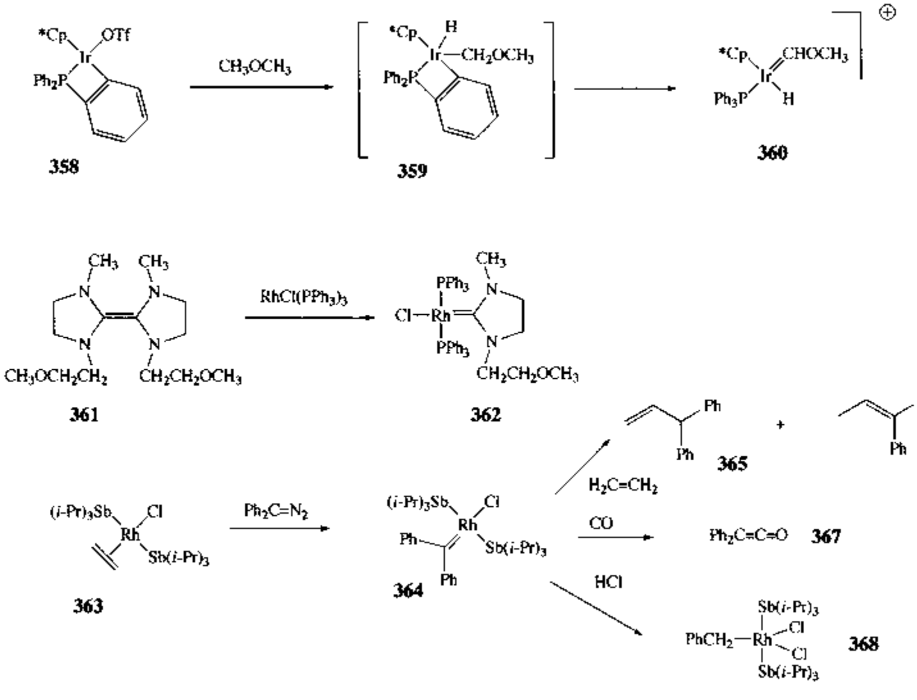
Scheme 65.

1.3.5.5. Group VIII metal complexes of higher cumulenes. The metal–higher cumulene complexes are produced from the coupling of Group VIII metal halides with propargyl alcohols which contain no hydrogens β- to the OH group. Several examples of this reaction were reported in 1997. The cationic ruthenium–allenylidene complex **349** (Scheme 65) was prepared from the coupling of the indenylruthenium complex **348** with diphenylpropargyl alcohol [274]. The reaction of the allenylidene complex with alcohols led to the corresponding α,β-unsaturated Fischer carbene complex **350**. Reaction of the allenylidene complexes with alkynyl anions (and other nucleophiles) led to neutral γ-substituted alkynylruthenium complexes (**351**). The synthesis and reactivity pattern for the allenylidene–ruthenium complex **352** were studied [275]. Electrophilic sites within the allenylidene ligand in complex **357** were calculated to be at the α- and γ-carbons, while the nucleophilic site was at the β-carbon. A variety of nucleophiles were tested in their reaction with allenylidene complex **352**, and attack at the α- and γ-positions was noted. Similar studies were conducted on related cumulene–metal complexes [276–280].

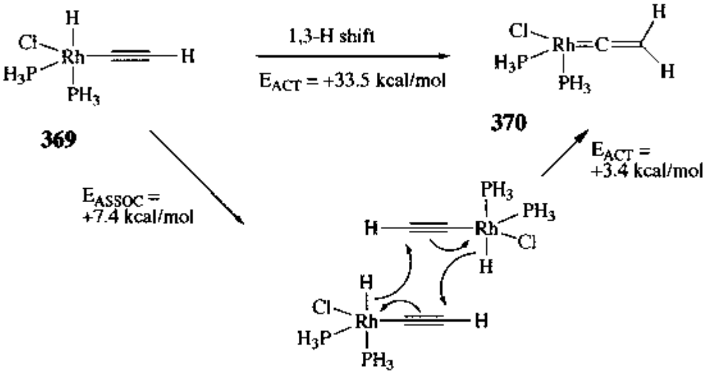
1.3.6. Group IX metal–carbene complexes

The iridium–carbene complex **360** (Scheme 66) was prepared via reaction of dimethyl ether with the *o*-methylated iridium complex **358** [281], presumably via oxidative addition into the C–H bond of dimethyl ether, followed by reductive elimination to the unchelated phosphine, followed by α-hydride elimination. The rhodium–carbene complex **362** was prepared from the cleavage of the alkene **361** by Wilkinson's catalyst [282]. A similar ruthenium complex was also prepared from alkene **361**. These complexes serve as catalysts for alkene cyclopropanation reactions using ethyl diazoacetate. A structurally similar rhodium–carbene complex was reported to have antimicrobial activity [283]. Stable carbene complexes (**364**) were produced in high yield from couplings of various diaryldiazo compounds with rhodium (I) chloride complexes (**363**) [284]. The reaction of carbene complex **364** with a variety of unsaturated organic substrates was examined. Coupling with ethylene afforded the net C–H insertion products **365** and **366**. Coupling with carbon monoxide afforded the diphenylketene (**367**); the analogous reaction involving isocyanides afforded ketimine derivatives. Reaction with hydrochloric acid led to alkylmetal–dihalide complex **368**.

A theoretical study of the conversion of rhodium–alkyne complexes to the corresponding vinylidenes was conducted [285]. Mechanisms involving conversion to hydrido–alkynyl complex **369** (Scheme 67), followed by either a 1,3-hydrogen



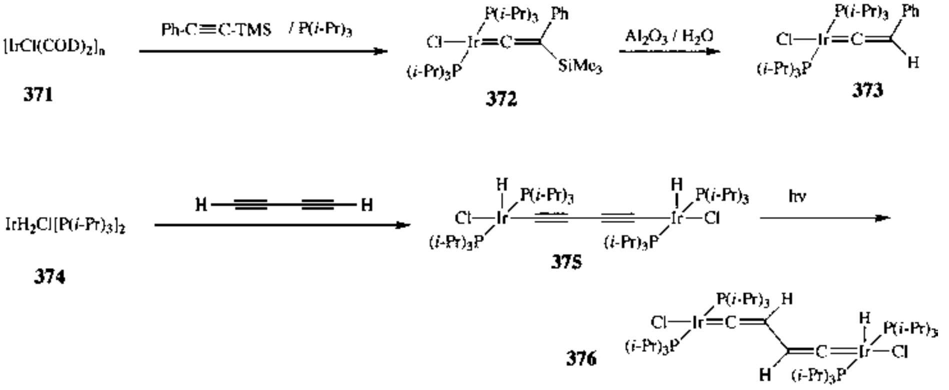
Scheme 66.



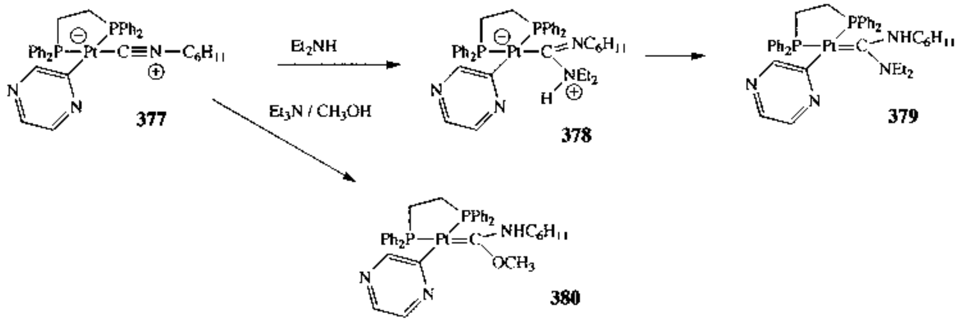
Scheme 67.

shift or a bimolecular hydride transfer were considered. The bimolecular mechanism was found to be the energetically more reasonable pathway. The energy of activation for the 1,3-hydrogen shift pathway was calculated to be 33.5 kcal mol^{-1}. For the bimolecular mechanism, the energy of association was calculated to be 7.4 kcal mol^{-1}, while the energy of activation for the bimolecular hydride transfer was calculated to be 3.4 kcal mol^{-1}. Even in a real system containing triisopropylphosphine ligands, the overall energy of activation for the bimolecular mechanism was calculated to be 17.0 kcal mol^{-1}. A study of the conversion of acetylene bound to a rhodium surface to the corresponding vinylidene was conducted [286]. The rearrangement of the initially-formed acetylene adduct to the vinylidene adduct occurred over the temperature range 140–220 K. The energy of activation for this process was determined to be 39 kJ mol^{-1}. A one-step mechanism involving surface-assisted migration of the hydrogen atom was proposed.

Iridium–vinylidene complexes (**372**, **373**, **376**, Scheme 68) were prepared from the coupling of iridium chloride or hydride derivatives with terminal alkynes or



Scheme 68.

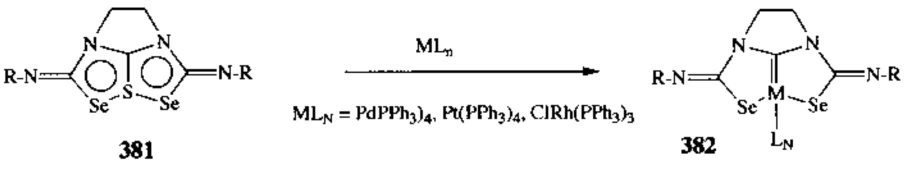


Scheme 69.

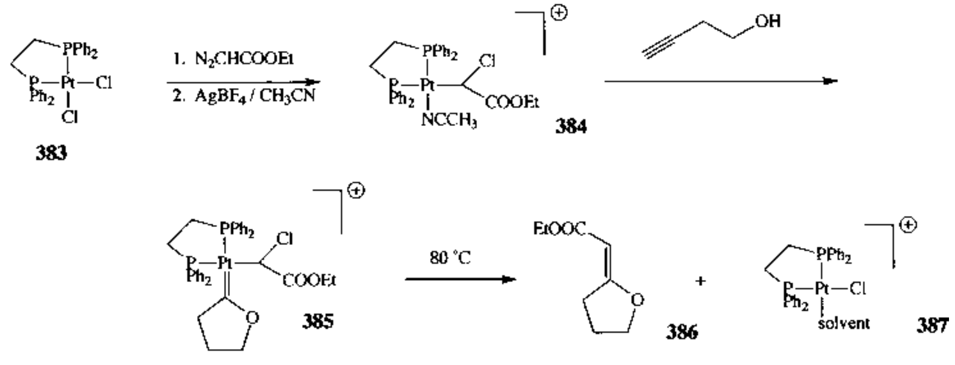
trimethylsilylalkynes [287]. Silylvinylidene–iridium complexes were desilylated using aluminum oxide or potassium fluoride. The reaction of 1,3-butadiyne with the iridium–dihydrogen complex **374** afforded the diacetylene-bridged bimetallic complex **375**, which converted to the corresponding bis(vinylidene)-bridged bimetallic **376** upon photolysis.

1.3.7. Group X and XI metal–carbene complexes

Platininum– and gold–carbene complexes were prepared from the reaction of metal isocyanides with alcohols or amines. The mechanism for the conversion of platinum isonitrile complexes (**377**, Scheme 69) and amines to the corresponding diheteroatom-stabilized carbene complexes (**379**, **380**) was studied [288]. The extra nitrogen of the pyridine-type ligand is a requirement in the synthesis of the carbene complex to assist with the proton transfer required in the conversion of initial adduct **378** to the carbene complex. A similar study was conducted for the conversion to platinum isonitrile complexes to alkoxycarbene complexes (**380**) using alcohols and triethylamine, and for the interconversion of alkoxycarbene complexes and aminocarbene complexes [289]. Bis carbene–platinum complexes could be prepared from bis isonitrile complexes [290]. The polycarbene–gold complex derivative of the aminocarbohydrate antibiotic neomycin could be prepared using similar reactions [291]. Various gold–carbene complexes having liquid crystal properties were prepared using similar reactions [292]. Platinum– and gold–carbene complexes were observed in the FAB spectrum of diazo compounds in the presence of platinum and gold complexes [293].



Scheme 70.



Scheme 71.

A series of thiadiselenadiazapentalene derivatives (**381**, Scheme 70) were converted to the chelated carbene complexes (platinum, palladium, rhodium) (**382**) upon treatment with a series of late transition metal phosphine complexes [294,295]. The reaction is a net desulfurization where the carbon–sulfur double bond is replaced by a carbon–metal double bond. The sulfur atom was transferred to one of the triphenylphosphine ligands, and triphenylphosphine sulfide was observed as a byproduct.

Platinum alkyl complex **384** (Scheme 71), obtained from the reaction of platinum dichloride complex **383** with ethyl diazoacetate, coupled with 3-butyn-1-ol to afford the cyclic Fischer carbene complex **385** [296]. Upon thermolysis, the carbene complex was transformed to the unsaturated ester derivative **386** and platinum complex **387**. This process was examined for a variety of homopropargyl alcohol derivatives and found to be general. The catalytic formation of unsaturated ester derivatives through the coupling of ethyl diazoacetate with homopropargyl alcohols was only marginally successful.

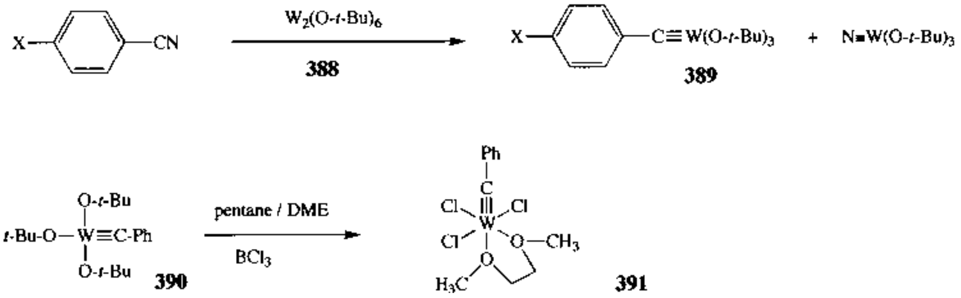
2. Metal–carbyne or metal–alkylidyne complexes

2.1. Reviews

A review focusing on the hydroboration of metal–carbon multiple bonds has appeared [297].

2.2. Synthesis/or generation

A series of tungsten–alkylidyne complexes (**389**, Scheme 72) were prepared via a nitrile metathesis reaction involving aryl nitriles and ditungsten complex **388** [298]. The Complex **389** (and several analogs) were readily transformed into carbyne complex **391** [299].

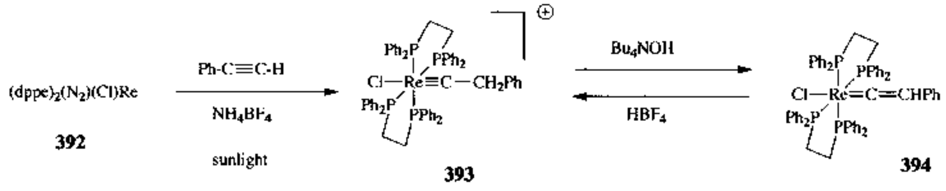


Scheme 72.

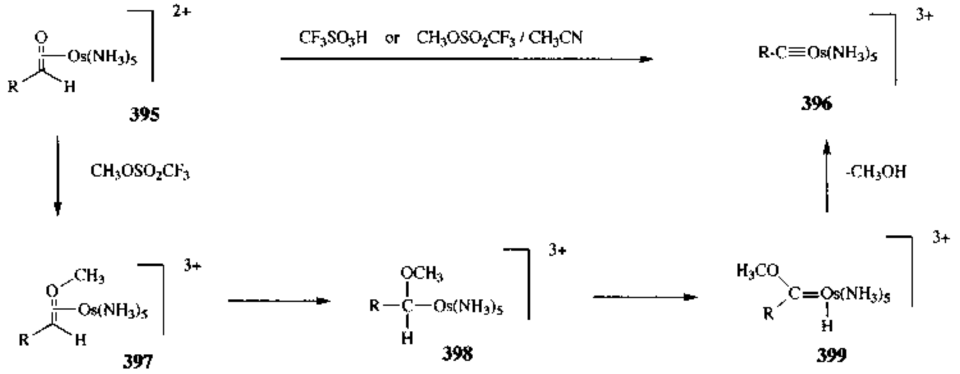
Cationic rhenium–carbyne complexes (**393**, Scheme 73) were prepared by sunlight irradiation of terminal alkynes in the presence of cationic rhenium–dinitrogen complex **393** [300]. Deprotonation of the carbyne complex **393** afforded the neutral rhenium–vinylidene complex **394**, which could be converted back into the cationic carbyne complex **393** by protonation. The electrochemistry of the carbyne and vinylidene complexes was examined. The cationic carbyne complexes have considerably greater oxidation potentials than the vinylidene complexes. The protonation process was examined in detail using stopped-flow kinetics [301]. Studies of the acid–base induced interconversion of osmium–carbyne complexes and osmium–vinylidene complexes were reported also [302,303].

Formation of carbyne–osmium (II) complexes of general structure **396** (Scheme 74) from aldehyde–osmium complexes (**395**) was investigated [304]. Treatment of the aldehyde complex **395** with either trifluoromethanesulfonic acid or methyl triflate/acetonitrile afforded the corresponding carbyne complex **396**. Treatment with methyl triflate in DME afforded the methylated aldehyde complex **397**. A mechanism involving conversion of the methylated aldehyde complex to osmium–alkyl complex **398**, followed by α-hydride elimination and elimination of methyl was proposed. A different reaction pathway was followed using α,β-unsaturated aldehyde complexes.

The synthesis and decomposition reactions of molybdenum–alkyl [305] and tungsten–alkyl [306] derivatives of general structure **400** (Scheme 75) were examined. For compounds where R = cyclopentyl or cyclohexyl, the α-hydride elimination process (forming **401**) was more facile than the β-hydride elimination (forming **402**). Thermolysis at higher temperatures ultimately afforded the cyclopentene and

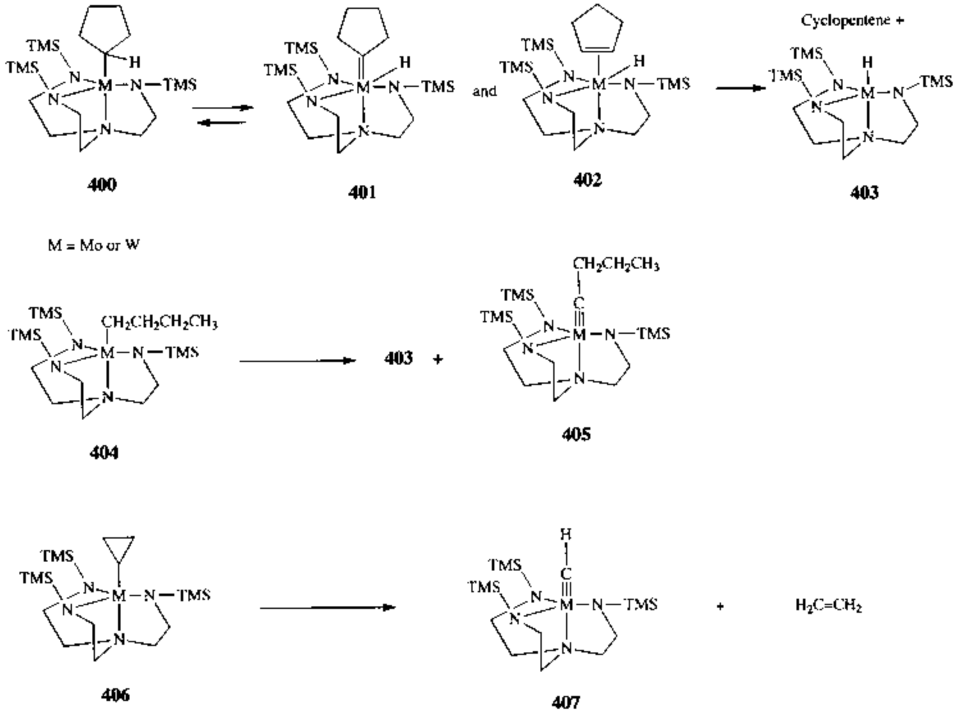


Scheme 73.

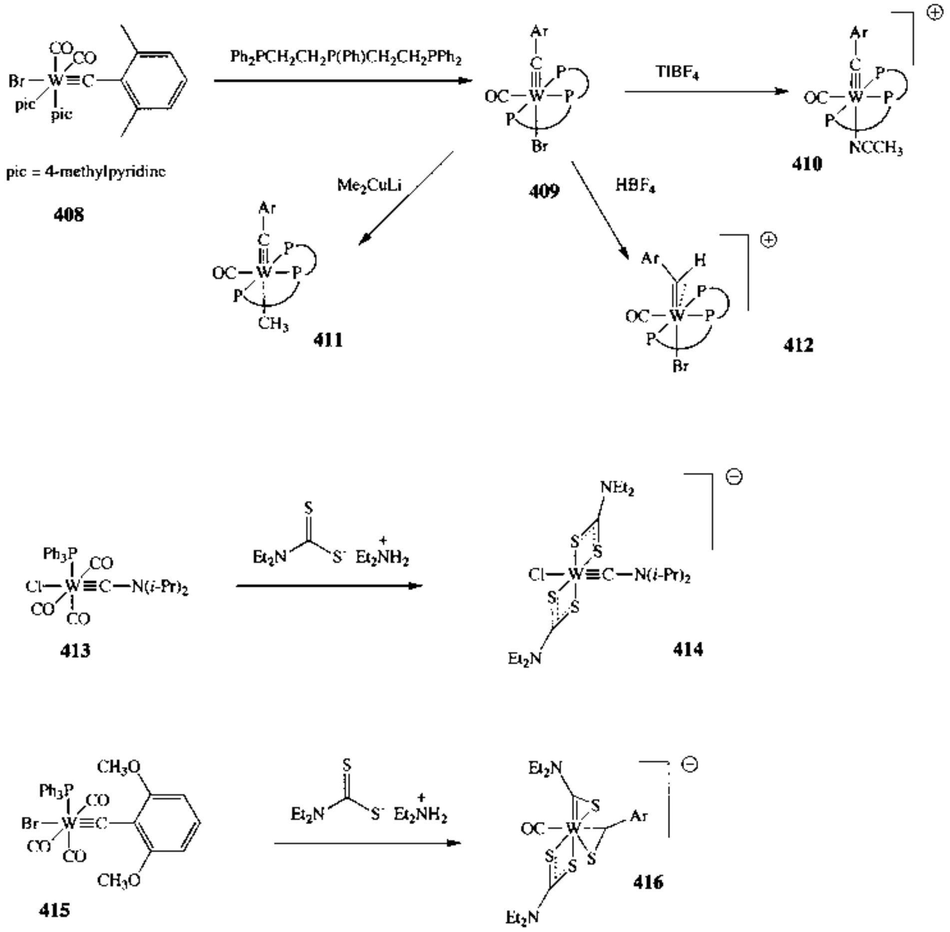


Scheme 74.

metal hydride **403** (the β-hydride elimination products). Complexes featuring primary alkyl groups (**404**) afforded alkylidyne complexes (**405**) upon thermolysis. The cyclopropyl complex **406** afforded the alkylidyne complex **407** and ethylene, a mechanism involving metallacyclobutene formation followed by the loss of ethylene and α-hydride elimination was proposed. An alkylidyne complex was also formed



Scheme 75.



Scheme 76.

upon thermolysis of the cyclobutyl complex. The tungsten and molybdenum complexes provided very similar distributions of products, however, the tungsten complexes were generally observed to be more reactive than the molybdenum complexes; in many cases, the tungsten–alkylidyne complexes were formed at or below room temperature.

2.3. Reactivity

2.3.1. Ligand exchange reactions

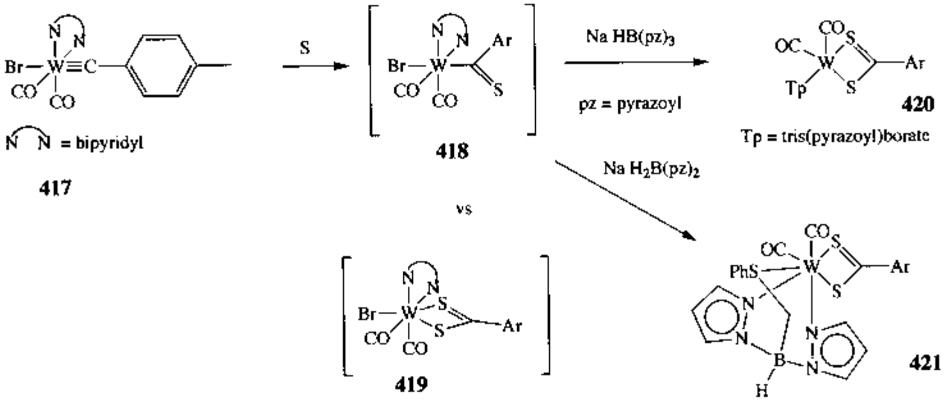
The reaction of the tungsten–carbyne complex **408** (Scheme 76) with the tridentate phosphine ligand afforded the carbyne complex **409** [307] The reactivity of complex **409** was examined. Reaction with CO or acetonitrile in the presence of thallous hexafluorophosphate led to the corresponding cationic carbyne complex

(**410**). Reaction with fluoroboric acid led to the corresponding carbene complex (**412**) featuring an agostic interaction. Reaction with lithium dimethylcuprate afforded the methyl–tungsten carbyne tungsten complex **411**. The reaction of the aminocarbyne– and arylcarbyne–tungsten (**413**, **415**) and molybdenum complexes with dithiocarbamate ligands was investigated [308]. The aminocarbyne–tungsten complex afforded the ligand exchange product **414**; the molybdenum analog of **414** was very unstable. The arylcarbene complex **415** afforded the product analogous to **414** if the sodium salt of the dithiocarbamate ligand was employed, however, the diethylammonium salt of the dithiocarbamate ligand led to the unusual complex **416**, which arises through migration of a sulfur atom of one of the dithiocarbamate ligands. An alternative one-pot synthesis of complexes **414** and **416** from tungsten hexacarbonyl was also presented. Other studies of the reaction of carbamates with dithiocarboxylate and dithiophosphonate ligands [309], and phosphine and isocyanide ligands [310] were reported also.

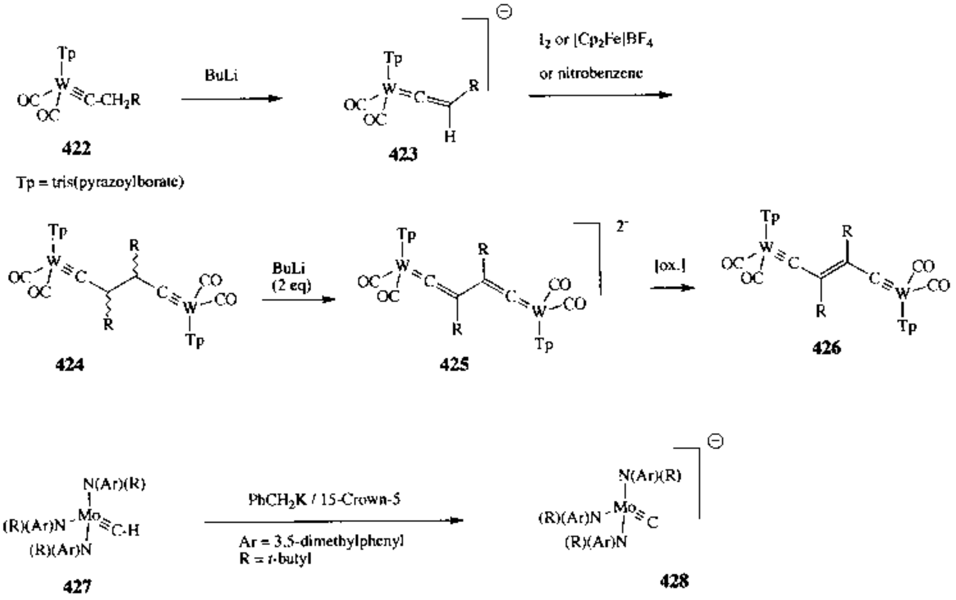
2.3.2. Addition reactions of metal–carbyne complexes

The reaction of tungsten–carbyne complexes with sulfur has been studied [311]. The reaction of complex **417** (Scheme 77) with sulfur followed by the tris(pyrazoyl)borate ligand afforded the dithiocarboxylate complex **420**. A mechanism involving conversion to thioacyl complex **418**, followed by conversion to the dithiocarboxylate complex in the presence of the added ligand was proposed. The reaction with sulfur in the presence of bis(pyrazoyl)borate afforded the bis(pyrazoyl)borate complex **421**. The benzylic sulfide linkage was proposed to arise via hydroboration of the alleged thioacyl complex intermediate; this observation was also supportive of the intermediacy of the thioacyl complex **418** and not the thiocarbamate complex **419**. Carbyne complexes were transformed directly to thioacyl complexes using propylene sulfide [312].

Other reported reactions involving additions to the carbon–carbon triple bond include: (1) formation of a cationic arseno–acyl complex from the coupling of



Scheme 77.



Scheme 78.

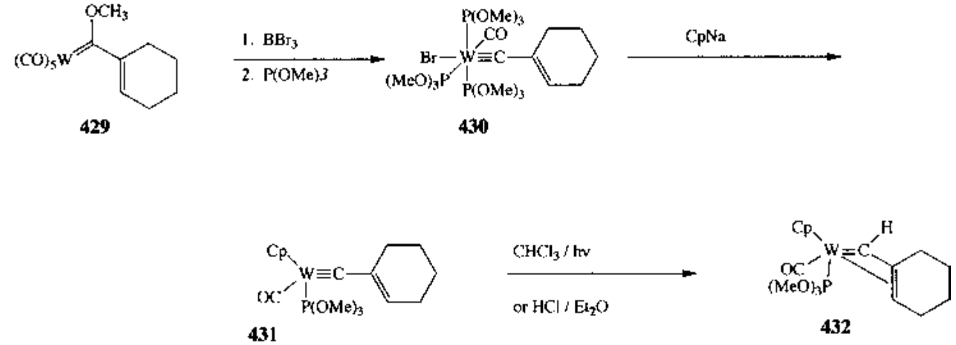
carbyne–tungsten complexes with arsenic halides [313], (2) addition of carboranyl-ruthenium complexes to a tungsten–carbyne complex, resulting in a heterobimetallic alkylidene complex [314], and (3) hydroboration reactions [315].

2.3.3. Reactions involving carbanions derived from metal–carbyne complexes

A study of the reaction of anions derived from neutral tris(pyrazolyl)borate metal–carbyne complexes of general structure **422** (Scheme 78) was conducted [316]. These complexes were deprotonated by *n*-butyllithium to afford anionic metal vinylidene complexes (**423**). Treatment of the vinylidene complex with an oxidant (iodine, nitrobenzene, or ferrocenium ion) affords the bis carbyne complex **424**. When $R \neq H$, a mixture of diastereomers was observed. The formation of the dianion of the bis carbyne complex **424**, followed by oxidation, affords the alkene-linked bis carbyne complex **426**. If $R = H$, the alkene linkage of **426** could be transformed to the alkyne by another anion formation-oxidation sequence. The first complex featuring a terminal carbide ligand (**428**) was prepared by deprotonation of the methylidyne–molybdenum complex **427**, followed by a crown ether [317].

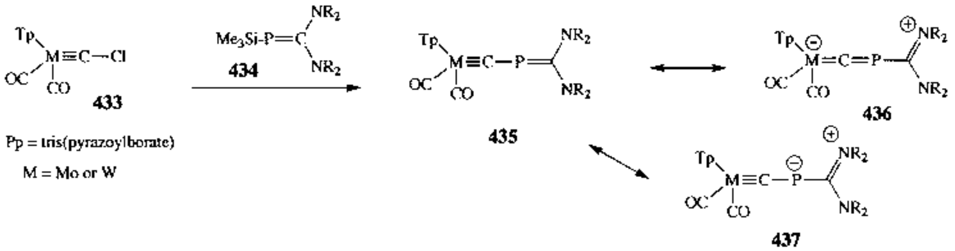
2.3.4. Other processes involving metal–carbyne complexes

The photoreactions of vinylcarbyne–tungsten complex **430** (Scheme 79) were studied [318]. Although the same product, **432**, was obtained either through photolysis in chloroform or simple protonation, different mechanisms were proposed. Since the photolysis reaction was unaffected by addition of acid scavengers, a mechanism involving single electron transfer followed by hydrogen abstraction was proposed.



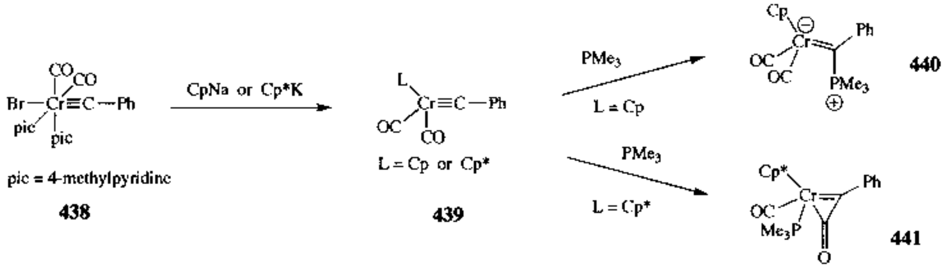
Scheme 79.

The coupling of molybdenum– and tungsten–chlorocarbyne complexes (**433**, Scheme 80) with the phosphorus compound **434** has been studied [319]. The reaction afforded the corresponding phosphorus-substituted complexes **435**. There is a signification contribution from the vinylidene-like resonance structure **436** and phosphide **437** in these complexes.



Scheme 80.

The preparation, ligand substitution chemistry, and electrochemistry of cyclopentadienyl-ligated chromium–carbyne complexes (**439**, Scheme 81) were examined [320]. The reaction pathway for coupling of complex **439** with trimethylphosphine was very ligand-dependent. Complex **439** (L = Cp) afforded the zwitterionic complex **440** upon exposure to trimethylphosphine, while simple CO insertion and ligation, forming complex **441**, were observed for complex **439** (L = Cp*).



Scheme 81.

Tungsten–carbyne complexes were effective catalysts for the polymerization of acyclic dienes [321]; this process was given the name ADIMET (acyclic diene metathesis polymerization). Metal–carbyne complexes have been proposed as intermediates in the reductive dimerization of carbon monoxide using a rhodium (I) catalyst and phenyl dimethylsilane [322]. A study of the second hyperpolarizabilities (γ) for the $[\mathrm{Mn{\equiv}CH}]^+$, $[\mathrm{Mn{=}CH_2}]^+$, and $[\mathrm{Mn{-}CH_3}]^+$ were calculated using ab initio calculations [323]. The metal alkyl was predicted to have a higher γ value than the metal carbene or carbyne complexes.

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