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The chemistry of the carbon–transition metal double and triple bond: annual survey covering the year 1998☆

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Contents

Abbreviations: ROMP, ring opening metathesis polymerization; RCM, ring closing metathesis.

☆ For 1997, see: J.W. Herndon, Coord. Chem. Rev. 181 (1999) 177.

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Abstract

This survey is intended to be a comprehensive summary of articles, which report on the synthesis, reactivity, or properties of compounds that feature a multiple bond between carbon and a transition metal. Reactions that employ metal carbene complexes as transient intermediates generated through well-established routes [this subject was reviewed in 1998: M.P. Doyle, M.N. Protopopova, Tetrahedron 54 (1998) 7919] are not covered unless there is some effort to characterize the carbene complex intermediate. Although a determined effort has been made to include patents, in general only patents that focus on carbene complexes and not polymer products will be included. Only compounds which feature a multiple bond between one carbon atom and one transition metal are discussed in this survey, thus bridging carbene and carbyne complexes are not covered unless there is a multiple bond to at least one transition metal. The complexes of stable carbenes with transition metals have not been included; since the π-donation component of these complexes is minimal, there is no formal carbon–metal multiple bond [see J.C. Green, R.G. Scurr, P.R. Arnold, F.G.N. Cloke, J. Chem. Soc. Chem. Commun. (1997) 1963, and 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: Multiple bond; Alkylidene complexes; Alkylidyne complexes

1. Metal–carbene or metal–alkylidene complexes

1.1. Review articles

Several reviews covering aspects of metal–carbene complex chemistry appeared in 1998. Many reviews focusing on some aspect of olefin metathesis were published, including the following specific subjects: (1) general reviews of the olefin metathesis reaction in organic synthesis [1,2], (2) selective olefin metatheses [3], (3) ring closing metathesis in organic synthesis [4], (4) cross metathesis reactions [5], (5) enyne metathesis reactions [6], (6) olefin metathesis using well-defined catalysts [7], (7) synthesis of natural compounds via the cycloolefin metathesis reaction [8], and (8) aqueous phase olefin metathesis [9]. Other specific subjects reviewed in which there is a heavy focus on carbene complexes include: (1) asymmetric synthesis using carbene complexes [10], (2) transition metal allenylidene and cumulenylidene complexes [11], (3) the use of tungsten alkynyl compounds in organic synthesis [12], (4) the chemistry of η^3-vinylcarbene complexes [13], (5) the reaction of ruthenium complexes with acetylenes [14], (6) bridging cumulenediylidene complexes [15], (7) dithioacetals as precursors to titanium alkylidenes [16,17], (8) titanium carbene-mediated reactions [18], (9) the reactions of Group VI carbene complexes with ylides [19], (10) ruthenium-based catalysts for organic synthesis [20], and (12) Fischer-type carbene complexes [21]. 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) epothilone total syntheses [22], (2) ruthenium-catalyzed reactions for organic synthesis [23], (3) transition metal–cyclic aryne and cumulene complexes [24], (4) second order nonlinear optical properties of transition metal complexes [25], (5) ruthenium catalysts for the selective catalytic transformations of alkynes [26], (6) a general study of complexes of functionalized ylides [27], (7) the last 40 years of research in catalysis [28], (8) transition metals in organic synthesis for 1996 [29] and 1997 [30], (9) compounds featuring a carbon–metal σ-bond (including carbenes and carbynes) for metals in Groups IV–VII [31] and metals in Groups VIII–X [32], (10) polymers with valuable optical properties [33], (11) metathesis ring-chain equilibrium in cyclobutene and 1-methylcyclobutene [34], and (12) synthesis of salinomycin [35].

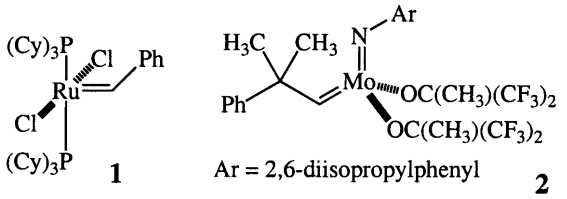


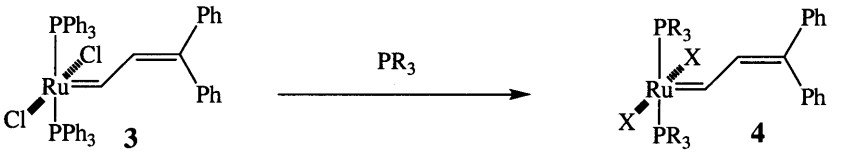
Fig. 1. Structures of alkene metathesis catalysts **1** and **2**.

1.2. Alkene metathesis

Alkene metathesis was the major reaction process reported for metal–carbene complexes in 1998, and this special section is devoted to papers which focus on this process. Many examples of both polymerization (mostly ring opening metathesis polymerization (ROMP)) reactions and small-molecule syntheses appeared. Only metathesis reactions initiated by a discrete transition metal–carbene complex, or metathesis reactions which discuss the carbene complex intermediates of this reaction have been included here.

1.2.1. General studies of alkene metathesis catalysts

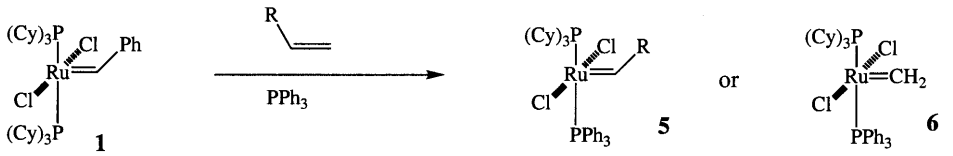
Several mechanistic studies related to alkene metathesis appeared in 1998. The thermochemistry of phosphine ligand substitution in ruthenium complex **3** (Scheme 1) was reported for a variety of phosphine ligands [36]. The ligand substitution process was most exothermic with the tricyclohexylphosphine ligand, and least exothermic with tribenzylphosphine; the observed effect was attributed to stabilization of the complex by σ-donation. The coupling of ruthenium alkylidene complexes with strained alkenes was studied in the gas phase [37]. The relative rates for reaction of the phosphine-dissociated carbene complex with various alkenes was determined, and a similarity to solution-phase chemistry was noted; the relative reactivity was norbornene > cyclopentene > 1-butene. Metathesis-active tungsten carbene complexes were studied by molecular modeling of the reactants, intermediates, and products of the metathesis reaction [38].



Scheme 1.

A study concerning the regiochemistry of alkene insertion in the reaction of the Grubbs catalyst (see Fig. 1; structure **1**: Grubbs catalyst, structure **2**: Schrock catalyst) with monosubstituted alkenes was conducted (Scheme 2) [39]. In cases where the alkene substituent is not bulky (Ph, *n*-Bu, *n*-Pr), the α-substituted ruthenium carbene complex (**5**) was formed, whereas the methylene complex (**6**) was

formed when the alkene substituent was bulky (*t*-Bu). In the reaction with *p*-substituted styrene derivatives, the electron rich alkenes (*p*-substituent = OMe) were kinetically more reactive than electron poor alkenes (*p*-substituent = NO_2).



Scheme 2.

Numerous attempts to develop new catalysts for alkene metathesis were reported in 1998; some representative examples are depicted in Fig. 2. Several derivatives of the Grubbs catalyst were synthesized and tested in their ability to undergo either ROMP or RCM processes, including: (1) a bimetallic complex (**7**) featuring a chlorine bridge from the carbene–ruthenium unit to an arene–metal (ruthenium or osmium complex); many derivatives of this complex were kinetically faster than Grubbs catalyst in the ROMP of 1,5-cyclooctadiene [40], (2) a salicylimide–ruthenium complex (**8**); the complex where R = NO_2 was kinetically faster than Grubbs catalyst in the RCM of diethyl diallylmalonate [41], (3) ruthenium–vinylidene complexes [42], (4) a tris(pyrazolylborate)ruthenium complex, which showed no metathesis activity at 70°C unless HCl, CuCl, or $AlCl_3$ was added [43], (5) analogs where the phosphines are replaced by stable carbene ligands (**9**), which catalyze the ROMP of 1,5-cyclooctadiene at 25°C and the RCM of 1,7-octadiene at 60°C [44], (6) a cationic ruthenium carbyne complex (**10**), which successfully catalyzes the ROMP of several strained alkenes and the cross metathesis of cyclopentene and methyl acrylate [45], and (7) ruthenium vinylidene-tris(pyrazolyl)borate complexes, which catalyze the ROMP of norbornene [46,47]. A number of other new metathesis catalysts or catalyst systems were studied, including: (1) dialkyltitanocene complexes, which were tested in their ability to effect the ROMP of norbornene; the effects of alkyl groups [48] and Cp ring substituents were emphasized [49], and (2) an alumina-bound analog of the Schrock catalyst [50]. Other studies of the alkene metathesis reaction discuss: (1) the inhibition of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/Me_4Sn$ metathesis catalyst system by aldehydes and ketones, which was attributed to carbonyl olefination reactions of the metal–alkylidene intermediates [51], and (2) the source of the carbene complex in the $RuCl_3{\cdot}xH_2O$/ROH metathesis catalyst

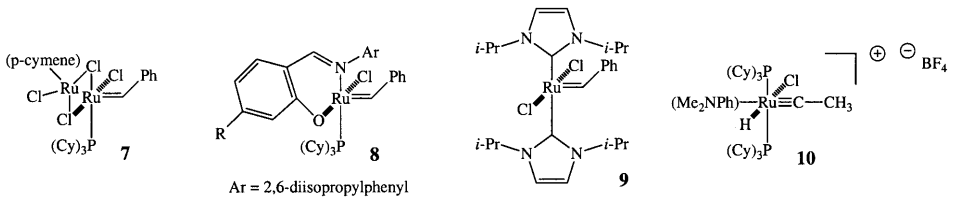


Fig. 2. Representative examples of new catalysts for alkene metathesis.

system [52]. Several patents were issued for the development of olefin metathesis catalysts [53–56].

1.2.2. Ring opening metathesis polymerization

The ring opening metathesis polymerization (ROMP) reaction remains 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 1998 (Fig. 3). Examples of ROMP using metal carbene complexes include: (1) ROMP of a diene-bridged ferrocene (**11**) using a tungsten–alkylidene complex [57], (2) ROMP of water-soluble norbornene and oxanorbornene derivatives (**13**) using a water-soluble analog of the Grubbs catalyst [58], (3) ROMP of oxanorbornene derivatives (**12**); the polymers were later transformed to carbohydrate derivatives after ozonolysis [59], (4) ROMP of norbornenedicarboxylic anhydride and oxanorbornenedicarboxylic anhydride using various ruthenium catalysts, including the Grubbs catalyst [60], (5) ROMP of dicyclopentadiene (**14**) using tungsten(VI) chloride/ethylaluminum dichloride and unsuccessful attempts to crosslink the polymer via ROMP of the residual cyclopentene units [61], (6) ROMP of 2-azanorbornene derivatives featuring chiral substituents (**15**) using the Schrock catalyst [62], and (7) ROMP of homochiral and racemic *endo*,*exo*-5,6-dimethylnorbornene [63].

1.2.3. Nonpolymer-forming ring opening metathesis reactions

The tandem ring opening-cross metathesis of cyclopropenone ketals (**16**) with monosubstituted alkenes using the Grubbs ruthenium catalyst was investigated (Scheme 3) [64]. Initial reaction with the monosubstituted alkene is required to initiate the reaction since cyclopropenone ketals do not react directly with the Grubbs catalyst. A tandem ring-opening metathesis-RCM-cross metathesis process was demonstrated for norbornene derivatives having remote alkene (e.g. **18**) substituents; treatment of **18** with allyltrimethylsilane (**19**) and either the Grubbs or Schrock catalyst afforded hydrindene derivative **20** [65].

1.2.4. Cross metathesis reactions

The cross metathesis reaction of various monosubstituted alkenes (e.g. **21**, Scheme 4) and either allyl acetate or *cis*-1,4-diacetoxy-2-butene (**21**) was investi-

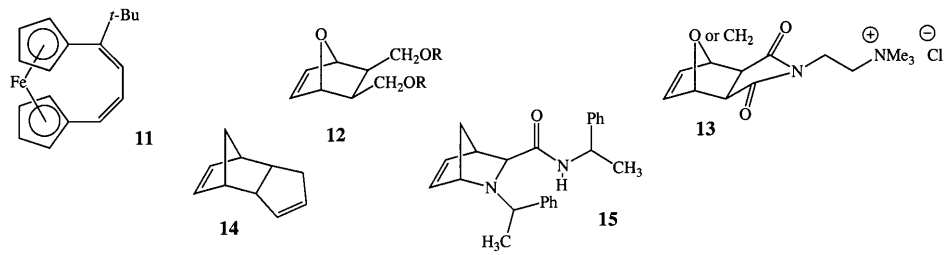
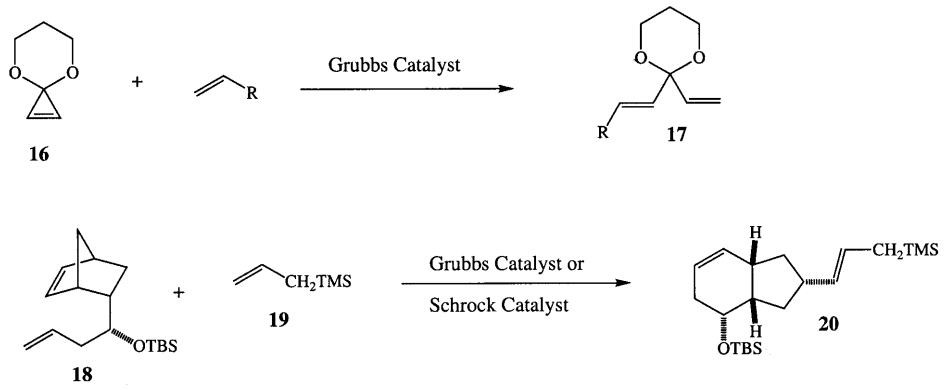
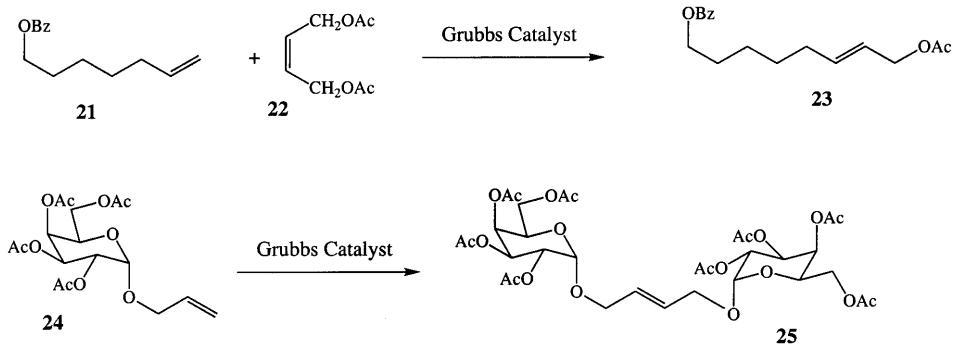


Fig. 3. Representative substrates for the ROMP reaction.



Scheme 3.

gated; diacetoxybutene was the superior source of acetoxyethylidene unit, and highly efficient cross-metatheses were observed using this compound [66]. Metathesis-dimerization of *O*-allyl glycosides (i.e. **24**) using the Grubbs catalyst afforded the dimeric compounds (**25**) in excellent yield as a 5:1 *E*:*Z* mixture [67]. Cross metathesis, RCM, and enyne metathesis were successfully demonstrated for a variety of substrates featuring the β-lactam ring system [68]. A vast combinatorial library was produced by treatment of a mixture of alkenes, including allylbenzene, 4-methyl-1-pentene, 1-hexene, 4-allylcyclopentene, with Grubbs catalyst [69]. A combinatorial library of alkanediamide-linked oligomeric amino acid derivatives was prepared by cross-metathesis of terminal alkenoyl amide derivatives, followed by hydrogenation [70,71]. The acyclic diene metathesis (ADMET) oligomerization reaction of a series of *p*-divinylbenzene derivatives was also reported [72].



Scheme 4.

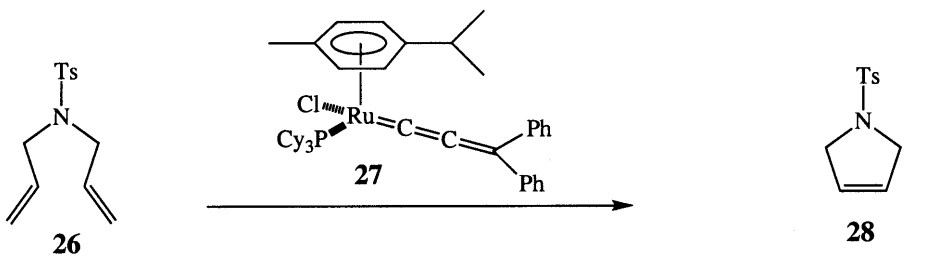
1.2.5. Ring closing metathesis

The ring-closing metathesis reaction (RCM) 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.

Theoretical studies of numerous simple reaction processes, including [2 + 2]-cycloaddition with ethylene, phosphine dissociation, *cis–trans* isomerization, and carbene rotation, were reported for methylenebis(phosphine)ruthenium(II) dichloride, a simple model for the Grubbs catalyst [73].

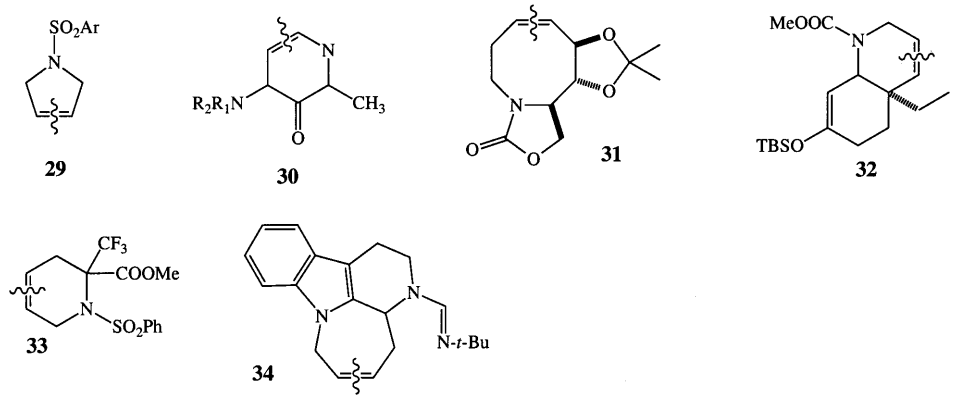
A ruthenium–allenylidene catalyst (**27**, Scheme 5) was prepared and tested in the RCM reaction of diallylsulfonamides (Scheme 5). This readily available catalyst was less reactive than Grubbs catalyst, however both the RCM reaction [74] and the enyne metathesis reaction [75] were highly efficient at 80°C. Water soluble ruthenium complexes for the RCM reaction were prepared using phosphine ligands having polar groups [76].



26 **27** **28**

Scheme 5.

Numerous examples of the formation of nitrogen heterocycles using the RCM reaction were reported in 1998 (Fig. 4, the indicated bond was formed via the RCM reaction). *N*,*N*-diallyl-*N*-arylsulfones afforded the corresponding cyclic sulfonamides (**29**) upon treatment with the Grubbs catalyst [77,78]. A variety of cyclic amides (e.g. **30**) were prepared from the RCM reaction [79,80]. Formation of an eight-membered ring amide (**31**) using the RCM reaction was a key step in the



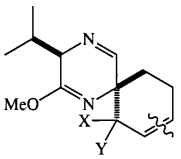
29 **30** **31** **32** **33** **34**

Fig. 4. Representative nitrogen heterocycles prepared via the RCM reaction.

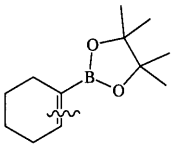
synthesis of the glucosidase inhibitor (+)-australine [81]. Intermediates for the preparation of aspidesperma alkaloids (**32**) were synthesized using the RCM reaction [82]. Cyclic α-amino acids featuring an α-trifluoromethyl group (**33**) were prepared using the RCM reaction [83]. Intermediates for the synthesis of geissoschizine alkaloids (**34**) were prepared using the RCM of allylindole derivatives [84].

The RCM reaction has been employed for the synthesis of a variety of carbocyclic ring systems (Fig. 5, the indicated bond was formed via the RCM reaction). A comparison of the RCM reaction of allylic alcohols (**35**) versus the corresponding enones (**36**) revealed that the allylic alcohols were better substrates for the RCM reaction [85]. In a related study, a comparison of allylic alcohols and the corresponding acetate esters (**37**) in the RCM reaction revealed greater generality for the allylic acetates [86]. Similar systems featuring a hydroxymethyl group in the newly formed ring were also demonstrated [87]. The RCM reaction has successfully been used for the synthesis of cyclic vinylborane derivatives (e.g. **38**) [88,89]. Synthesis of bicyclo[m.n.1] ring systems (e.g. **39**) using the RCM reaction was reported; five- six- and seven-membered rings were prepared in high yield [90]. Various carbohydrate-linked dialkenes were tested in the RCM reaction, which result in carbocycles fused to carbohydrate systems (e.g. **40**) [91]. The reaction was efficient for six-membered ring formation, however the efficacy of five- and eight-membered ring closure was highly dependent of the relative stereochemistry of the alkene substituents and the ring size under construction. The RCM reaction was also employed for the preparation of 4-aminocyclohexene derivatives [92]. The RCM reaction was the key step in the synthesis of cyclic α,β-unsaturated amides from polymer-bound amides linked through an α,β-unsaturated amide [93].

Many examples of oxygen heterocycle synthesis using the RCM reaction were reported in 1998 (Fig. 6, the indicated bond was formed via the RCM reaction). The RCM reaction has been employed for synthesis of: (1) highly oxygenated seven- and eight-membered ring oxygen heterocycles [94], (2) carbohydrate-substituted lactone derivatives (e.g. **41**) (cross-metathesis reactions were also investigated) [95], (3) five- and six-membered ring conjugated lactone derivatives (e.g. **42**) using the Grubbs catalyst and titanium isopropoxide to break up oxygen–ruthenium chelates [96], (4) spiro-fused oxygen heterocycles from *O*-allyl-*C*-allyl glycosides [97] or non-carbohydrate precursors [98], (5) intermediates for brevitoxin/ciguatoxin



35, X = H, Y = OH
36, X,Y = O
37, X = H, Y = OAc



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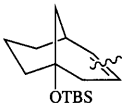

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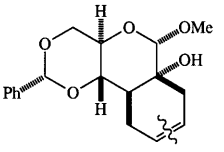

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Fig. 5. Representative carbocyclic rings prepared via the RCM reaction.

synthesis (e.g. **43**) using the RCM reaction [99–101], (6) dihydropyrans using an enol ether as one of the RCM components [102], (7) chromene derivatives (e.g. **45**, Scheme 6) using the molybdenum-catalyzed RCM of *o*-styryl cyclic allylic ethers (**44**) [103]; this reaction was the cornerstone of a stereoselective synthetic route to the anti-hypertensive agent nebivolol [104], (8) chromenes using *o*-styryl acyclic allylic ethers [105], (9) benzoxapins using the RCM of *o*-allylphenyl allyl ethers; synthesis of larger ring systems was less successful [106], (10) intermediates for halichondrin B total synthesis (**46**) using a double RCM reaction of 3,5-bis(homoallyloxy)-1-cyclopentene derivatives (**45**) [107], (11) six-membered ring α,β-unsaturated lactones by the RCM reaction of acrylate esters of homoallylic alcohols [108], (12) synthesis of 2-methoxydihydropyran derivatives [109], and (13) preparation of 2,5-dihydrofurans for the synthesis of muconin [110].

A variety of cyclic phosphonates were prepared from the RCM reaction of alkene-containing phosphonates (Scheme 7) [111]. A preference for cyclizing one

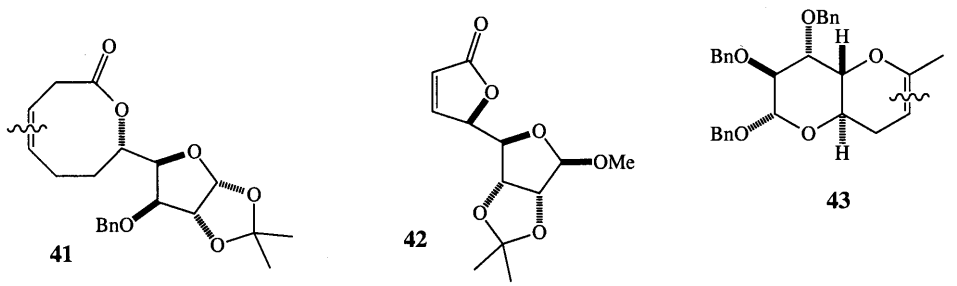
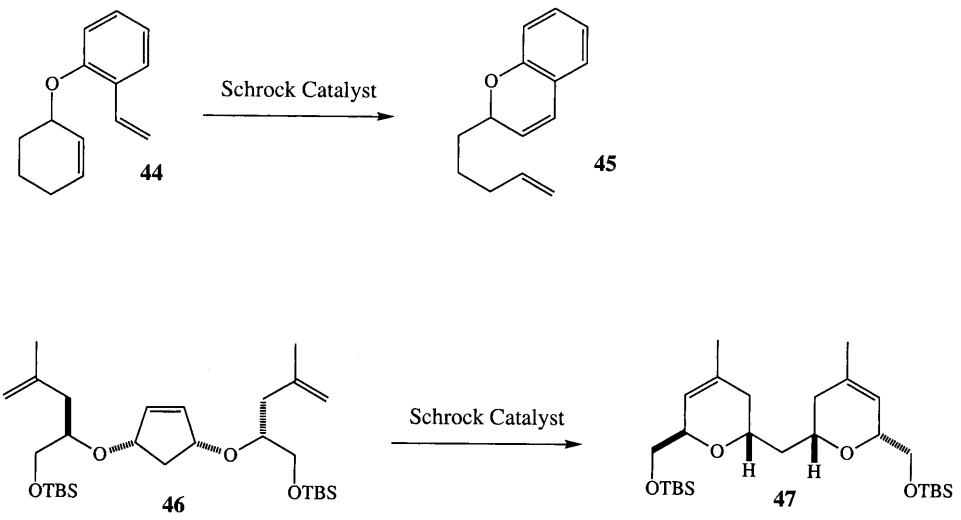
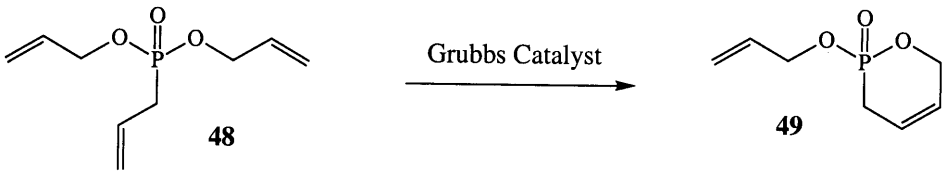


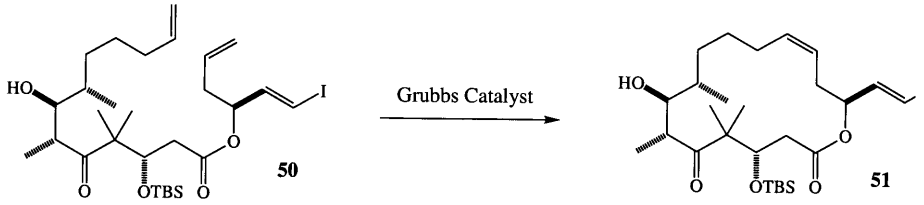
Fig. 6. Representative oxygen heterocycles prepared via the RCM reaction.



Scheme 6.



Scheme 7.



Scheme 8.

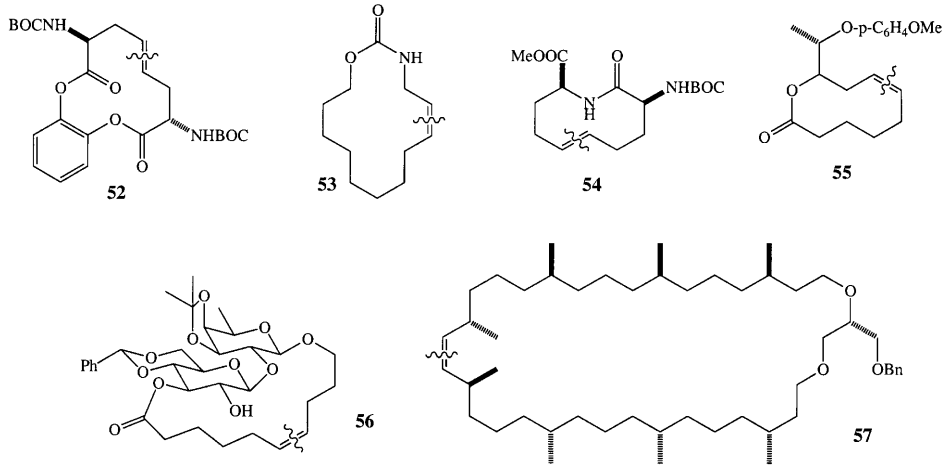


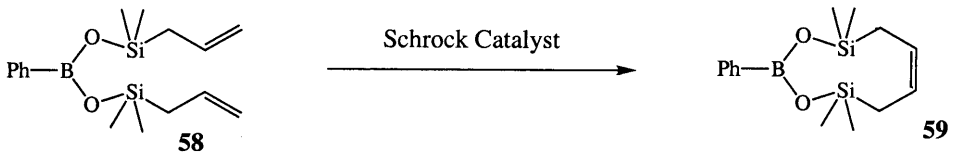
Fig. 7. Representative macrocycles (ring size ≥ 10) prepared using the RCM reaction.

alkene connected to the phosphorous via a carbon and one connected via an oxygen (depicted in Scheme 7 for the conversion of **48** to **49**) was noted.

The RCM reaction was a key step in the total synthesis of the anticancer drug Epothilone A and its derivatives (Scheme 8) [112,113]. The RCM reaction of diene **50** and similar structures afforded Z–E mixtures of the macrocyclic product (e.g. **51**).

Numerous other examples of successful macrocyclic ring closure using the RCM reaction have appeared (Fig. 7, the indicated bond was formed via the RCM reaction). RCM of the catechol-tethered amino acids using the Grubbs-catalyst led to the corresponding macrocyclic amino acid derivatives (e.g. **52**) as a 2:1 mixture

of alkene stereoisomers [114]. A similar RCM of amino acid derivatives using a 1,3-benzenedimethanol tether was also reported [115]. The reaction of urethane-tethered bis alkenes with the Grubbs catalyst resulted in the formation of the macrocyclic urethanes (e.g. **53**) [116]. Synthesis of macrocyclic amides and imides using the RCM reaction was reported; the reaction was claimed as *Z*-selective since the amount of *Z*-isomer was substantially greater than predicted based on theoretical calculations [117]. A peptide β-turn mimic (e.g. **54**) was prepared by RCM of a dimeric α-3-butenylamino acid derivative [118]. The RCM reaction was tested for oligopeptide derivatives featuring *O*-allylated serine or homoserine residues [119]. A variety of papers reported on formation of macrocyclic esters (e.g. **55**) based on the RCM reaction [120,121]. A macrocyclic ester bridged by a disaccharide (**56**) was prepared using the RCM reaction and the Grubbs vinylcarbene catalyst [122]. Calixarene-bridged macrocycles were prepared by the RCM of terminal alkenylalkylcalixarene ether derivatives; the RCM was successful if the alkene and ether are spaced by three methylene units, however ADMET polymerization was a serious competing reaction or shorter tethered derivatives [123]. Macrocyclic membrane lipids (**57**) were prepared using the RCM of glycerol-tethered diterpenyl alkenes; a mixture of the 36-membered RCM product (**57**), accompanied by the cyclic dimer (72-membered ring), and the acyclic dimer was obtained [124,125].



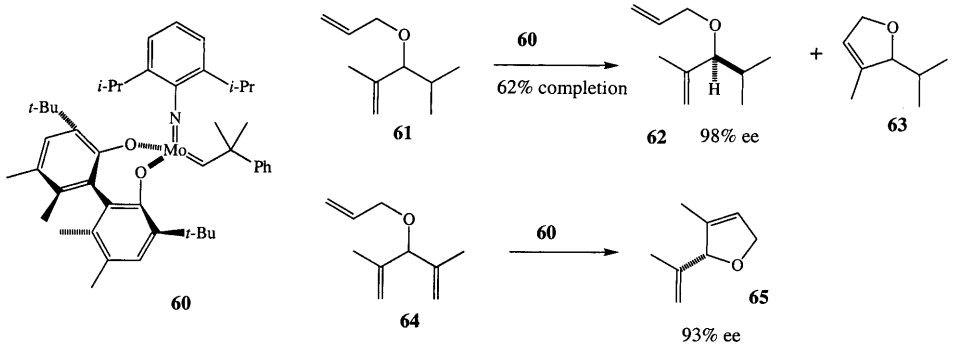
Scheme 9.

In several cases, metallacycles were prepared using the RCM reaction (e.g. **58** → **59**, Scheme 9). The 2-sila-1,3-dioxepene ring system was prepared using the RCM reaction of allylic alcohol–dichlorodiphenylsilane adducts [126]. The RCM of various bis(allylsilyloxy)boranes (e.g. **58**) was reported using the Schrock catalyst [127]. The reaction of diallyl-silanes, phosphines, sulfides, and ethers was accomplished through RCM using a tungsten catalyst [128].

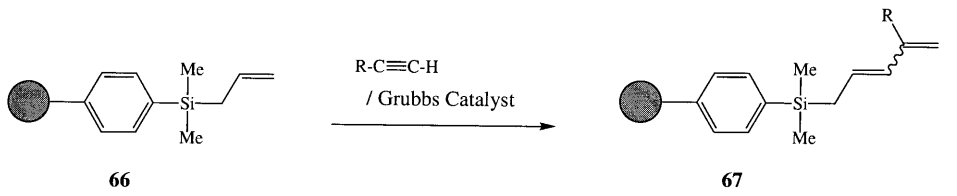
The asymmetric RCM reaction was reported for chiral racemic allylic ether dienes (e.g. **61**, **64**) and homochiral molybdenum catalyst **60** (Scheme 10) [129]. Kinetic resolution of allylic ethers (e.g. **61**) was examined using this catalyst. A very high ee of recovered starting material (98%) were achieved at 63% completion. This catalyst could also effect the enantioselective RCM of allylic ethers containing enantiotopic alkene groups (e.g. **64**) [130]. Other molybdenum carbene complexes featuring chiral ligands were less effective for the kinetic resolution of racemic dienols [131].

1.2.6. Alkene metathesis involving alkyne components

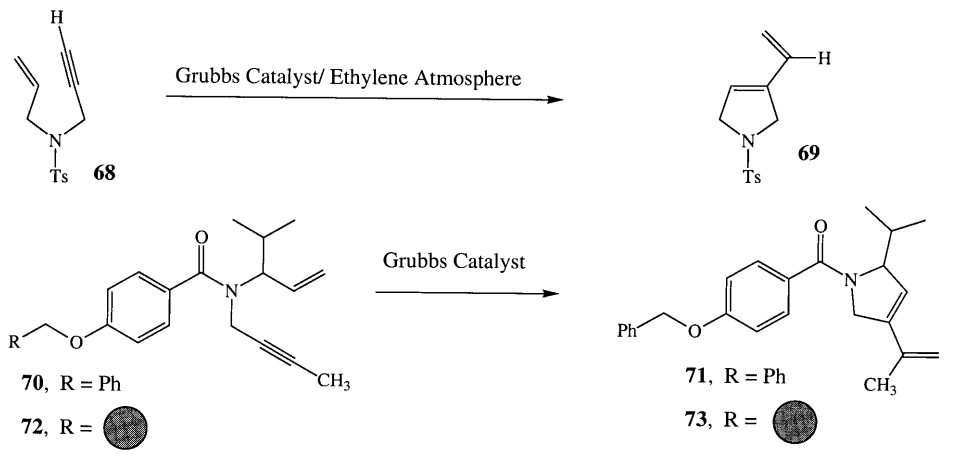
The highly efficient intermolecular enyne metathesis of polymer-bound allylsilanes (**66**, Scheme 11) and terminal alkynes, leading to polymer-bound dienes (**67**)



Scheme 10.



Scheme 11.



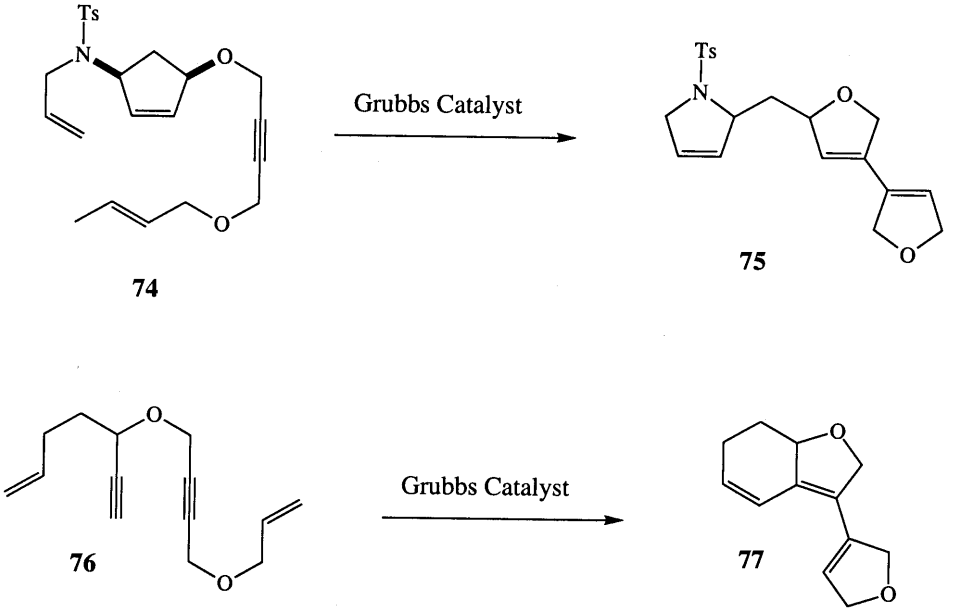
Scheme 12.

was reported [132]. The intermolecular enyne metathesis was also demonstrated for polymer bound alkynes and various monosubstituted alkenes [133].

Several examples of intramolecular enyne metathesis were reported in 1998. Optimal yields of enyne metathesis product for *N*-allyl-*N*-propargyl-*N*-sulfonamide derivatives (e.g. **68**, Scheme 12) and longer tethered analogs were obtained in an

ethylene atmosphere; even terminal alkyne **68** afforded the cyclic diene (**69**) efficiently [134]. Solution and solid phase intramolecular enyne-metathesis reactions were reported for *N*-allyl-*N*-propargylamide derivatives (**70** and **72**), which proceed with similar efficiency [135]. The formation of carbocyclic amino acid derivatives through enyne-metathesis of 2-allyl-2-propargyl-2-amino acid derivatives was reported [136]. Synthesis of oxygen heterocycles containing the brevitoxin/ciguatoxin skeleton was accomplished using enyne metathesis of alkoxyacetylene derivatives [137]. A tandem RCM–enyne metathesis (**74**→**75**, Scheme 13) and double tandem RCM–enyne metatheses (**76**→**77**) of appropriate polyene–polyyne systems afforded multiple ring systems in a single synthetic operation [138]. In a mechanistically related process, the polymerization of terminal alkynes featuring biphenyl groups was accomplished using the Schrock catalyst [139].

Ring closing alkyne metathesis (**78**→**79**, Scheme 14) was demonstrated for a variety of dialkyne derivatives linked by a tether of at least ten atoms using a



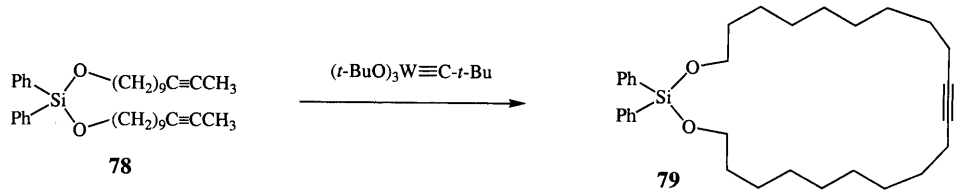
Scheme 13.

tungsten carbyne catalyst [140]. The reaction required high dilution conditions and was restricted to internal alkynes. This is the first example of ring closing alkyne metathesis.

1.3. Individual carbene or alkylidene complexes classified according to metal

1.3.1. Group IV metal–carbene complexes

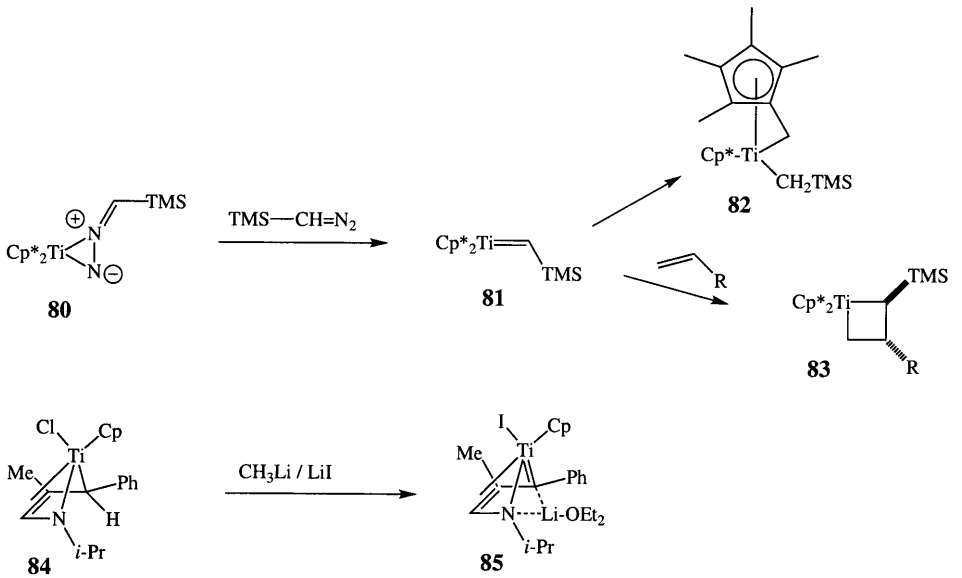
Both isolable titanium–carbene complexes and reactions which involve titanium alkylidene complexes are covered in this section. Routine uses of the Tebbe



Scheme 14.

and related reagents for carbonyl methylenation reactions are not covered in this survey.

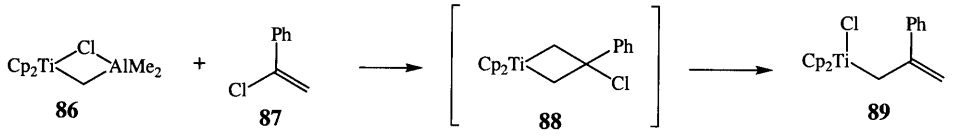
Stable titanium alkylidene complexes (**81**, Scheme 15) were generated from the coupling of titanium(II)–ethylene complexes and trimethylsilyldiazomethane; this coupling initially afforded a stable titanium-diazo complex (**80**), which underwent conversion to the alkylidene complex at 25°C [141]. These complexes underwent coupling with alkenes to generate titanacyclobutanes (**83**); decomposition afforded the intramolecular C–H activation product **82**. Similar reaction processes were reported for aryldiazomethane analogs [142]. Chelated titanium–alkylidene complexes (**85**) were synthesized by deprotonation of 1-azadiene–titanium complexes (**84**) with methyllithium [143].



Scheme 15.

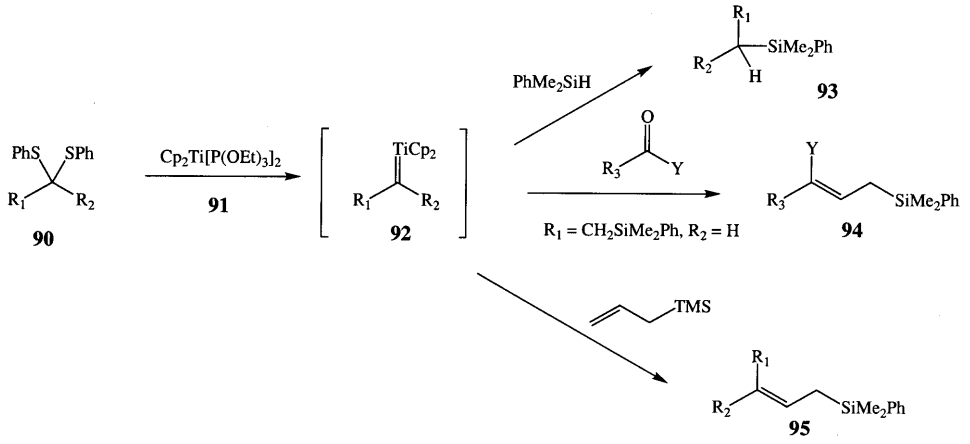
The formation of allyltitanium complexes (**89**, Scheme 16) via the reaction of alkenyl chlorides (**87**) with the Tebbe reagent (**86**) was reported [144]. A mechanism involving [2 + 2] cycloaddition of the alkene titanium–methylene complex, affording titanacyclobutane **88**, followed by β-elimination of chloride was proposed. Dimethyltitanocene was not effective in this transformation; the Lewis acid

byproduct, $AlMe_3$, from the Tebbe reagent is essential in the chloride displacement step.



Scheme 16.

A study of alkene polymerization by the methyltitanocene/methyl aluminoxane catalyst system revealed that methyltitanium and not methylenetitanium complexes were involved in the reaction [145]. A mechanistic proposal suggesting that titanium–alkylidenes are involved in the McMurry coupling reaction was also presented [146].

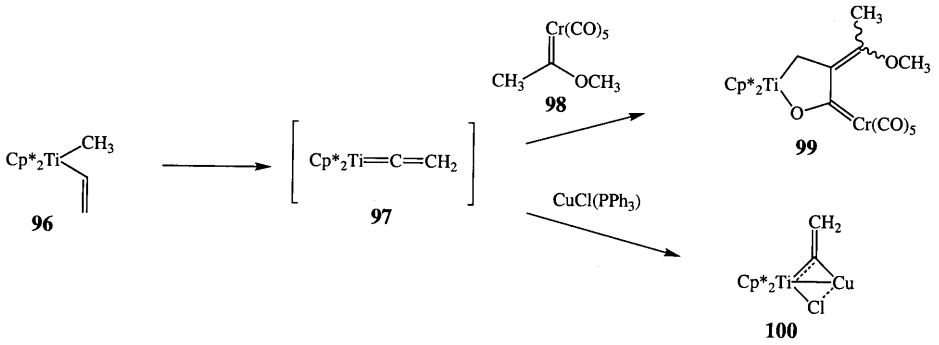


Scheme 17.

Several examples of the formation of titanium alkylidene intermediates (**92**, Scheme 17) from dithioacetals (**90**) and low-valent titanium (**91**) were reported in 1998. Examples include: (1) the synthesis of silanes, germanes and stannanes (e.g. **93**) through coupling of the alkylidene intermediate with Group IV metal hydrides [147], (2) the synthesis of allylsilanes (**94**) via coupling of the α-silylalkylidene intermediates with aldehydes, ketones, esters, or thioesters [148], (3) syntheses of allylsilanes (**95**) via a metathesis process involving dithioacetal-derived titanium alkylidenes and allyltrimethylsilane [149], (4) the synthesis of alkylidenecyclobutanes from the coupling of cyclobutanone thioketal with carbonyl compounds in the presence of titanium(II) species [150], and (5) the synthesis of enol ethers and vinylic sulfides by coupling of orthodithioester derivatives with carbonyl compounds [151].

Titanium vinylidene complexes (e.g. **97**, Scheme 18), generated in situ from decomposition of divinyltitanium species or alkyl–vinyltitanium species (**96**), have

been studied. A heterobimetallic complex featuring an vinylidene ligand bridging titanium and copper (**100**) was prepared by decomposition of a (methyl)-vinyltitanium species in the presence of copper(I) salts [152]. Coupling of titanium vinylidene complexes with Fischer alkoxycarbene complexes (**98**) led to the oxametallacyclic Fischer carbene complexes (**99**), however the analogous reaction with aminocarbene–chromium complexes failed [153]. Titanium vinylidene complexes were successfully trapped by reaction with imines and carbodiimides, leading to 4-methylene-2-azatitanacycles [154]. Attempts to trap titanium–vinylidene intermediates as titanacyclobutenes via coupling with alkynes failed [155]. Coupling of titanium vinylidene intermediates with imines afforded alkenyltitanium–imine complexes [156].

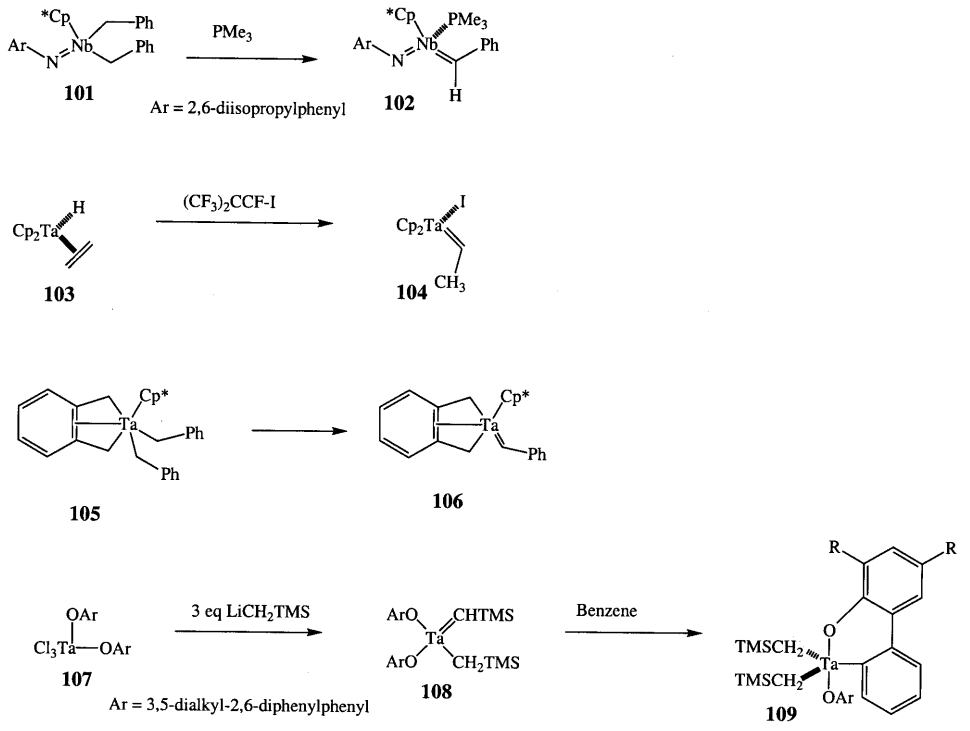


Scheme 18.

1.3.2. Group V metal–carbene complexes

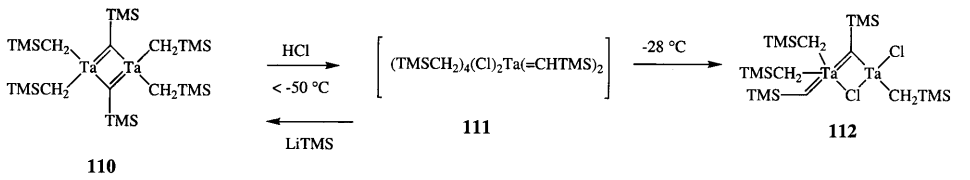
Several papers emphasizing the synthesis of Group V metal–carbene complexes appeared in 1998, and most of these papers focus on tantalum carbene complexes. Newly synthesized Group V metal–carbene complexes are depicted in Scheme 19. A niobium–benzylidene complex (**102**) was prepared via α-hydride elimination/reductive elimination form dibenzylcomplex **101** in the presence of trimethylphosphine [157]. Tantalum–ethylidene complex **104** was prepared from the reaction of tantalum–ethylene complex **103** with secondary perfluoroalkyl iodides [158]. An electron-transfer mechanism was proposed.

Several studies emphasizing the reactivity of tantalum–alkylidene complexes appeared in 1998. Stable tantalum–alkylidene complexes (**106**) were prepared from decomposition of dibenzyltantalum complexes (**105**) at 20°C, and tested as ROMP catalysts; in some cases, dialkyltantalum species which did not form stable tantalum alkylidenes were still effective as ROMP catalysts [159]. A theoretical study of the tantalum(I)-catalyzed conversion of methane/carbon dioxide to acetic acid suggested that cationic alkylidene–tantalum(I) complexes are intermediates in this process [160]. Tantalum–alkylidene complexes (**108**) were prepared from treatment of bis(3,5-dialkyl-2,6-diphenylphenoxy)trichlorotantalum(V) derivatives (e.g. **107**) with three equivalents of trimethylsilyllithium [161]. When no alkyl group was



Scheme 19.

present at the 3- and 5-positions of the aryloxy ligand, intramolecular C–H activation occurred, leading to complex **109**; the rate of this process was slower for complexes featuring alkyl groups at the 3- and 5-positions.



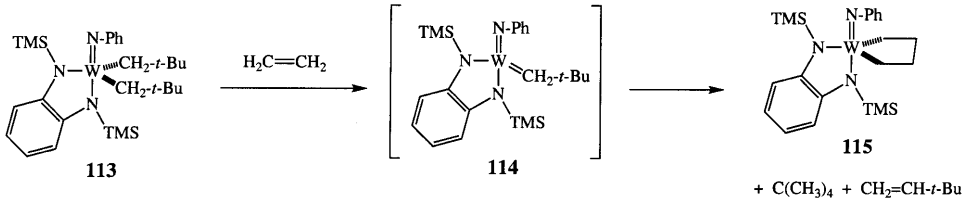
Scheme 20.

The reaction of tantalum bis bringing alkylidene complexes (**110**, Scheme 20) with HCl afforded an unstable monomeric complex (**111**), which reformed an alkylidene-bridged dimeric complex upon warming above − 28°C or upon exposure the trimethylsilyllithium [162].

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

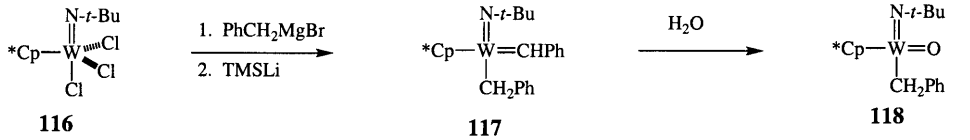
1.3.3.1. Schrock-type carbene complexes. A significant portion of this subject material has already been presented in the alkene metathesis section; the Schrock catalyst belongs to this class.

Group VI metal–alkylidene complexes were proposed as intermediates in the decomposition of several alkyl–metal complexes. In the reaction of tungsten–imido complex **113** (Scheme 21) with ethylene, tungsten–alkylidene complex **114** was proposed as an intermediate in eventual conversion to metallacyclopentane complex **115**, neopentane, and 3,3-dimethyl-1-butene [163]. Chromium–alkylidene complexes were proposed as intermediates in the decomposition of alkylchromium(III) complexes [164] and alkylchromium(IV) complexes [165,166]. Molybdenum–alkylidenes were proposed as intermediates in the polymerization of alkynes by molybdenum hexacarbonyl/phenol and in the addition of phenol to alkynes [167].



Scheme 21.

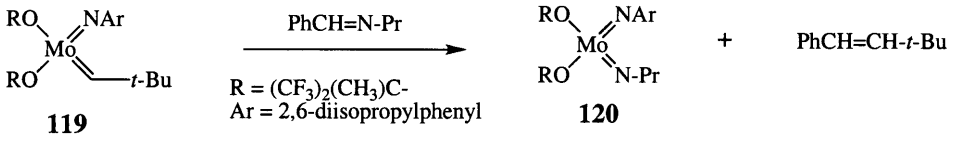
The tungsten(IV) alkylidene complex **117** (Scheme 22) was prepared by treatment of the corresponding trichloride complex **116** with excess benzyl Grignard reagent followed by trimethylsilyllithium [168]. Treatment of **117** with water led to replacement of the alkylidene ligand by an oxo ligand (complex **118**), accompanied by formation of toluene. Molybdenum–carbene–oxo complexes were prepared through the reaction of hydrido-molybdenum complexes and arylacetylenes; the oxo ligand was thought to arise from a water impurity [169].



Scheme 22.

The Schrock carbene complex and derivatives (e.g. **119**, Scheme 23) underwent reaction with imines to afford diimido-molybdenum complexes (**120**) and alkenes [170]. These complexes also served as catalysts for metathesis of imines.

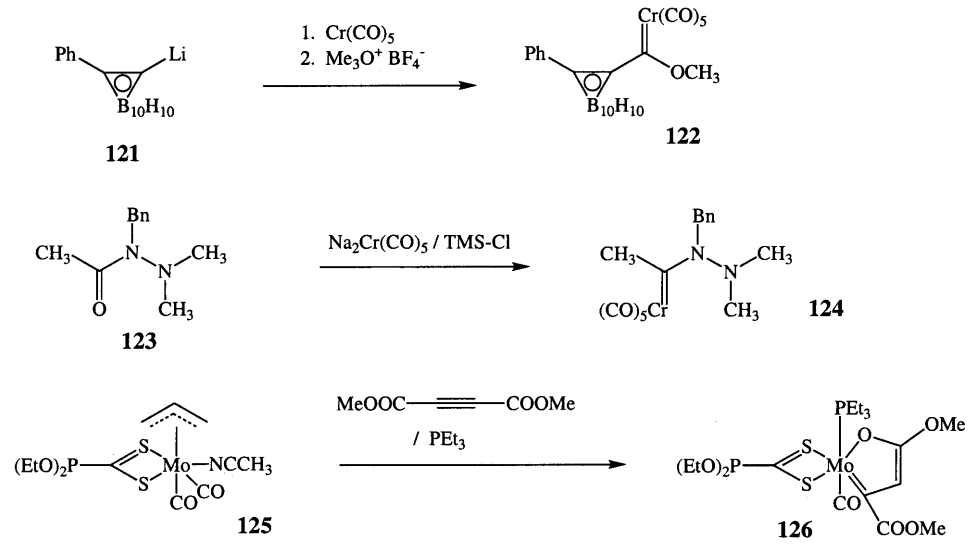
A theoretical study was undertaken involving the [2 + 2]-cycloaddition of ethylene and various compounds containing a molybdenum–element double bond [171]. The cycloaddition was most favorable for the Mo=Si system ($\Delta H = -24.1$ kcal



Scheme 23.

mol^{-1}) followed by the Mo=C system ($\Delta H = -15.6$ kcal mol^{-1}). Cycloadditions of molybdenum oxo compounds (Mo=O) were least favorable ($\Delta H = +12.0$ kcal mol^{-1}). A theoretical study comparing structural aspects of Fischer carbene and Schrock carbene complexes of tungsten [$(CO)_5W{=}CH_2$ vs. $(CO)_5W{=}CHOH$ vs. $X_4W{=}CH_2$] was also reported [172]. The Fischer carbene complexes featured a lower bond order in the tungsten–carbon bond; the carbene ligand in Fischer carbene complexes is better σ-donor but poorer π-acceptor than a carbonyl ligand.

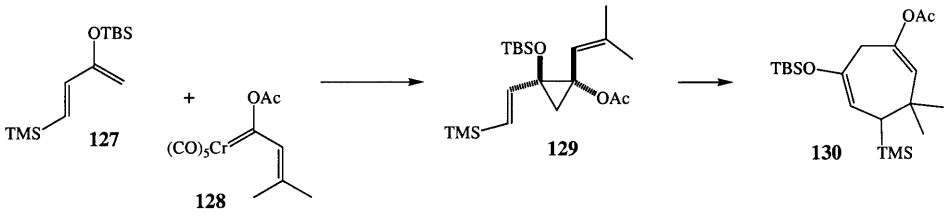
1.3.3.2. Publications focusing on synthesis of Fischer carbene complexes of Group VI metals. The most common procedure used for the synthesis of Group VI metal–carbene complexes is the Fischer synthesis, which involves coupling of an organolithium reagent with a Group VI metal carbonyl derivative, followed by alkylation of the resulting acylate. Novel carboranyl-substituted chromium- and tungsten carbene complexes (e.g. **122**, Scheme 24) were synthesized by this route [173]. Another well established route is through the reaction of chromium pentacarbonyl dianion with either acid chlorides or in situ-generated chloroimines. Examples of carbene complexes synthesized using this route include hydrazino complexes (e.g. **124**) [174], which were formed as configurationally stable *E*- and *Z*-isomers owing



Scheme 24.

to hindered rotation about the carbene carbon–nitrogen bond; carboethoxy-substituted carbene complexes were also prepared using this method [175]. Other less common procedures for the synthesis of Group VI metal–carbene complexes were also reported in 1998. The molybdenum carbene complex **126** was prepared from the coupling of allylmolybdenum complex **125** with dimethyl acetylenedicarboxylate, followed by triethylphosphine [176].

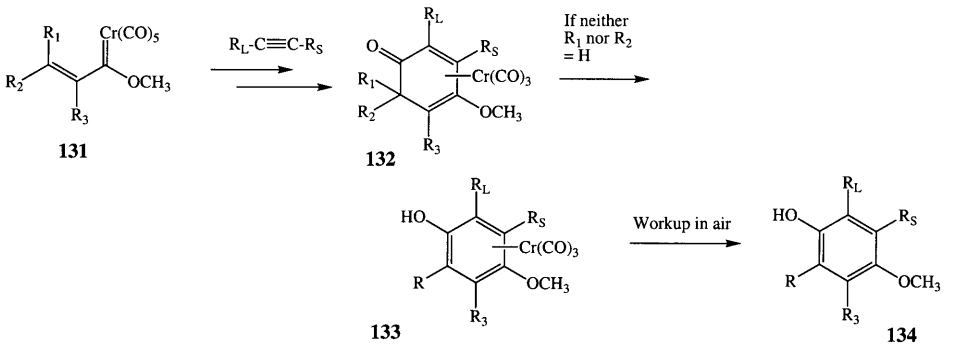
1.3.3.3. Reaction of Group VI metal–carbene complexes with alkenes and dienes. This section focuses on reactions of Group VI metal–carbene complexes which involve coupling with alkenes at the carbene–carbon. Other examples of the coupling of carbene complexes with alkenes where the reactive site is elsewhere can be found under the heading: cycloaddition reactions occurring at the C–C π-bond of α,β-unsaturated metal–carbene complexes (Section 1.3.3.7). Cyclopropanation is a common reaction pathway for the coupling of Fischer carbene complexes with polarized alkenes. Cyclopropanation was observed in the coupling of electron-rich dienes (e.g. **127**, Scheme 25) with (acetoxy)vinylcarbene–chromium complexes (**128**); the resulting divinylcyclopropanes (**129**) were transformed to cycloheptadiene derivatives (**130**) by mild thermolysis [177]. Chromium carbene complexes were identified as intermediates (by spectroscopy) in the (cyclooctene)$Cr(CO)_5$-catalyzed cyclopropanation of alkenes by diaryldiazo compounds [178].



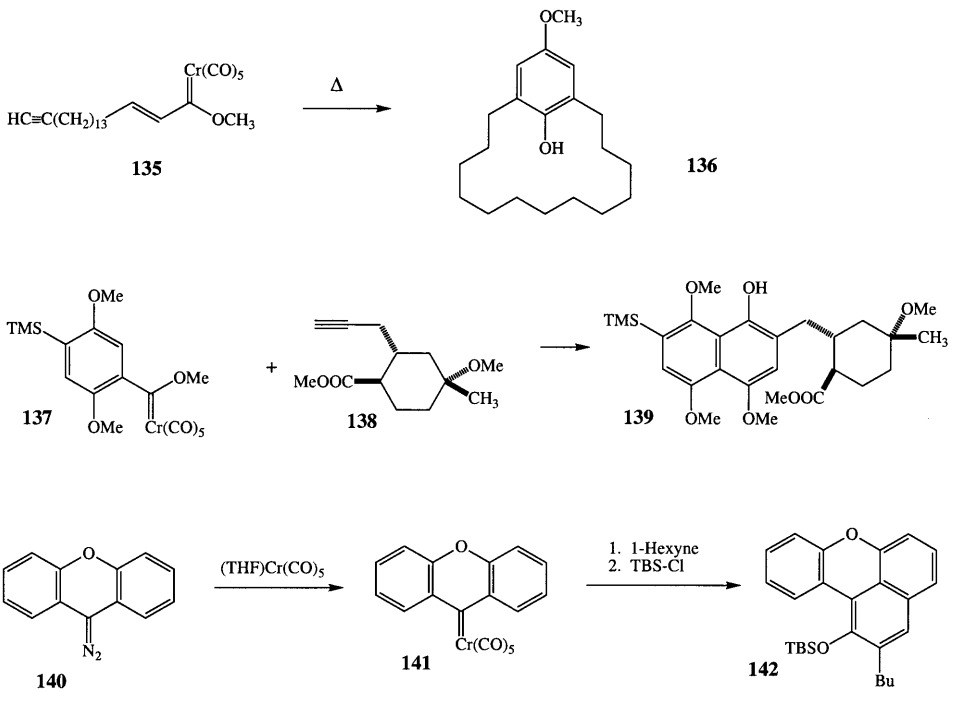
Scheme 25.

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 (e.g. **131**, Scheme 26) and alkynes (commonly known as the Dötz reaction) were reported in 1998. The general reaction equation is depicted in Scheme 26; specific examples are depicted in Scheme 27. Examples include: (1) coupling of alkynes and cyclic α-oxygenated-β-chloro-α,β-unsaturated carbene complexes (which are readily available and more stable than the non-chlorinated analogs) [179,180], (2) coupling of alkynes with chiral *m*-cyclophanylcarbene complexes, which afforded naphthol–chromium complexes with a moderate degree of stereocontrol [181], (3) intramolecular coupling of alkynes and alkenylcarbene featuring 6-atom and 13-atom tethers (**135**, Scheme 27), which afforded m-cyclophanes (**136**) exclusively employing the 13-atom tether, and mostly dimeric cyclophanes using the six-atom tether [182], (4) synthesis of *C*-aryl glycosides via the coupling of alkynylglycals with arylcarbene–chromium complexes [183], (5)

synthesis of the carbon core of menogaril (**139**) through coupling of arylcarbene complex **137** and an elaborate alkyne (**138**) in acetonitrile [184], (6) benzannulation reactions involving non-heteroatom-stabilized chromium carbene complexes (e.g. **141**) [185], (7) benzannulation reactions using cyclooctyne [186], and (8) benzannulations using cyclic carbene complexes featuring an exocyclic alkene [187].



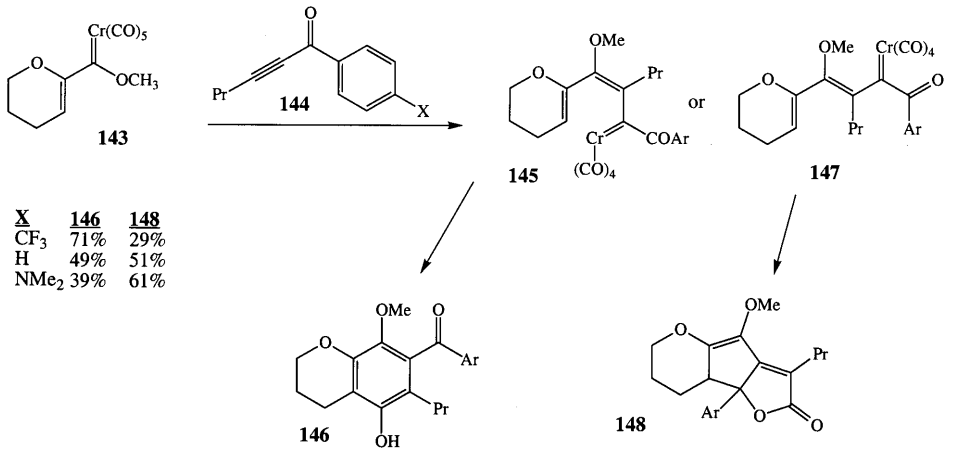
Scheme 26.



Scheme 27.

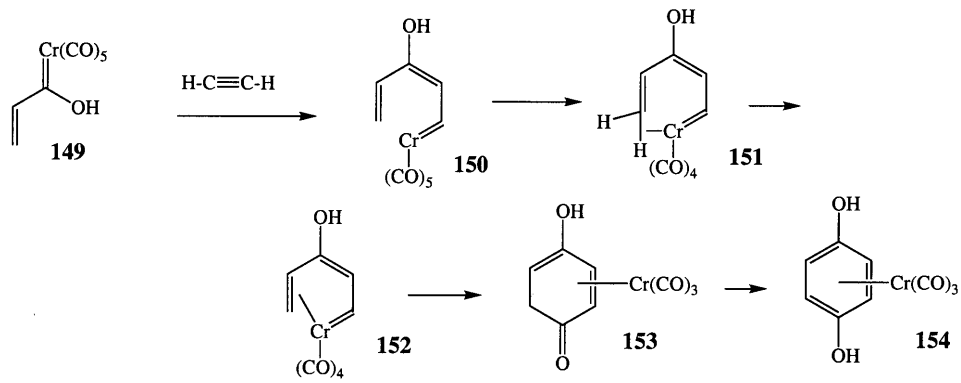
A detailed study of electronic effects in an early step of the Dötz benzannulation, vinylcarbene complex (**145** and **147**, Scheme 28) formation, was conducted [188].

The reaction of alkenylcarbene complex **143** and the aroylacetylene **144** afforded mixtures of the benzannulation product **146** (from the *Z*-vinylcarbene complex **145**) and the van Halban–White product **148** (from the *E*-vinylcarbene intermediate **147**). The electron-density of the aromatic ring had a profound effect on this product distribution. Electron-donating groups favored the benzannulation product due to a preference for *trans* orientation of the methoxy and the more electron-withdrawing substituent at the α-carbon in **145** and **147**. A similar electronic dependence was also noted for aryloxycarbene complexes.



Scheme 28.

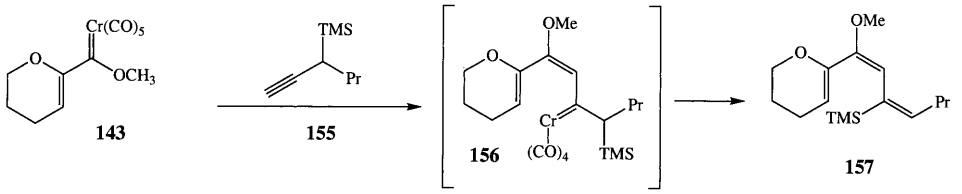
A theoretical study of the conversion of alkenylcarbene–chromium complexes to phenols (the Dötz benzannulation reaction) was undertaken [189]. The authors proposed that the lowest energy pathway available (Scheme 29) for this transformation involves initial [2 + 2]-cycloaddition of the alkyne and the coordinatively saturated pentacarbonylcarbene complex; this suggestion is contrary to the gener-



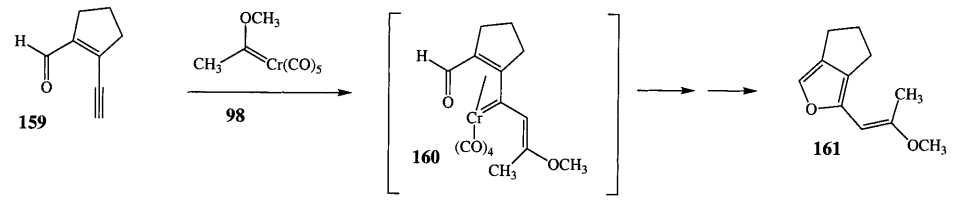
Scheme 29.

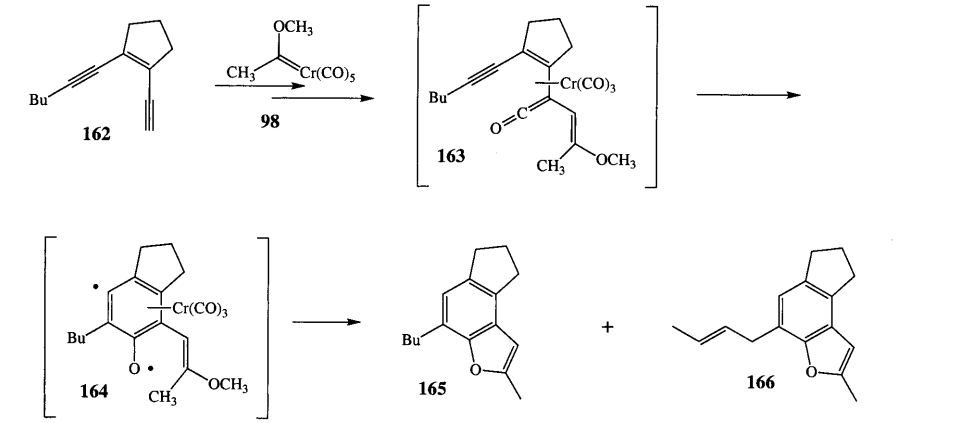
ally accepted mechanism for this transformation, which involves CO-dissociation as the initial step. In a related paper, the authors also suggested that the dienylcarbene intermediate of the Dötz benzannulation reaction features an agostic interaction between chromium and the δ-C–H bond (**151**) [190].

1.3.3.5. Nonbenzannulation reactions of Group VI metal–carbene complexes with alkynes. The coupling of α,β-unsaturated carbene complexes (e.g. **143**, Scheme 30) with propargylsilanes (**155**) resulted in the formation of 1,3,5-triene derivatives (**157**) [191]. The competing Dötz benzannulation reaction was a minor reaction pathway in this coupling.



Scheme 30.

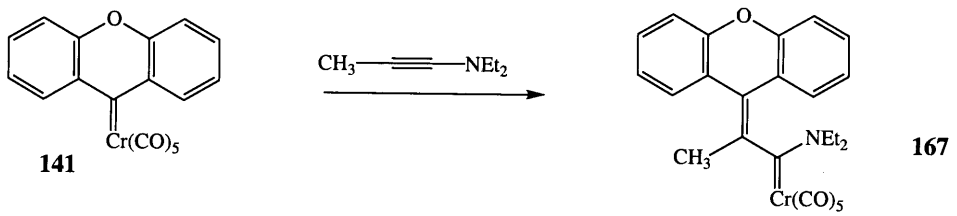




Scheme 31.

The reaction of Fischer carbene complexes with highly conjugated acetylene derivatives was explored. The reaction of methylcarbene complex **98** (Scheme 31) with enyne–aldehydes (**159**) and enyne–ketones led to vinylfuran derivatives (**161**) [192]. A mechanism involving nucleophilic attack of the carbonyl oxygen at the carbene carbon the vinylcarbene complex intermediate **160** (forming a carbonyl ylide) followed by demetallation was proposed. Coupling with conjugated enediyne derivatives (e.g. **162**) led to benzannulation products (**165** and **166**) via a diradical mechanism [193]. Formation of the major product **166** involves Moore cyclization of enyne–ketene intermediate **163**, followed by sequential intramolecular hydrogen atom transfers from intermediate diradical **164** to give an enol ether–phenol, which is converted to the benzofuran derivative **166** during workup. Reaction of diradical **164** with an external hydrogen atom source (the solvent dioxane) leads to butyl derivative **165**. The initially formed diradical could also be captured in a radical cyclization reaction.

A variety of non-heteroatom-stabilized carbene complexes (e.g. **141**, Scheme 32) were prepared from diazo compounds and pentacarbonyl(1,5-cyclooctadiene)chromium(0), and coupled with ynamines or alkoxyacetylenes to give heteroatom-stabilized alkenylcarbene complexes (e.g. **167**) [194]. Similar reactions using ethyl diazoacetate afforded either *O*-bound ester complexes or *N*-bound diazo complexes [195].

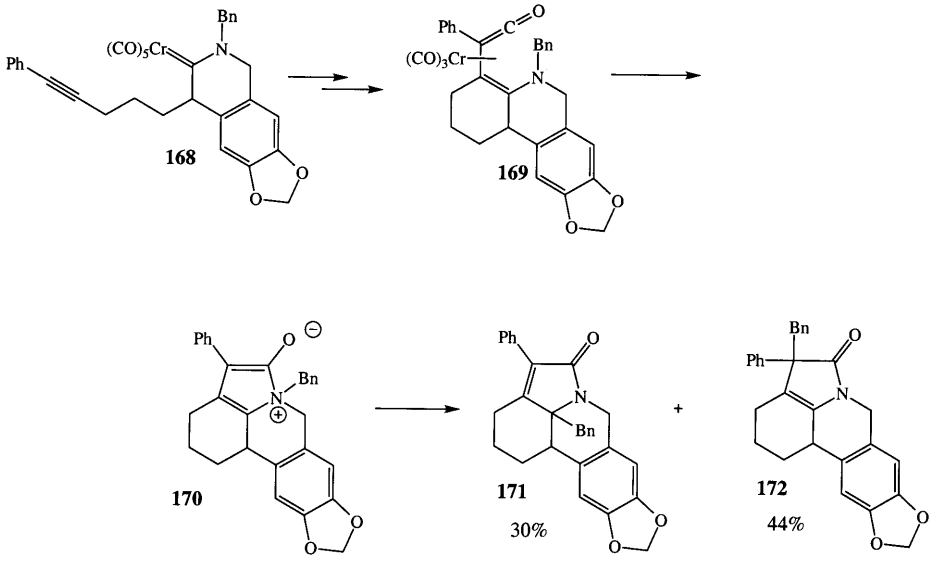


Scheme 32.

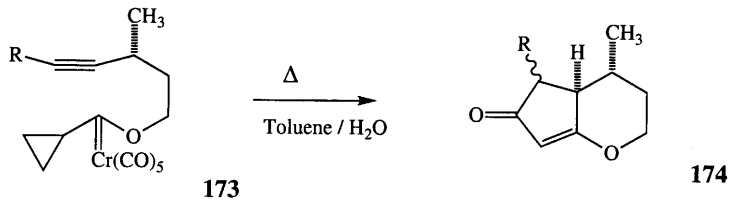
A variety of pyrrolidone derivatives (e.g. **171** and **172**, see Scheme 33) were prepared from the coupling of aminocarbene–chromium complexes with alkynes [196,197]. The reaction proceeds via alkyne insertion, followed by CO insertion and formation of an ylide (**170**) by nucleophilic attack of the nitrogen at the ketene carbon. A 1,2- or 1,4-alkyl shift then leads to the observed products. Trapping of the vinylketene intermediates in the reaction of carbene complexes with alkynols was also reported [198].

The intramolecular cyclopentannulation reaction (Scheme 34) of alkynes and cyclopropylcarbene–chromium complexes, which feature a propargylic stereocenter, afforded cyclopentapyran derivatives (e.g. **174**) with a high degree of stereocontrol at the ring fusion [199]. One of the examples was later transformed into an intermediate for vitamin D_3 synthesis.

1.3.3.6. Photolysis reactions of Group VI metal–carbene complexes. Several publications concerning the formation of chromium ketene complexes (e.g. **176** and **179**,



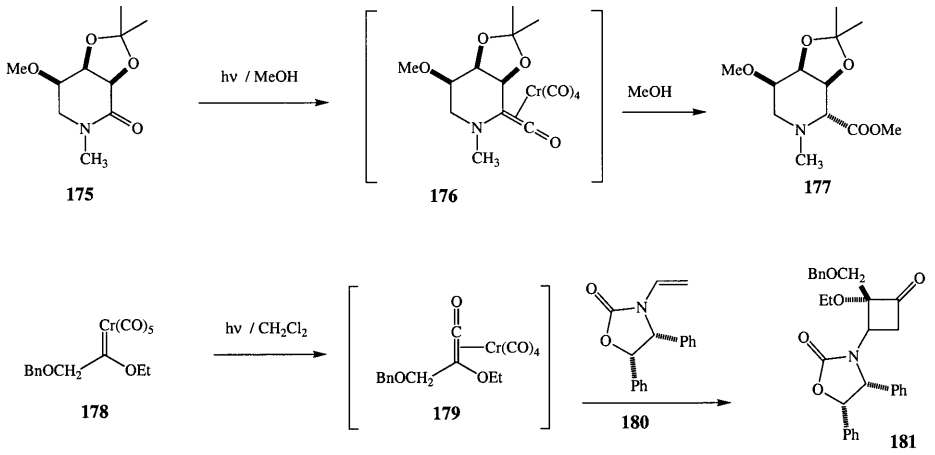
Scheme 33.



Scheme 34.

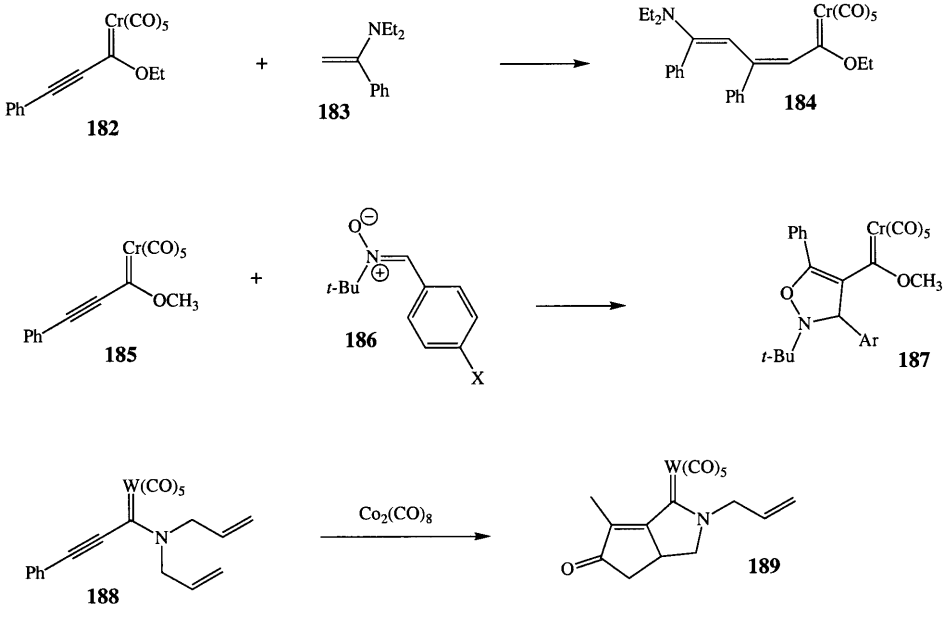
Scheme 35) through photolysis of Fischer carbene–chromium complexes appeared in 1998. Photolysis of carbohydrate-derived aminocarbene complex **175** leads to the chain-extended carbohydrate derivative **177** after trapping of the initially generated ketene complex (**176**) with methanol [200]. Photolysis of cyclic carbene complexes in the presence of homochiral enamides (e.g. **180**) afforded the expected cyclobutanone derivatives (**181**) with a high degree of diastereoselectivity; these were later transformed to the spiroketals [201] or cyclobutane nucleosides [202]. Photolysis of carbene complexes tethered to electron-rich aromatic rings afforded products resulting from intramolecular Friedel–Crafts reaction of the ketene intermediates [203].

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 carbene complex is a surrogate for an 'activated ester') were reported in 1998. The



Scheme 35.

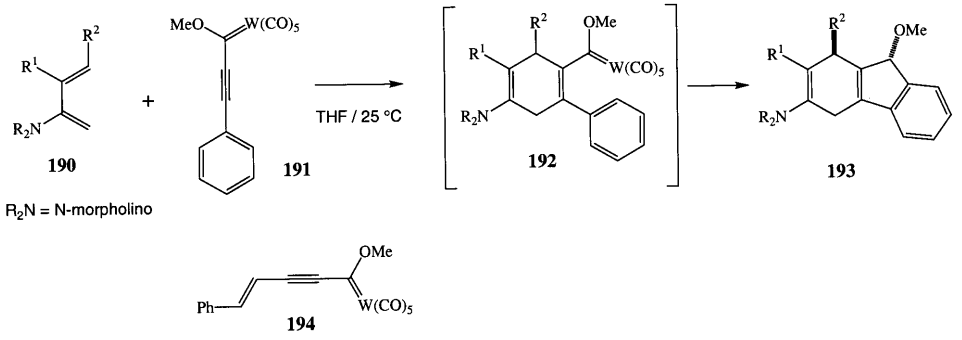
following reaction processes (Scheme 36), in which the carbene complex functionality survives the reaction, were reported for α,β-unsaturated Group VI metal–carbene complexes: (1) coupling of enamines (e.g. **183**) with alkynylcarbene complexes (e.g. **182**), leading to 5-amino-α,β,γ,δ-unsaturated carbene complexes (**184**) [204,205], which in some cases cyclize to cyclopentadiene derivatives, (2) the stereoselective 1,3-dipolar cycloaddition reaction of nitrilimines with optically active



Scheme 36.

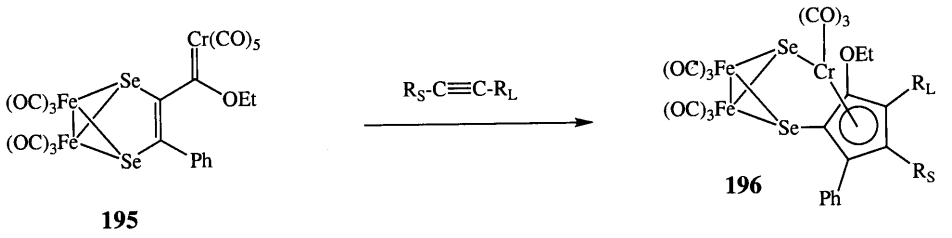
α,β-unsaturated carbene complexes [206], (3) the 1,3-dipolar cycloaddition reaction of nitrones (**186**) with alkynylcarbene–chromium and –tungsten complexes [207], (4) the imino Diels–Alder reaction of alkynylcarbenes and 1-azadienes, which was accompanied by [2 + 2]-cycloaddition of the resulting enamine with a second equivalent of carbene complex [208], (5) addition of cyclic iminoesters to alkynylcarbene complexes, which afforded β-amino-α,β-unsaturated carbene complexes; in the case involving a dihydropyrrole derivative, a second mole of alkylcarbene added to the resulting enamine in a [2 + 2] manner [209], (6) Pauson–Khand reactions of (diallylamino)alkynylcarbene–tungsten complexes (e.g. **188**) [210], (7) Diels–Alder reactions of (boroxy)α,β-unsaturated carbene–chromium and –tungsten complexes [211], (8) extremely facile solution-phase *E*–*Z* isomerizations of β-amino-α,β-unsaturated carbene complexes [212], and (9) reaction of alkynylcarbene–chromium and tungsten complexes with urea derivatives, which afforded 2-pyrimidone-6-ylidene complexes after Michael addition and intramolecular heteroatom exchange [213].

In many cases, the reaction of 1,3-dienes and alkenylcarbene complexes produced other compounds in addition to simple Diels–Alder adducts (Scheme 37). The reaction of phenylethynylcarbene–chromium complexes (e.g. **191**) and 2-aminodienes (**190**) afforded products resulting from cyclopentannulation reaction (**193**) of the initial Diels–Alder adducts (**192**) [214,215]. In the alkenylethynyl analogs (e.g. **194**), the cyclopentadienes analogous to **193** could not be isolated owing to rapid Diels–Alder reaction with the starting carbene complex.



Scheme 37.

Further studies of trimetallic carbene complexes (e.g. **195**, Scheme 38), derived from the cycloaddition reaction between iron-bridging chalcogenide complexes and alkynylcarbene–chromium and –tungsten complexes were reported. Reaction with alkynes afforded the corresponding cyclopentadienyl complexes (**196**) [216]. Thermolysis in THF (no alkyne) afforded a similar type of chelated cyclopentadienyl complex [217,218]. Novel heterobimetallics linked through alkynylcarbene units were prepared by the coupling of ethynylcarbene complexes with various transition metal salts [219].



Scheme 38.

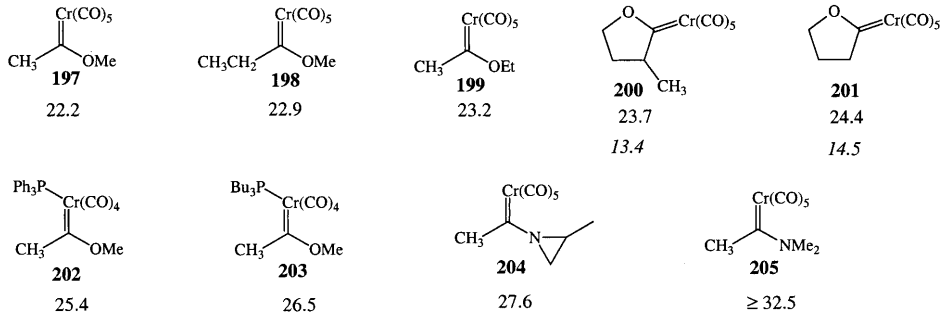
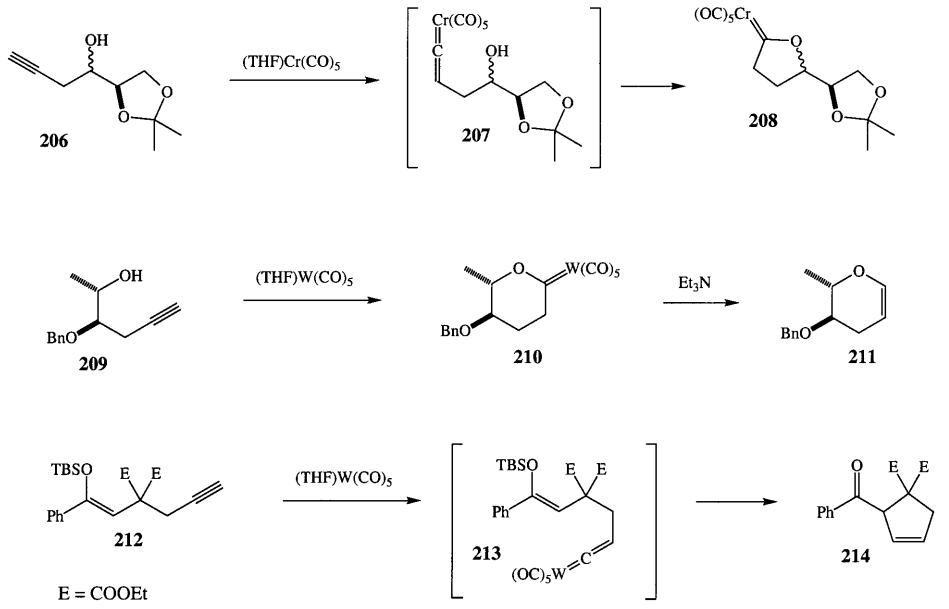


Fig. 8. Experimentally determined pK_a values for Fischer carbene complexes in acetonitrile (numbers in italics are for pK_a values determined in 50:50 water:acetonitrile).

1.3.3.8. Physical organic chemistry of Group VI Fischer carbene complexes. A detailed study of the thermodynamic and kinetic acidity of various Fischer carbene complexes was determined in 50:50 water:acetonitrile and in pure acetonitrile (see Fig. 8). A comparison of cyclic carbenes **200** and **201** revealed that the alkylated complex **200** was more acidic (pK_a 13.41 vs. 14.47). The enhanced acidity of complex **200** was attributed to the greater stability of the double bond obtained by deprotonation [220]. The pK_a of a variety of carbene complexes was determined in pure acetonitrile solvent; including some (**202**–**205**) which are not acidic enough to be measured in water. In most cases the pK_a was about 10 pK_a units higher in pure acetonitrile than when measured in 50:50 water:acetonitrile [221].

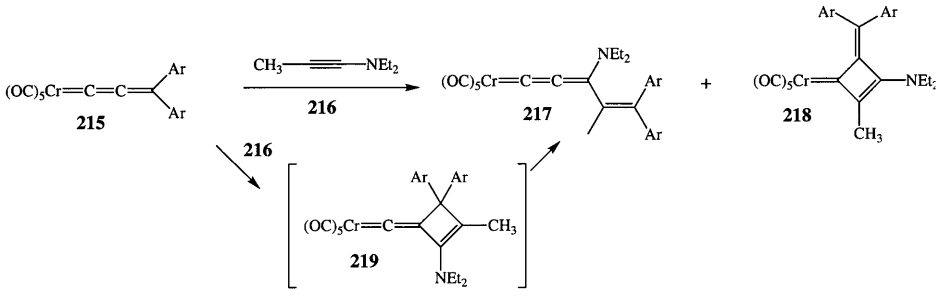
1.3.3.9. Synthesis and reactivity of Group VI metal–vinylidene complexes, and reactions which involve vinylidene–metal complexes as intermediates. Many examples of the coupling of alkynols with Group VI metal pentacarbonyl sources were reported in 1998 (Scheme 39). The general reaction pathway followed in these couplings is conversion of the alkyne to a metal–vinylidene complex (e.g. **206** → **207**), followed by intramolecular nucleophilic attack of the alcohol at the carbene carbon to generate a Fischer carbene complex (**208** or **210**). This conversion was reported for chiral auxiliary-substituted alkyne–alcohols (**206**) [222]. The cyclic carbene complexes were subsequently converted to the corresponding alkenylcarbene complexes via aldol-like processes, which underwent stereoselective Diels–Alder reactions directed by the chiral auxiliary. Highly oxygenated alkynol

derivatives (e.g. **209**) were converted to the corresponding glycal derivatives (**211**) by reaction with pentacarbonyl(THF)tungsten(0) followed by conversion of the carbene complex (**210**) to an alkene using triethylamine [223]. Iterative use of this reaction process provided an entry into ring systems present in brevitoxins and ciguatoxins [224]. The intramolecular capture of intermediate vinylidene–tungsten complexes (**213**, Scheme 40) with enol ethers resulted in cyclopentene derivatives (e.g. **214**) [225].



Scheme 39.

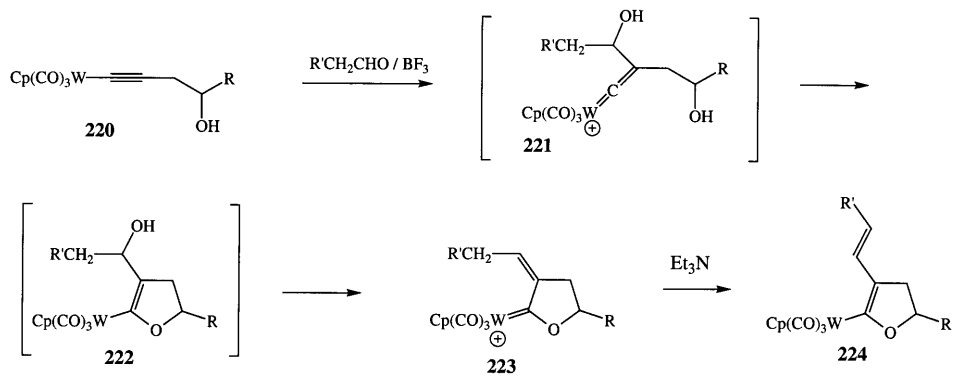
The reaction of allenylidene–tungsten and –chromium complexes (e.g. **215**, Scheme 40) with ynamine **216** was investigated [226]. In most cases, the alkenylvinylidene complex (**217**) was the major product, accompanied by the cyclobutenylidene complex (**218**). Complex **217** was proposed to arise from [2 + 2]-



Scheme 40.

cycloaddition at the β,γ C–C double bond followed by ring opening, while **218** is the [2 + 2]-cycloaddition product involving the α,β C–C double bond. Similar studies of longer cumulene complexes were undertaken [227]. The [2 + 2]-cycloaddition of chromium–vinylidene complexes and alkynyliron complexes was also reported [228].

Group VI metal–vinylidene complexes were also generated via electrophilic attack on alkynyl–metal complexes at the β-position (Scheme 41). The reaction of aldehydes and alkynyltungsten complexes featuring a homopropargyl alcohol group (**220**) afforded α-alkylidene-cyclic carbene complexes (**223**), which were deprotonated with triethylamine to provide η^1-dienylmetal complexes (**224**) [229]. Initiation of similar chemistry via intramolecular Lewis acid-catalyzed coupling of acetals and alkynyltungsten complexes was also reported [230]. Electron-rich benzylethynyltungsten complexes [$ArCH_2C{\equiv}C{-}W$] underwent a cyclization reaction upon protonation, resulting in indanone derivatives [231]. Neutral tungsten–vinylidene complexes isoelectronic with **221** (CO replaced by NO^+) could be deprotonated to afford the anionic alkynyltungsten complexes isoelectronic with **220** [232].



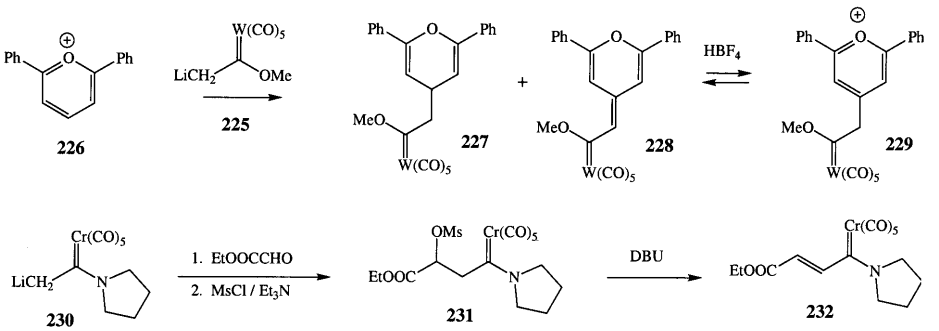
Scheme 41.

A theoretical study of the rearrangement of alkyne–tungsten(IV) complexes [F_4W–(HC ≡ CH)] to the corresponding vinylidene complexes ($F_4W{=}C{=}CH_2$) was undertaken [233]. The reaction process was determined to be endothermic ($\Delta G = +$ 10.4 kcal mol^{-1}) and have a very high energy of activation (85.5 kcal mol^{-1}).

In an isolated study, a molybdenum–vinylidene complex was generated by photolysis of a bridging ferrylcarbene–dimolybdenum complex [234].

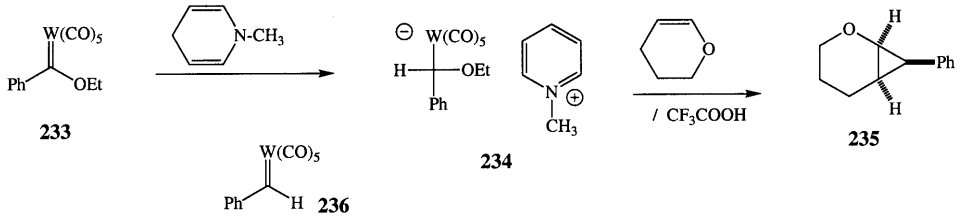
1.3.3.10. Reaction involving carbanions derived from Group VI metal–carbene complexes. Several examples of reactions which involve deprotonation of a Group VI Fischer carbene complex at the α-position, followed by reaction with an electrophile were reported in 1998 (Scheme 42). The coupling of carbene complex-derived carbanions (e.g. **225**) with pyrylium salts (**226**) afforded pyrone derivatives (**227** and **228**) featuring a carbene complex-containing substituent in the 4-position [235]. The oxidation of the 4-alkylpyrone to the 4-alkylidenepyrone was induced by the

pyrylium salt. Protonation of carbene complex **228** regenerated a pyrylium salt (**229**) The reaction of aminocarbene–chromium complex-derived carbanion **230** and glyoxal ester, followed by methanesulfonyl chloride afforded the anticipated alkylated carbene complex **231**, which afforded the γ-oxo-α,β-unsaturated carbene complex **232** upon base-induced elimination [236]. This aminocarbene complex underwent efficient benzannulation at 60°C with a variety of alkynes. The successful synthesis of α,β-unsaturated carbene complexes through the coupling of carbene complex anions with enolizable aldehydes, followed by elimination of water was also reported [237]. Acylation of carbene-complex derived carbanions resulted in relatively unstable β-oxocarbene complexes, which transformed to the β-methoxyenones [RCOC(R′)=C(R″)OMe] at 25°C [238]. The reaction of aminocarbene complex-stabilized carbanions with alkenylnitro compounds provided the expected Michael adducts as well as the corresponding oxime–amides [$R_2NCOCH_2CH(Ar)C(R)$=NOH] which result from oxidation of the carbene complex by a nitro group oxygen [239]. Oxidation of carbene complex derived anions with iodine in methanol afforded one-carbon chain-extended α-methoxy-α,β-unsaturated esters [RCH=C(OMe)COOR] [240].



Scheme 42.

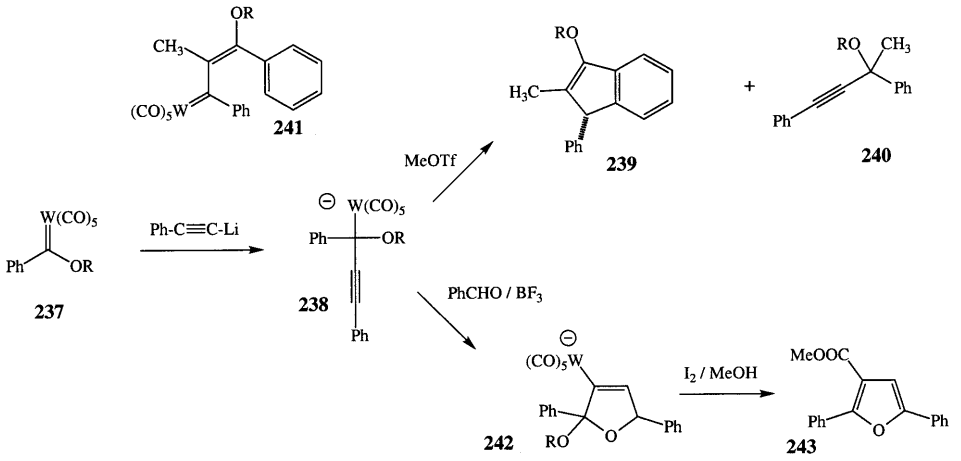
1.3.3.11. Reactions involving the addition of nucleophiles to the carbene carbon. The coupling of dihydropyridine derivatives with Fischer carbene–tungsten complexes led to complexes featuring a hydrogen at the original carbene carbon (e.g. **234**, Scheme 43), which serve as a synthon for hydridocarbene complexes (e.g. **236**) after



Scheme 43.

protonation [241]. The reaction of complex **234** with acid in the presence of enol ethers or enamines led to the non-heteroatom-substituted carbene cyclopropanation product **235** as a 95:5 *cis*:*trans* mixture (the major isomer is depicted) [242,243].

New reaction processes were reported for anionic propargyl–tungsten complexes (e.g. **238**, Scheme 44), which were derived from addition of alkynyl anions to Fischer carbene complexes (**237**) [244]. Reaction of propargyltungsten complex **238** (R = *l*-menthyl) with methyl triflate led to a mixture of indene **239** and propargyl ether **240**. A mechanism involving 1,3-shift of tungsten prior to alkylation, affording phenylvinylcarbene complex **241**, followed by cyclization (see Scheme 37) was proposed for formation of indene **239**. Formation of **239** occurred with a moderate degree of stereoselectivity relative to the chiral auxiliary; no stereoselectivity was observed in the formation of **240**. Furan (e.g. **243**) and pyrrole ring systems were formed from the coupling of the propargyltungsten species with aldehydes, carbon dioxide, imines, or isocyanates [245].

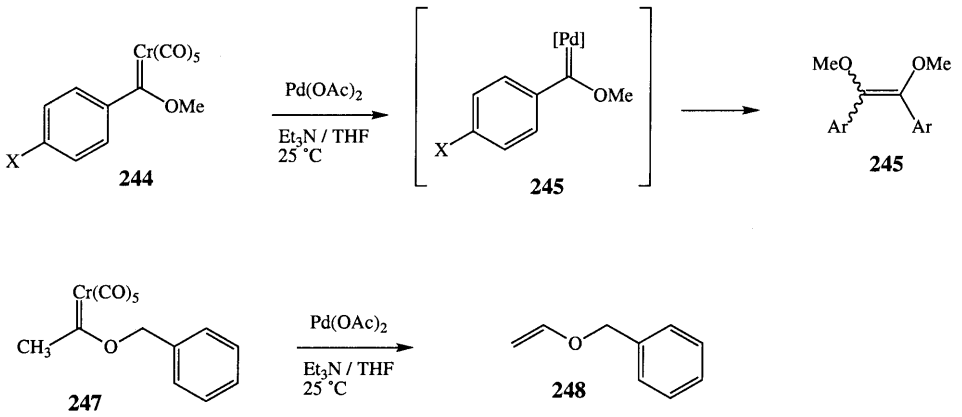


Scheme 44.

Other processes which involve the addition of nucleophiles to the carbene carbon include: (1) reaction of Fischer carbene–chromium complexes [R–C(OMe)=$Cr(CO)_5$] with α-halo organolithium reagents (R′–CHBrLi), which affords olefination products [R–C(OMe)=CHR′] in good yield [246], (2) the reaction of chiral carbene complexes with Group XIV metal–hydrides, which leads to the corresponding α-amino-silane or -stannane with a high degree of stereoselectivity (de = 96%) [247], and (3) the reaction of alkoxycarbene–chromium complexes with thiolate anions, which forms an intermediate identified as the tetrahedral substitution intermediate at pH 11 [248].

1.3.3.12. Other reactions of Group VI metal–carbene complexes. The reaction of Fischer carbene–chromium complexes with palladium (II) acetate was investigated (Scheme 45) [249]. Carbene dimerization (**244** → **246**) was the major reaction

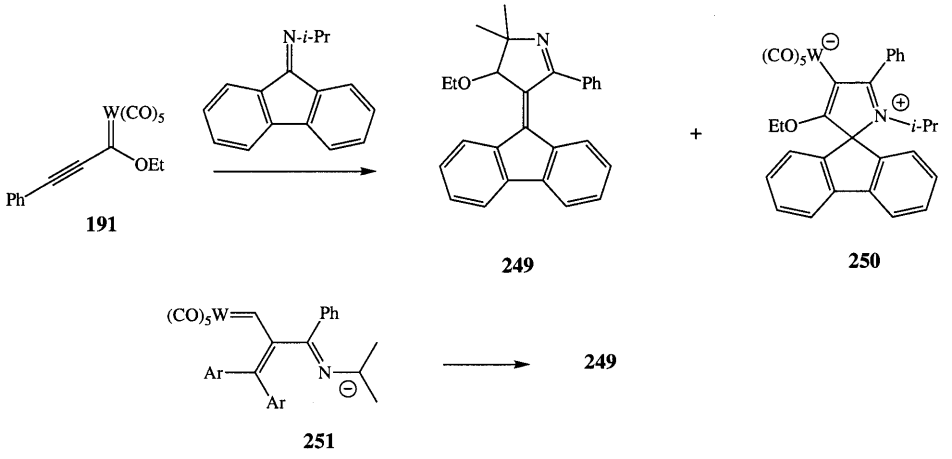
pathway for (alkoxy)arylcarbene complexes. Alkylcarbene complexes (e.g. **247**) were transformed to enol ethers (**248**). (Amino)arylcarbene complexes coupled with electron-deficient alkenes to provide carbonyl anion addition products. In all of these processes, a mechanism involving conversion of the chromium carbene complex to a palladium–carbene complex (**245**) was proposed.



Scheme 45.

Reaction of cyclic diaminocarbene–Group VI metal complexes with acid chlorides was investigated [250,251]. Reaction with excess acid chloride afforded the acyclic isocyanide complex $[(RCO)_2N(CH_2)_2–N{\equiv}C–W(CO)_5]$; a mechanism involving acylation of one nitrogen of the carbene complex, followed by ring opening and a second acylation was proposed.

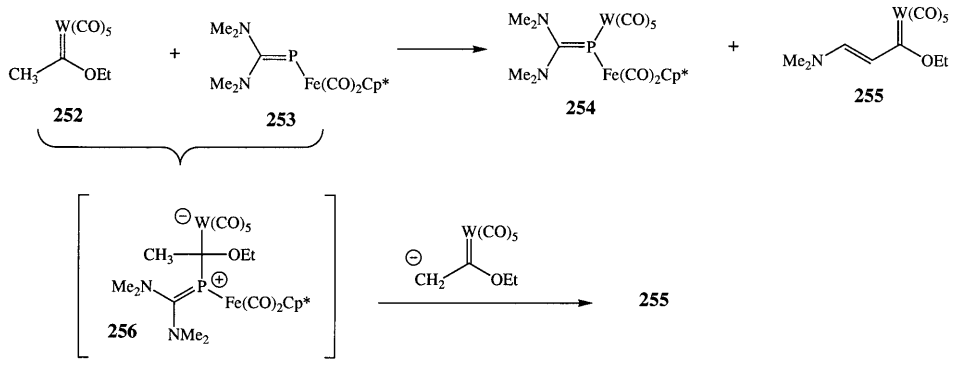
Reaction of alkynylcarbene complexes with imines resulted in an unusual cycloaddition reaction depicted in Scheme 46 [252]. The minor cycloadduct, **250**, was



Scheme 46.

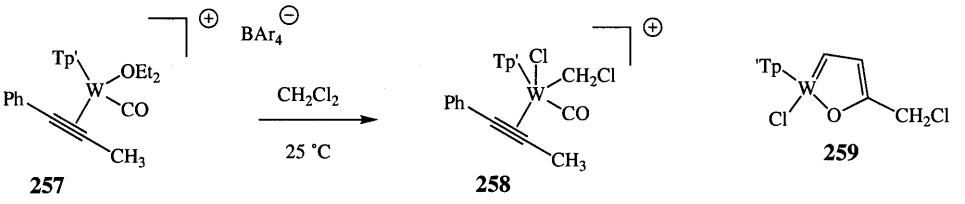
formed via Michael addition of the imine nitrogen followed by intramolecular cyclization. The major cycloadduct, **249**, arises through [2 + 2]-cycloaddition and ring opening, leading after deprotonation to intermediate **251**, which provides **249** after cyclization and demetallation.

The coupling of Fischer carbene complexes and phosphaalkene–iron complexes (e.g. **253**, Scheme 47) has been reported [253]. The major products from coupling with alkylcarbene complex **252** were the Group VI metal–phosphaalkene complex **254** and the α,β-unsaturated carbene complex **255**. A mechanism involving nucleophilic attack of the phosphorus atom at the carbene carbon, followed by attack of the carbene complex-derived anion at the phosphaalkene carbon of the resulting species **256**, followed by β-elimination was proposed. Predominantly products resulting from Michael addition of phosphorus were obtained from the coupling of alkenylcarbene complexes and **253**, while products resulting from [2 + 2]-cycloaddition were observed in the coupling of **253** with alkynylcarbene complexes. The reaction of aminocarbene–chromium complexes and phosphaalkenyl chlorides, resulting in (2*H*-azaphosphirene) complexes, was also reported [254,255].



Scheme 47.

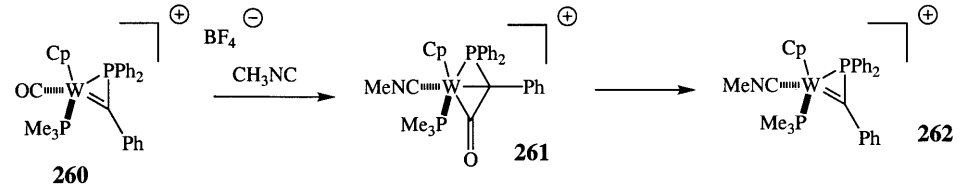
Carbene–tungsten complex **259** (Scheme 48) was generated from cationic tungsten alkyne complex **257** at 25°C in dichloromethane [256]. A mechanism involving oxidative addition into the C–Cl bond of dichloromethane, followed CO insertion, alkyne insertion, and *O*-coordination was proposed.



Tp' = tris(3,5-dimethylpyrazolyl)borate Ar = 3,5-bis(trifluoromethylphenyl

Scheme 48.

Reaction of cationic carbonyl(phosphinocarbene)tungsten complex **260** (Scheme 49) with isocyanides led to the isocyanide-ligated phosphinoketene complexes (**261**), which could be transformed to isocyanide(phosphinocarbene)tungsten complexes (**262**) by heating in THF [257].



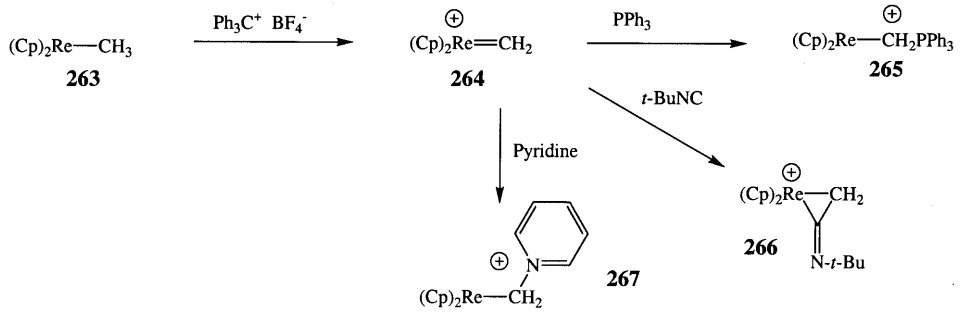
Scheme 49.

Fischer carbene–chromium complexes were studied by X-ray near edge spectroscopy (XANES) [258]; energy shifts arising from modification of the carbene ligand were found to correlate with chromium-53 NMR chemical shifts.

Group VI metal carbene complexes were suggested as intermediates in several processes. Cationic tungsten carbene complexes were suggested as intermediates in the conversion of tungsten-substituted oxanorbornene derivatives to phenols [259].

1.3.4. Group VII metal–carbene complexes

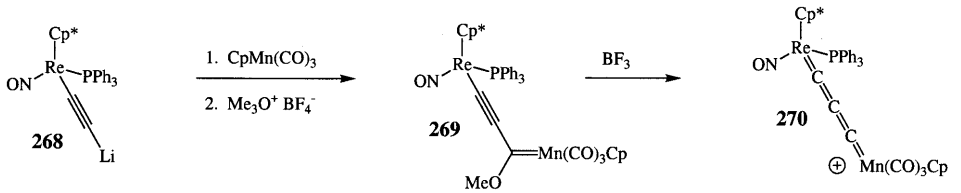
Several novel routes to Group VII metal–carbene complexes were reported in 1998. Cationic rhenium–carbene complexes (e.g. **264**, Scheme 50) were prepared via hydride abstraction from rhenium alkyls using triphenylmethyl cation and other oxidants [260]. These carbene complexes reacted at the carbene carbon with a variety of nucleophiles, including pyridine, phosphines, and isocyanides. Other reactions included conversion of the metal–carbon double bond to other element double bonds by reaction with amine oxides (C=O formation), sulfur (C=S formation), or diazo compounds (C=C formation). New carbene–rhenium complexes were synthesized from the desulfurization reaction of tetramethylthiourea with dirhenium decacarbonyl in the presence of ultraviolet light [261]. Traditional methods for the synthesis of new carbene complexes of Group VII metals were also



Scheme 50.

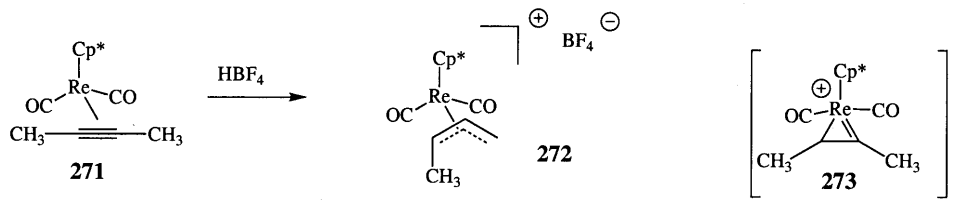
reported. Synthesis and alcohol exchange reactions, emphasizing carbohydrate-derived alcohols, were reported for manganese–carbene complexes [$Cp(CO)_2Mn{=}C(Ph)OR$] [262]. A rhenium analog of the process in Scheme 39, formation of cyclic alkoxycarbene complexes from alkynols, was also reported [263].

A variety of bimetallic systems featuring one alkyne–rhenium bond and one carbene–metal bond were generated from the rhenium lithioacetylene complex **268** (Scheme 51) using the route of Fischer [264]. Bimetallics involving an alkynyl ruthenium and a carbene–tungsten, carbene–manganese, and carbene–iron bond were reported. In the manganese and iron cases, an all carbon cumulene linkage (e.g. **270**) could be generated by treatment of the carbene complex with a Lewis acid. Similar cumulenylidene-bridged polymetallics featuring rhenium cumulenylidene at one end and a bridging cumulenylidene osmium at the other end were also reported [265]. The four-carbon cumulene bridge was also studied by density functional theory. The structure of this bridge can be either a 1,4-dialkynyl (–C≡C–C≡C–), a cumulenylidene (=C=C=C=C=), or a 2-yne-1,4-ylidyne (≡C–C≡C–C≡) linkage, depending upon the electronic configuration at the metals [266].



Scheme 51.

Several papers from 1998 report on reaction processes where Group VII metal carbene complexes are reactive intermediates. Cationic rhenium–carbene complexes (**273**, Scheme 52) were proposed as intermediates in the acid-catalyzed conversion of rhenium–alkyne complexes (**271**) or allene complexes to rhenium–allyl complexes (**272**), and observed by low-temperature NMR [267,268]. The carbene intermediates generated from diphenylacetylene were more stable than those from 2-butyne since hydrogen shift processes are blocked. Other processes involving Group VII metal carbene complex intermediates include: (1) reduction of man-

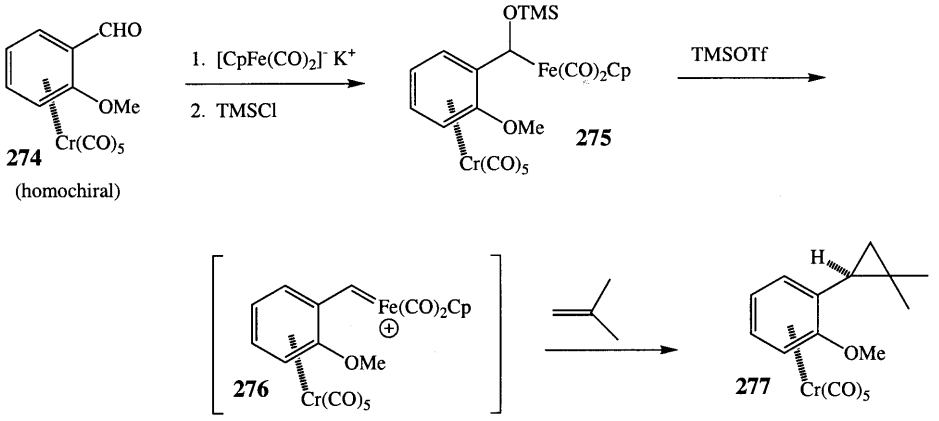


Scheme 52.

ganese acyl complexes (Mn–COR) to carbonyloxyalkyl complexes [Mn–CH(OOCR′)R] using hydrogen and carbon monoxide, which was proposed to involve hydroxycarbene–manganese complexes as intermediates [269], and (2) reaction of chromium-complexed arylmanganese complexes with phenyllithium followed by alkylating agents [270].

1.3.5. Group VIII metal–carbene complexes

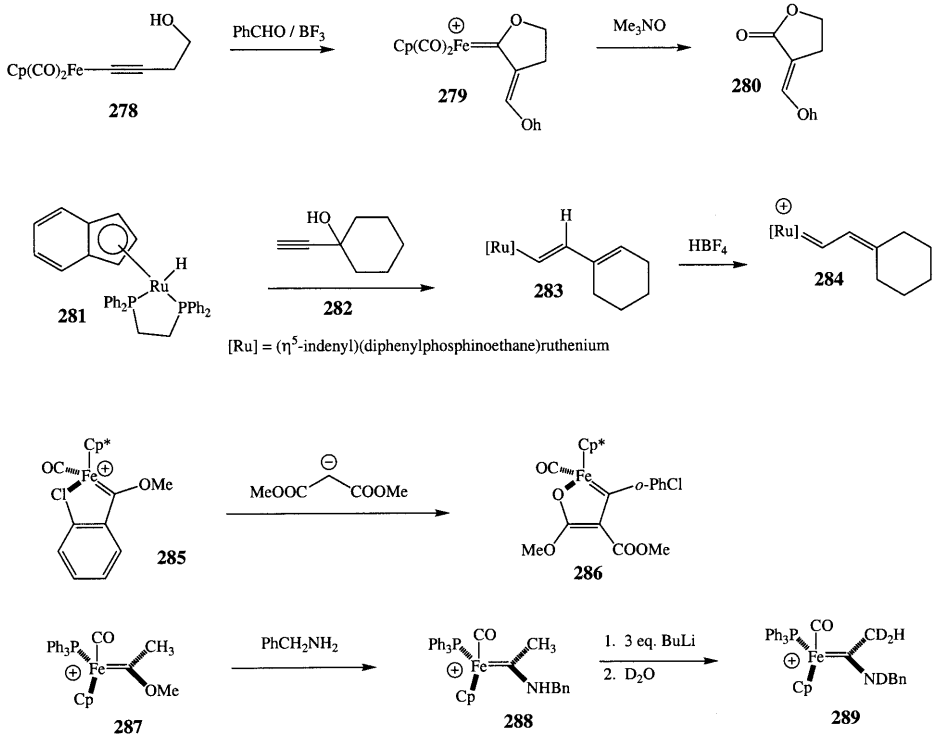
1.3.5.1. Cationic metal–carbene complexes which are not cumulenes. Cationic iron–carbene complexes are commonly used as cyclopropanating agents, and several examples of this transformation appeared in 1998. A homochiral iron–carbene complex (**276**, Scheme 53), derived from a homochiral aldehyde **274**, afforded chiral cyclopropane **277** with a high degree of diastereoselectivity [271]. Cyclopropane **277** was an intermediate in the enantioselective synthesis of cyclopropanecarboxylic acid derivatives. Cyclopropanations using cationic iron carbene complexes featuring the indenyl ligand in place of the Cp ligand (as in **276**) were also studied [272]; these carbene complexes were effective cyclopropanating agents and displayed greater *cis* selectivity than the corresponding cyclopentadienyl complexes. The mechanism of alkene cyclopropanation using cationic carbene complexes (generated from alkyliron–sulfonium salts) was investigated [273]. Cationic iron–carbene complexes were proposed as intermediates in other reaction processes, including the reduction of neutral acyliron species to the corresponding alkyliron species by silanes [274], and in the ring opening of cyclopropyliron complexes induced by SO_2 [275].



Scheme 53.

Several examples of stable cationic Group VIII metal carbene complexes were reported in 1998. Coupling of homopropargyl alcohol–alkynyliron complexes (e.g. **278**, Scheme 54) with aldehydes in the presence of Lewis acids provided stable alkoxycarbene iron complexes (**279**) [276], which were converted to the corresponding lactones (**280**) by treatment with trimethylamine-*N*-oxide. This reaction proceeds through a cationic vinylidene complex generated by electrophilic attack on

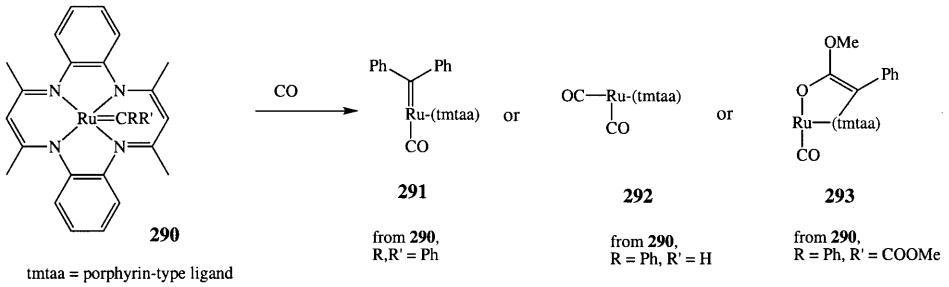
the alkyne. Cationic alkoxycarbene–iron complexes were also prepared by ring opening of spirobicyclo[4.2]hepta-2,4-diene with tricarbonylbis(cyclooctene)iron(0), followed by alkylation of the resulting acyliron complex [277]. Cationic alkoxycarbene–iron complexes were generated directly from lactones using a novel iron–zirconium reagent [278]. Cationic ruthenium–alkenylcarbene complexes (**284**) were generated from δ-protonation of η^1-dienylruthenium complexes (**283**) [279]. Nucleophilic attack on cationic ruthenium–vinylcarbene complexes occurs primarily at the γ-position [280]. The reaction of internally chelated cationic iron carbene complex **285** with enolates afforded the neutral oxygen chelates (**286**), which result from attack of the nucleophile at the carbene carbon [281]. Reaction of these complexes with alkoxide nucleophiles was also reported [282]. Cationic cycloheptatrienylidene–chromium tricarbonyl complexes containing an iron [–$Fe(CO)_2Cp$] group were synthesized by treatment of the iron-substituted cycloheptatriene–chromium tricarbonyl complex with triphenylmethyl cation [283]. The reaction of cationic chiral-at-iron carbene complexes (e.g. **287**) with amines, which led to aminocarbene complexes (**288**), and the reactivity of aminocarbene complexes were investigated [284]. The aminocarbene complex could be triply deprotonated. The reaction of the racemic alkoxycarbene complex with racemic α-phenethylamine led to a 1:1 mixture of diastereomers, suggesting that there is no molecular recognition in the amination reaction.



Scheme 54.

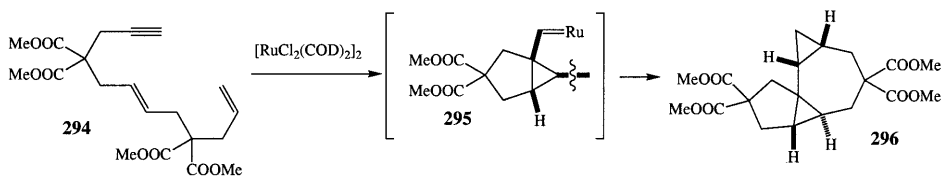
1.3.5.2. Neutral non-heteroatom-substituted metal–carbene complexes which are not cumulenes. Numerous additional examples of the synthesis and reactivity of this class of compounds has been presented in the alkene metathesis section. The Grubbs catalyst falls into this classification.

Ruthenium carbene complexes (**290**, Scheme 55) were prepared through the coupling of diazo compounds with ruthenium(II)–tmtaa complexes [285]. The reaction of these complexes with CO was examined. The reaction course was highly dependent on the groups attached to the carbene carbon; the diphenylcarbene complex afforded the simple CO adduct **292**, while the phenylcarbene complex afforded the dicarbonyl/carbene displacement product **293**. The carbomethoxy phenylcarbene complex led to a tmtaa–carbene coupling product **293**. Other ruthenium–porphyrin complexes also reacted with diazo compounds to afford carbene complexes. Ruthenium porphyrin-mediated cyclopropanation of styrene and other alkenes using ethyl diazomalonate was reported [286]; the ruthenium carbene complexes could be isolated from these reactions and were found to efficiently transfer carbene ligands to a variety of alkenes. The formation of ruthenium– and osmium–methylene complexes through the coupling of ruthenium hydride complexes with diazomethane was also reported [287].



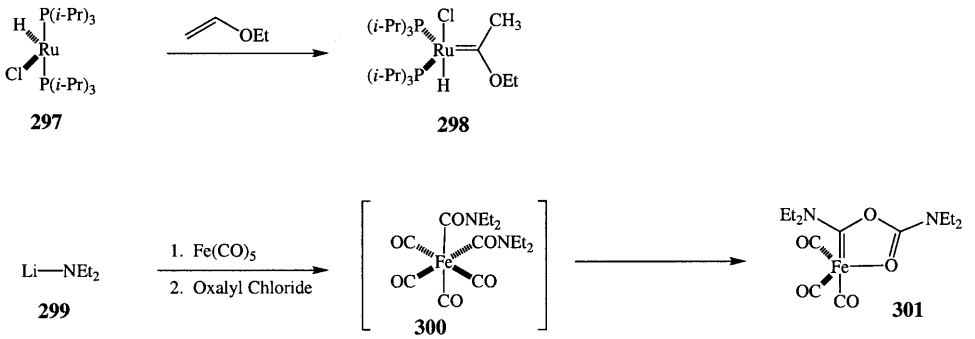
Scheme 55.

Ruthenium–carbene complexes (**295**, Scheme 56) were proposed as intermediates in the ruthenium-catalyzed cyclization of dienyne **294** to **296** [288]. Ruthenium–carbene complexes were proposed as intermediates in the high-temperature conversion of η^5-cyclohexadienone–ruthenium complexes to the corresponding η^5-cyclopentadienyl complexes, which is accompanied my migration of the carbon atoms of the cyclohexadienone ligand [289].



Scheme 56.

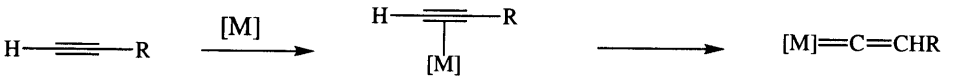
1.3.5.3. Neutral heteroatom-substituted Group VIII–metal carbene complexes. A heteroatom-stabilized ruthenium–carbene complex (**298**, Scheme 57) was prepared from the reaction of ethyl vinyl ether with hydrido–ruthenium complex **297**; a mechanism involving alkene insertion followed by α-hydride elimination was proposed and supported by deuterium-labeling studies [290]. Bis heteroatom-stabilized iron carbene complexes (**300**) were prepared by the treatment of iron pentacarbonyl with two equivalents of a lithium amide derivative, followed by oxalyl chloride [291], which rearranged to chelated carbene complex **301** at 25°C. Bimetallic complexes featuring iron–carbene and manganese–diene linkages were generated from a cycloheptatrienyl-η^3-iron(tricarbonyl)-η^4-manganese(tricarbonyl complex and phenyllithium using the Fischer synthesis; the iron–carbene unit underwent a spontaneous coupling with the cycloheptatrienyl ligand [292]. A bis-carbene iron complex was prepared in low yield by treatment of iron pentacarbonyl with 2,6-dimethylphenyllithium [293]. Phosphoranyl-substituted Fischer carbene–iron complexes were prepared by alkylation of the corresponding phosphoranyl-substituted acyliron anions [294].



Scheme 57.

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 Fig. 9. 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.

Numerous other studies of the synthesis and reactivity of Group VIII metal–vinylidene complexes appeared in 1998; representative examples of compounds in this classification are depicted in Fig. 9. The major synthetic route to metal vinylidenes involves the coupling of coordinatively unsaturated metals with terminal alkynes (Scheme 58) [295]. There are numerous pathways by which the alkyne complex can rearrange to the vinylidene complex. Examples of complexes prepared this way include: (1) cationic ruthenium vinylidene complexes (**302**) which feature a alkyne–cobalt complex as a substituent [296], (2) 2-amidopyridine-ligated ruthenium car-



Scheme 58.

bene complexes, which undergo reaction with the amide group in the ligand to afford stable amidocarbene complexes [297], (3) hydrido-vinylidene complexes (**303**), which was formed through insertion of the alkyne into the metal–hydride bond followed by α-hydride elimination, and supported through deuterium labeling studies [298], (4) neutral ruthenium–vinylidene complexes [299], which undergo alkyne insertion processes, (5) (hydrido)alkenylvinylidene–osmium complexes, which were converted to the corresponding alkenylcarbyne complex upon protonation or to the hydride migration product (a η^1-dienyl complex) upon treatment with carbon monoxide [300], (6) (alkenyl)trimethylsilylvinylidene–osmium complexes, which undergo migration of the alkenyl group to afford 2-dienylosmium complexes; a comparison with the ruthenium analogs was also undertaken [301], (7) bipyridine-ligated dicationic ruthenium vinylidenes (**304**), which react with aniline at the α-position, to ultimately afford cationic chelated aminocarbene–ruthenium complexes after ortho-metallation, the luminescent properties of these complexes were

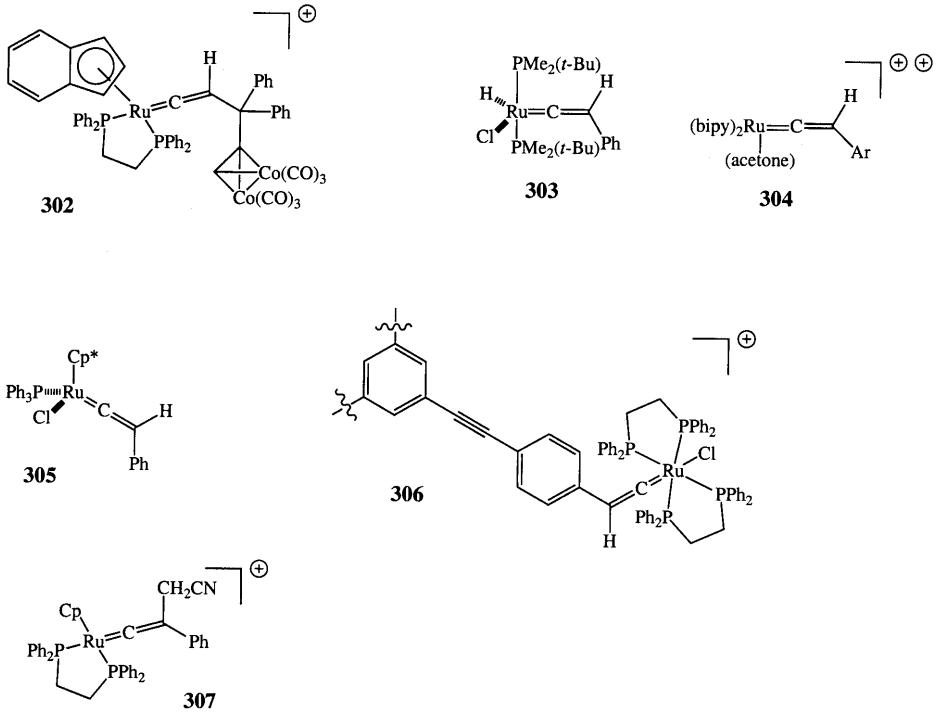
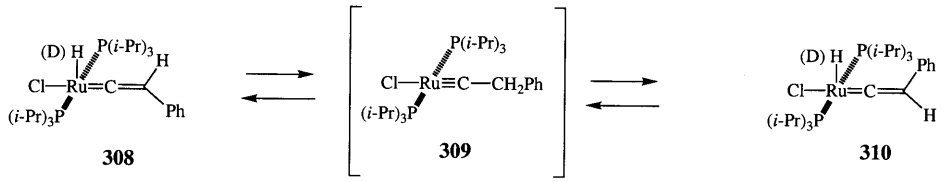


Fig. 9. Representative Group VIII vinylidene complexes.

studied [302], (8) neutral ruthenium–vinylidene complexes (**305**); ligand exchange reactions of this complex were studied [303], (9) chloro(hydrido)(vinylidene)-ruthenium complexes, which transform to the dichloro(carbene)ruthenium complexes upon treatment with HCl [304], (10) compounds featuring three cationic ruthenium vinylidene groups (**306**) by reaction of 1,3,5-tris(4-ethynyl-phenylethynyl)benzene with a ruthenium(II) chloride complex; the electrochemistry of this complex was investigated [305], (11) cationic ruthenium vinylidene complexes which also contain a ruthenium carbene ligand [306], (12) vinylidene–ruthenium complexes featuring an antimony ligand [307], and (13) failed attempts to synthesize an alkynyl(vinylidene)ruthenium complex from a cationic ruthenium vinylidene complex [308].

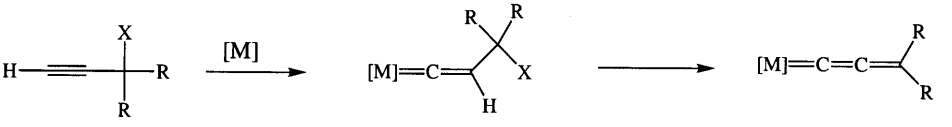
Other studies involving Group VIII metal vinylidene complexes include: (1) synthesis of an iminothiol-substituted vinylidene–ruthenium complex through the addition of phenyl isothiocyanate to an alkynylruthenium complex [309], (2) studies of the synthesis of cationic ruthenium vinylidene complexes (**307**) from the reaction of alkynylruthenium complexes with iodoacetonitrile, and subsequent conversion to the neutral cyclopropenylruthenium complexes by treatment with base [310], and (3) reaction of ruthenium vinylidene complexes with diiron nonacarbonyl, resulting in bridging acetylene–triiron complexes [311].



Scheme 59.

Deuterium-labeled ruthenium–vinylidene complex **308** (Scheme 59) was prepared and its rotational isomerization (**308** → **310**) examined [312]. The rotation occurs without scrambling of the vinylidene hydrogen and deuteride ligands, which is contrary to an earlier mechanistic suggestion (for osmium complexes) involving metal carbynes (**309**) as intermediates.

1.3.5.5. Group VIII metal complexes of higher cumulenes. 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 (Scheme 60), or by addition of electrophiles to the δ-carbon of alkynylethynyl–metal complexes;



Scheme 60.

representative examples of this class of compounds are depicted in Fig. 10. Newly synthesized Group VIII–metal cumulene complexes include: (1) cationic osmium–allenylidene complex **311**, which was observed to undergo addition of nucleophiles at the γ-position in competition with ligand exchange processes [313], (2) cationic ruthenium vinylidene complexes featuring the L_{OEt} ligand, which was studied by electrochemistry [314], (3) bimetallic cumulene–diiron complexes prepared by electrochemical oxidation of the corresponding diacetylene-bridged diiron complex [315], (4) ruthenium complexes featuring allenylidene and alkynyl ligands (e.g. **312**); non-linear optical properties were examined [316], (5) cationic osmium– and ruthenium–allenylidene complexes; electrochemistry was examined [317], (6) cationic ruthenium allenylidene complexes generated from the reaction of bis dppe–ruthenium(II) complexes with alkynylacetylene derivatives [318], (7) cationic iron allenylidene complexes (**313**) produced from the coupling of the iron(II)–halide complex with 1-trimethylsilyl-1,3-butadiyne in the presence of methanol and sodium tetraphenylborate [319], and (8) neutral ruthenium allenylidene complexes (**314**) prepared from the coupling of ruthenium hydride complexes with 1,1-diphenyl-2-propyn-1-ol in the presence of alumina [320]. A cumulene resonance structure (**315**) was a significant contributor for the corresponding alkynylruthenium complex [321].

A variety of reaction processes of Group VIII metal–cumulene complexes were reported in 1998. A common reaction pathway for these complexes is reaction with nucleophiles at the γ-position, resulting in alkynylmetal complexes, or attack at the γ-position, resulting in allenylmetal complexes. The reaction of cationic ruthenium–allenylidene complexes (e.g. **316**, Scheme 61) with pyrazole was examined, which resulted in the heterocyclic alkenylruthenium complex **319**; a mechanism involving nucleophilic attack at the α-position, affording intermediate **317**, followed by

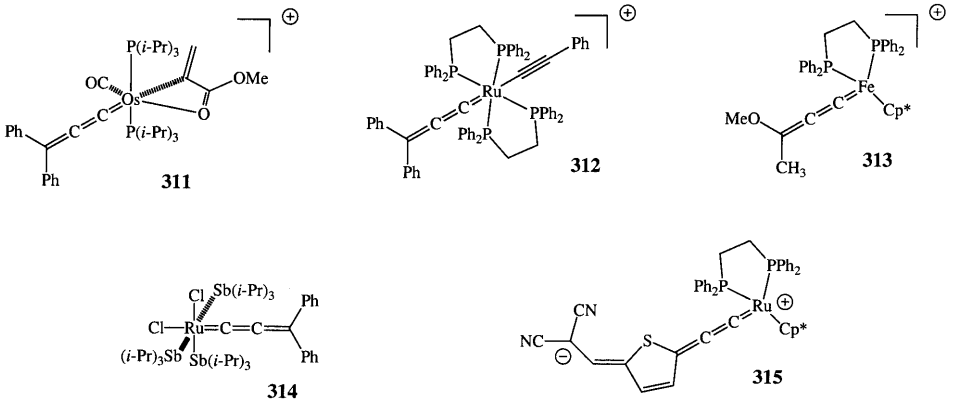
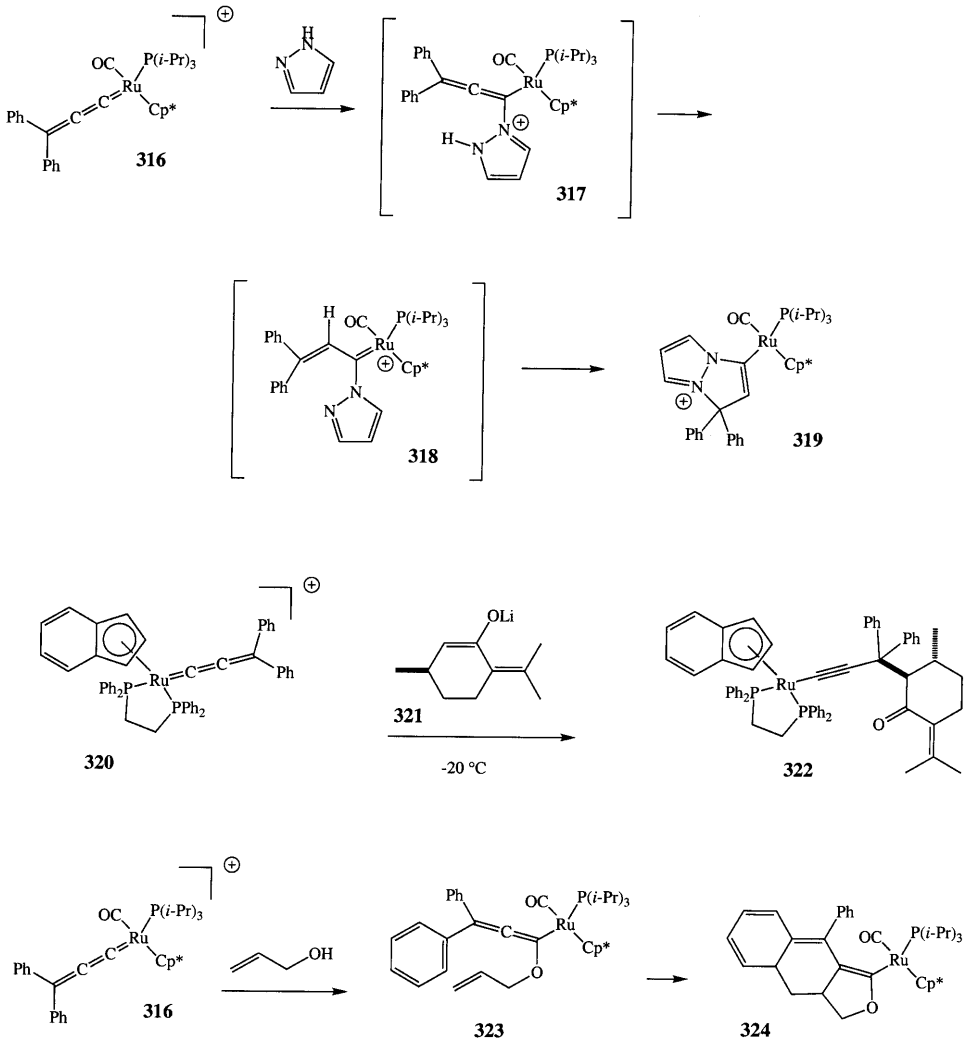


Fig. 10. Representative Group VIII metal–cumulene complexes.

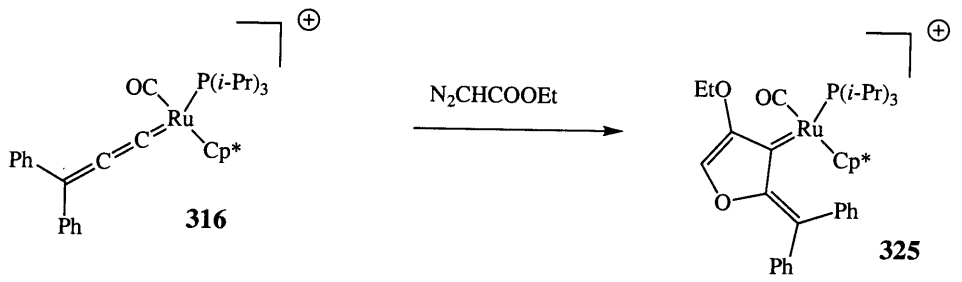


Scheme 61.

proton transfer and formation of alkenylcarbene complex **318**, followed by a second nucleophilic attack at the γ-position was proposed [322]. Coupling of ruthenium–allenylidene complexes with methoxide afforded alkynylruthenium complexes through γ-attack, while phosphine nucleophiles afforded allenylruthenium complexes through α-attack [323]. The coupling of cationic ruthenium allenylidene complexes (e.g. **320**) and ketone enolates was investigated; attack at the γ-position to produce the alkynylruthenium complex (**322**) was the major reaction pathway [324]. The coupling of cationic ruthenium allenylidene complexes and ferrocenylamines was investigated; attack at the γ-position to produce the nitrogen-

substituted 3-buten-1-ynyluthenium complex was observed [325]. The reaction of neutral allenylidene–ruthenium complexes and azide or isocyanate ions was investigated; ligand substitution was observed, however treatment of the azide adduct with CO led to the γ-azidoalkynyl complex [326]. Cationic ruthenium–allenylidene complex **316** was converted to the corresponding allyloxy–alkenyl complex (**323**) by reaction with allyl alcohol followed by deprotonation [327]. The allenylruthenium complex undergoes an unusual intramolecular Diels–Alder reaction involving a benzene ring, forming stable adduct **324**, which affords a cationic ruthenium carbene complex after protonation. Cationic ruthenium cumulenylidene complexes were prepared from 1,3-butadiyne; reaction of these complexes with a variety of nucleophiles resulted in attack at the γ-position to afford the γ-substituted allenylidene complex or the alkenylethynyl complex [328].

Other reaction processes were also reported for Group VII metal–cumulene complexes. The reaction of cationic ruthenium allenylidene complex **316** (Scheme 62) with ethyl diazoacetate afforded a cycloaddition product, alkenylcarbene complex **325** [329]. The reaction of neutral osmium–allenylidene complexes $\{Cl(Cp)[P(i\text{-}Pr)_3]Os{=}C{=}C{=}CPh_2\}$ with a variety of reagents was examined [330]. Coupling with dimethyl acetylenedicarboxylate proceeded by [2 + 2]-cycloaddition at the α,β-double bond followed by ring opening. Protonation afforded the cationic carbyne complexes $[Os{\equiv}C{-}CH{=}CR_2]$. Reaction with vinylmagnesium bromide proceeded by attack at the metal.

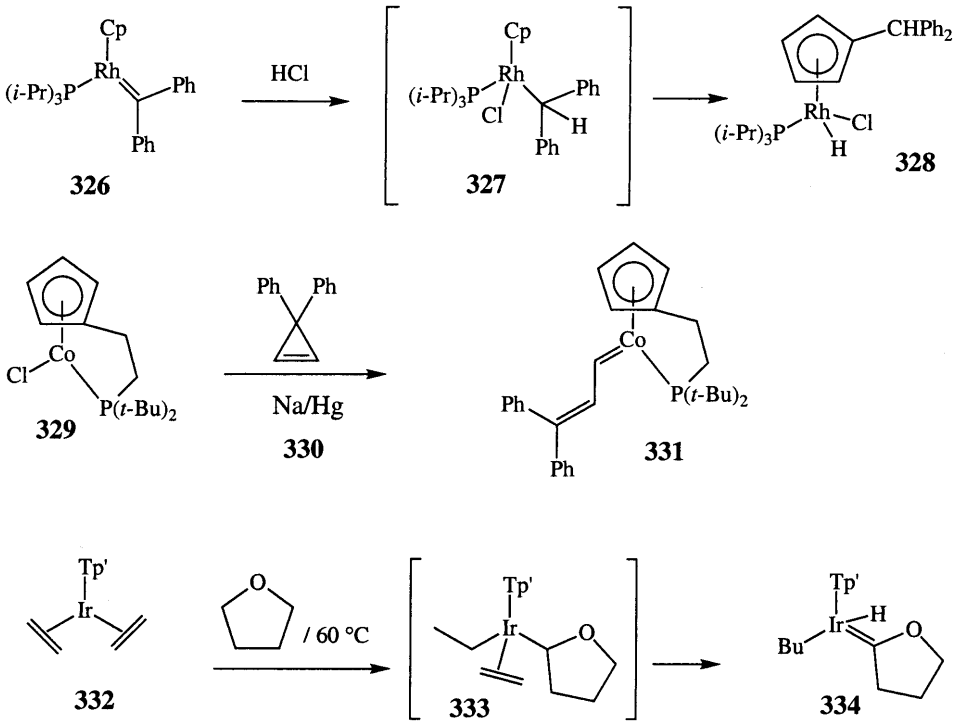


Scheme 62.

1.3.6. Group IX metal–carbene complexes

1.3.6.1. Simple carbene complexes. Rhodium–carbene complex **326** was treated with either acid or trifluorophosphine (Scheme 63); protonation and migration of the diphenylcarbene unit to the cyclopentadienyl ligand was the major reaction pathway; complex **328** was obtained from the reaction of **326** with HCl [331]. Protonation of the carbene carbon, resulting in **327**, followed by migration of the alkyl group, followed by migration of one of the original Cp group hydrogens back to rhodium was proposed and supported through deuterium labeling studies. Cobalt–carbene complexes (**331**) were prepared by the reductive coupling of cobalt

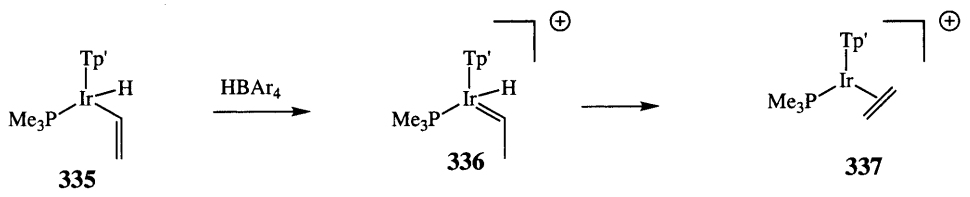
complex **329** with cyclopropenes; coupling of these complexes with phospaalkynes was also reported [332]. Heteroatom-stabilized iridium–carbene complexes were prepared from the reaction of iridium–diethylene complex **332** with cyclic ethers (e.g. THF, dioxane); a mechanism involving C–H activation (forming intermediate **333**), followed by ethylene insertion and α-hydride elimination was proposed [333]. Rhodium–thiocarbene complexes were obtained though treatment of a rhodium complex with thiocarbamoyl chlorides or with carbon disulfide followed by methyl iodide [334]. Iridium–carbene complexes were proposed as intermediates in the base-induced net dehydrochlorination of a cycloheptatrienyliridium chloride complex [335].



Scheme 63.

Several examples of the generation of Group IX metal–carbene complexes through protonation of the corresponding alkenyl complexes were reported in 1998. Cationic hydrido(ethylidene)iridium complexes (**336**, Scheme 64) were generated by protonation of the corresponding vinyliridium complex (**335**) and observed by low-temperature NMR; the carbene complex was transformed to the η^2-ethylene complex (**337**) at -47°C [336]. Cationic iridium–carbene complexes [Ir=C(CH_3)–CH(CH_3)–C(CH_3=NH] were generated by protonation of β-irido-α,β-unsaturated

imines [Ir–C(CH_3)=C(CH_3)–C(CH_3=NH] [337]. Cationic rhodium carbene complexes were proposed as intermediates in the acid-induced conversion of neutral trivinylrhodium complexes to cationic monovinyl π-allylrhodium complexes [338].



Tp' = tris(3,5-dimethylpyrazol-1-yl)hydroborate
Ar = 3,5-bis(trifluoromethyl)phenyl

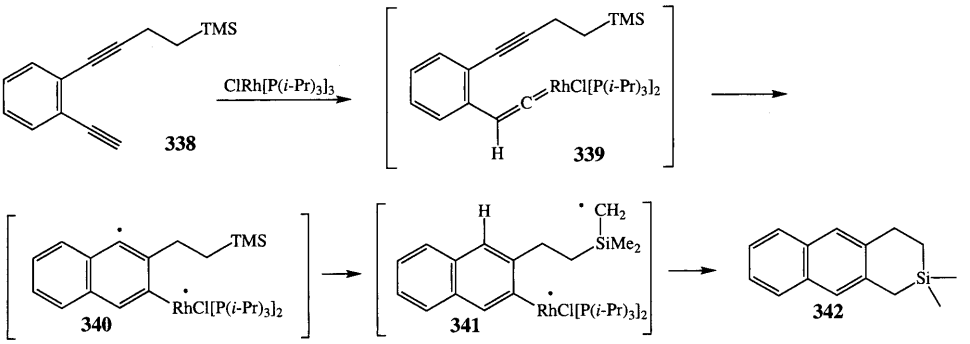
Scheme 64.

A theoretical study of the structure and the charge distribution of dirhodium–methylene complexes (commonly suggested as intermediates in the reaction of diazo compounds with dirhodium tetracarboxylates) was undertaken [339]. The isocyanide complexes of dirhodium tetraacetate were observed to have significant carbene character in the rhodium–carbon bonds [340].

1.3.6.2. Vinylidene complexes. Rhodium–vinylidene–chloride complexes [Cl–Rh=C=CHPh] were converted to the corresponding vinylidene–hydroxide complexes [HO–Rh=C=CHPh] by treatment with sodium hydroxide [341], which were transformed to the vinylidene–alkynyl complexes by treatment with terminal alkynes [RC ≡ C–Rh=C=CHPh]. Conjugated enediynes (e.g. **338**, Scheme 65) were transformed to the corresponding diradical intermediate **340** by treatment with a rhodium chloride complex; a enynylvinylidene intermediate (**339**) was proposed, which undergoes Myers-type cyclization to the diradical **340**; ultimately cyclization product **342** was obtained after intramolecular hydrogen atom transfer and radical–radical coupling [342].

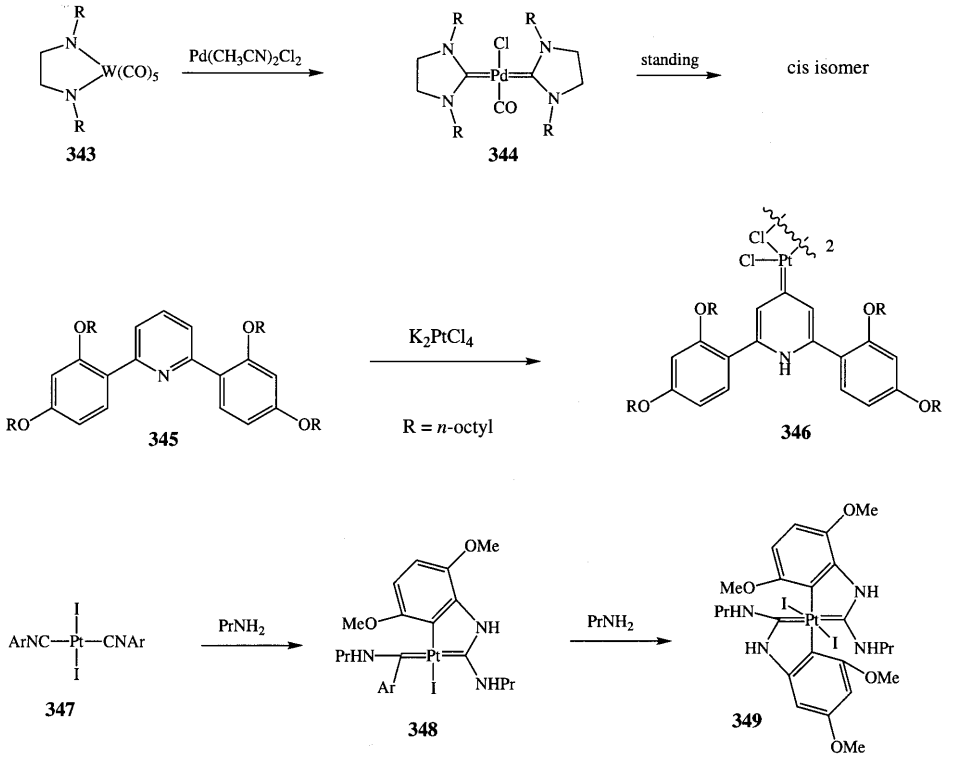
1.3.7. Group X metal–carbene complexes

Palladium bis(carbene) complexes (**344**, Scheme 66) were generated from the reaction of diaminocarbene–tungsten complexes (**343**) with bis(acetonitrile)-palladium (II) chloride; a similar synthesis of platinum and rhodium analogs was also reported [343]. Hydropyridinylidene–platinum complexes (**346**) were synthesized from the reaction of potassium tetrachloroplatinate with 2,6-diarylpyridine derivatives (**345**) featuring bulky aryl groups; less bulky aryl groups led to simple *N*-bound platinum complexes [344]. Platininum–carbene complexes (**348** and **349**) were prepared from the reaction of metal isocyanide complexes (e.g. **347**) with alcohols or amines [345]. If aryl isocyanide ligands featuring electron-rich aromatic rings were employed, an intramolecular C–H activation was accompanied by



Scheme 65.

conversion to the carbene complex. Other studies of Group X metal carbene complexes include: (1) formation of cyclic oligomeric platinum dicarbene complexes from the reaction of potassium tetrachloroplatinate, *t*-butyl isocyanide, and hydra-



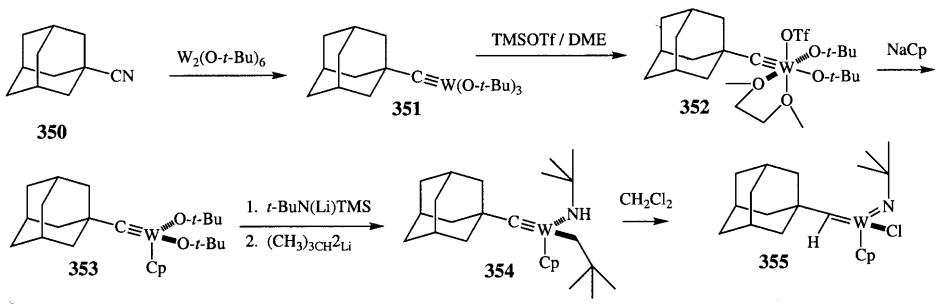
Scheme 66.

zine [346], (2) formation of cyclobutene-bridged diplatinum complexes (featuring one alkenyl–platinum and one carbene–platinum linkage) by treatment of a dimeric alkynylplatinum complex with thiols [347], and (3) nickel–carbene complexes, which were suggested as intermediates in the nickel-catalyzed ring opening of cyclopropenes and in the synthesis of cyclopropenes from the coupling of nickel–acetylene complexes with sulfone-stabilized carbanions [348].

2. Metal–carbyne or metal–alkylidyne complexes

2.1. Synthesis and/or generation

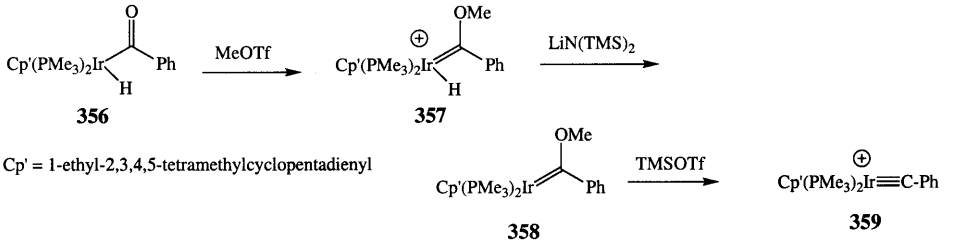
Tungsten adamantylidyne complexes (e.g. **351**–**354**, Scheme 67) were prepared via a nitrile metathesis reaction involving adamantanecarbonitrile (**350**) and a ditungsten complex [349]. A series of ligand exchange processes were examined for complex **351**. The amido–carbyne complex **354** was transformed to the imido–carbene **355** complex at 25°C in dichloromethane.



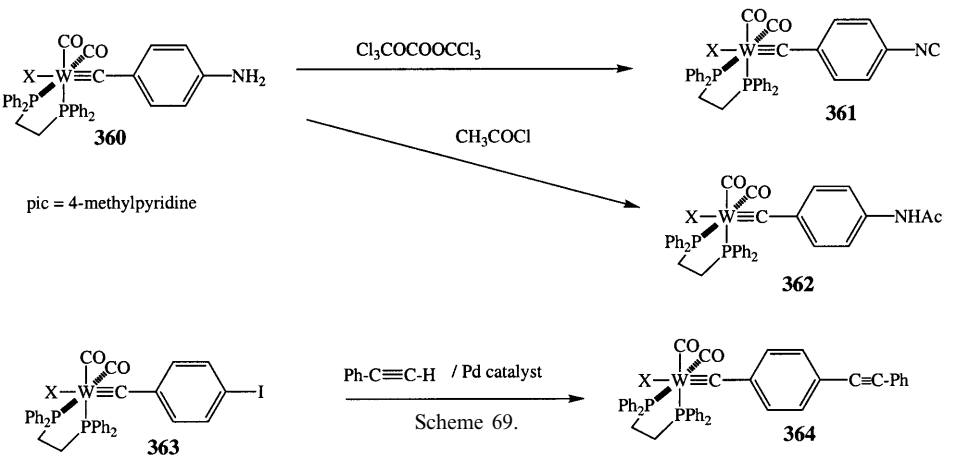
Scheme 67.

Cationic iridium–carbyne and carbene complexes were prepared from acyliridium complex **356** (Scheme 68) [350]. Methylation of acyliridium complex **356** provided cationic methoxycarbene complex **357**, which was deprotonated to afford the neutral carbene complex **358**. Treatment with trimethylsilyl triflate afforded cationic carbyne complex **359**. Tungsten-*p*-aminophenylcarbyne complexes (**360**, Scheme 69) were prepared and subjected to transformations typical of an amine group, including amide, isocyanide, and imine formation [351]. The analogous *p*-iodophenylcarbyne complex (**363**) was prepared, and underwent Sonogashira coupling to produce the *p*-alkynylphenylcarbyne–tungsten complex (**364**) [352]. Other reported syntheses of carbyne complex include: (1) formation of tricationic carbyne–osmium (IV) complexes from the reaction of η^2-furan-osmium (II) complexes with trifluoromethanesulfonic acid in methanol [353], and (2) formation of calixarene-bound tungsten–butylidyne and –butylidene complexes from the reac-

tion of calixarene–alkene complexes with butyllithium; these complexes were interchanged by protonation/deprotonation reactions [354].



Scheme 68.



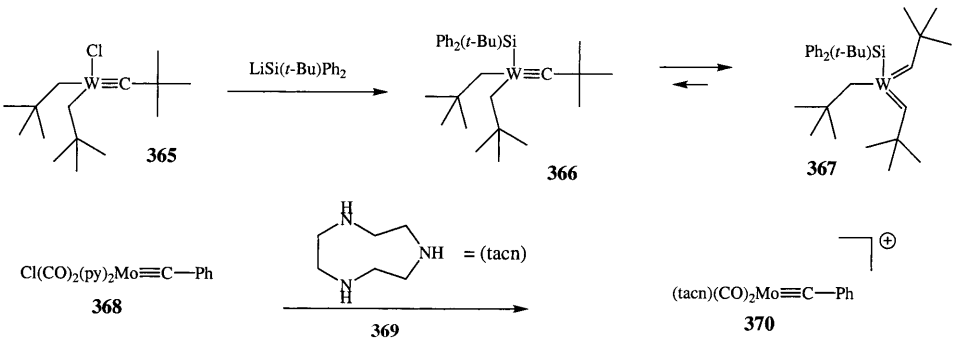
Scheme 69.

2.2. Reactivity

2.2.1. Ligand exchange reactions

The reaction of chlorotungsten–carbyne complex **365** (Scheme 70) with *t*-butyldiphenylsilyllithium afforded a mixture of the analogous silyl–tungsten complex (**366**) and the bis-carbene complex (**367**), which could be interconverted at room temperature [355]. Molybdenum carbyne complexes (**370**) featuring the tacn ligand (**369**) were prepared from carbyne complex **368** by ligand exchange processes [356]. The corresponding (Me_3tacn)-ligated molybdenum–carbyne complexes were similarly prepared, however ligation of the third nitrogen atom required addition of sodium tetraphenylborate [357]. Ligand exchange and addition processes were investigated for tungsten–carbyne–L_{OEt} complexes and amine/alkoxy ligands; in

most cases simple ligand exchange reactions occurred, however reaction with primary amines or alumina led to carbene-oxo or carbene imido complexes [358]. Ligand exchange and addition processes were investigated for Group VIII metal carbynes [M ≡ C–Ar], prepared by treatment of the corresponding dichlorocarbene complexes [Cl–M=CCl_2] with arylithiums [359]. A series of ligand exchange and addition of various electrophiles (HCl, Cl_2, $AgClO_4$) to the carbon–metal triple bond were examined.



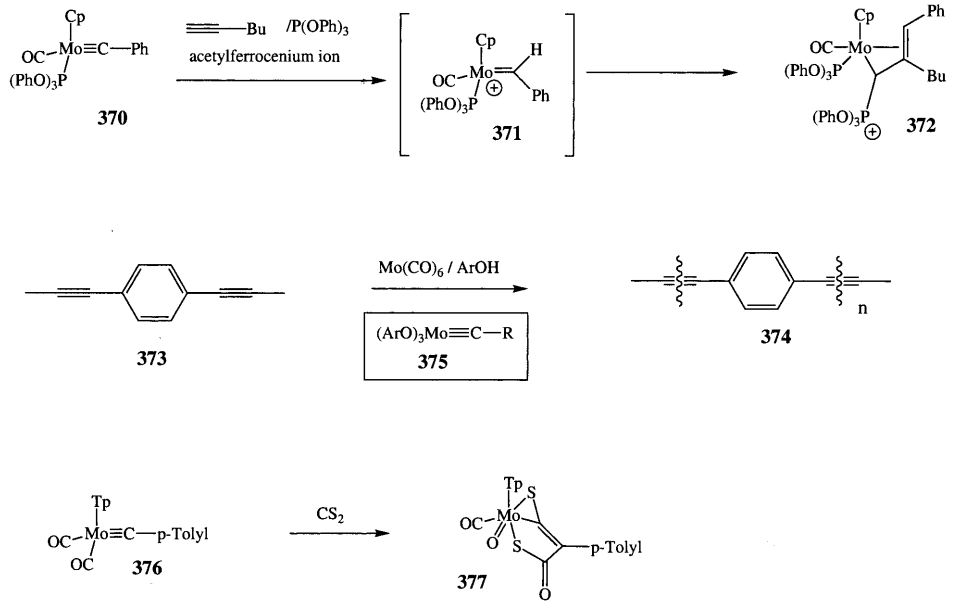
Scheme 70.

2.2.2. Addition reactions of metal–carbyne complexes

The following reaction processes (depicted in Scheme 71) involving addition to the carbon–carbon triple bond were reported in 1998: (1) oxidation of molybdenum carbynes (e.g. **370**) to the cationic carbene complex (**371**) followed by alkyne insertion, resulting in allyl complexes (**372**) [360], (2) polymerization of dialkynes using an in situ-generated molybdenum–carbyne complex (**375**); the process was referred to as ADIMET (acyclic diyne metathesis polymerization) [361], (3) ligation of boron hydrides to tungsten–carbyne complexes followed by synthesis of hetero-bimetallics through addition of metal carbonyl derivatives to the tungsten–carbon triple bond [362], (4) addition of carbon disulfide to molybdenum (II) carbene complex **376**, which leads to the unusual molybdenum oxo species **377**, which is inconsistent with a previous claim [363], and (5) formation of cationic carbene–tungsten complexes by protonation of neutral tungsten–carbyne complexes [364].

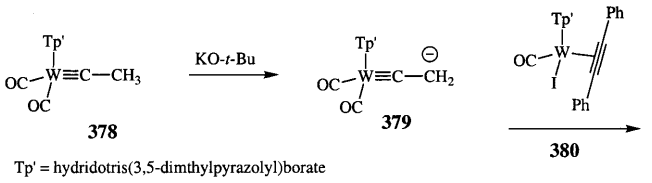
2.2.3. Reactions involving carbanions derived from metal–carbyne complexes

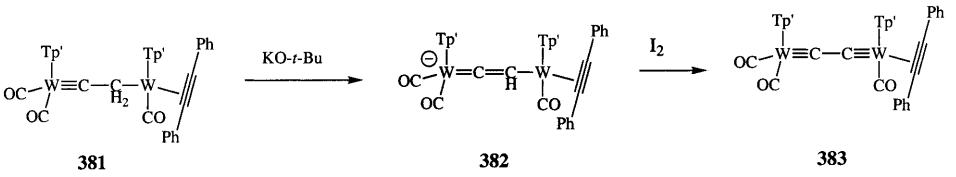
Tungsten carbyne derived anion **379** (Scheme 72) was generated by deprotonation of carbyne complex **378**. Coupling of this anion (and the molybdenum analog) with alkyne–tungsten iodide complex **380** afforded a bimetallic system, which was transformed to the dialkylidynyl bridged complex **383** after deprotonation and iodine oxidation [365]. The coupling of anions derived from tungsten carbyne complexes with various other electrophiles, including alkyl halides, ketones, and acyl halides, was also reported [366]. Two moles of the carbyne complex anion were



Scheme 71.

incorporated in reactions involving acyl halides, however the mono-addition product could be generated by a retro-aldol like process involving the di-addition product.

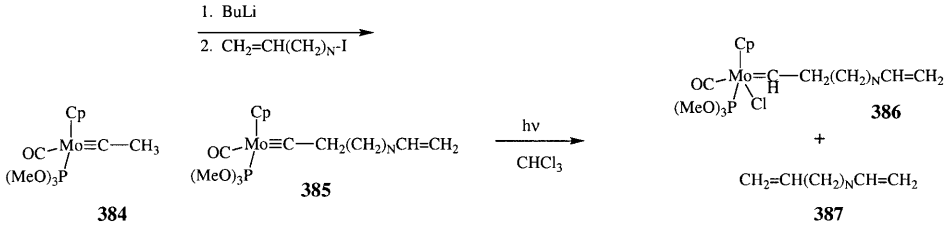




Scheme 72.

Deprotonation of molybdenum carbyne complex **384** (Scheme 73) followed by treatment with alkyl iodides featuring remote alkene functionality led to alkylated carbyne complexes **385** [367]. Photolysis of complexes **385** in chloroform was studied. The major products from these photolyses were the dienes **387** and the

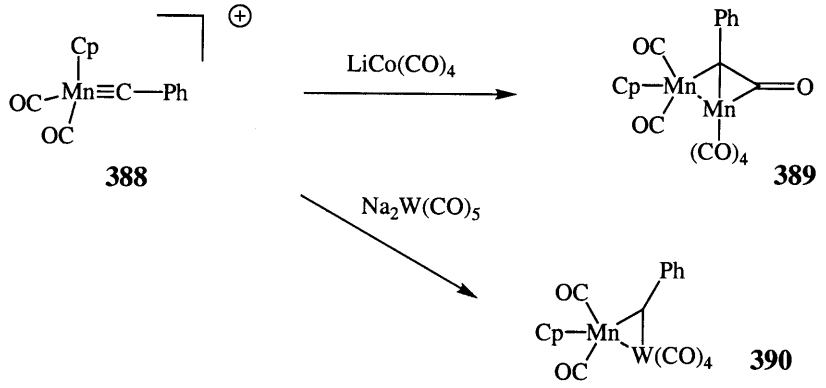
carbene complexes (**386**) containing chloride ligands. The proposed mechanism involves photooxidation of the metal followed by hydrogen atom abstraction from chloroform, affording a cationic carbene complex, which either decomposes to the corresponding diene (**387**) or reacts with chloride ion to produce carbene complex **386**.



Scheme 73.

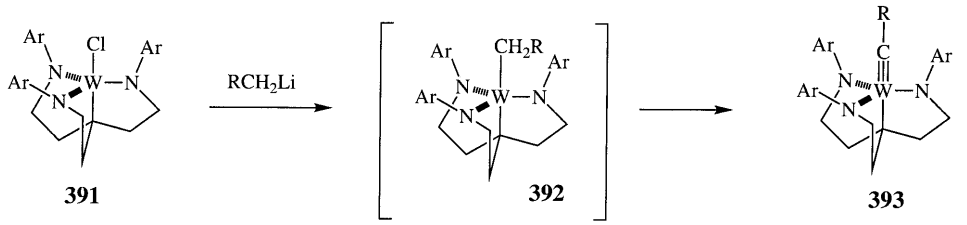
2.2.4. Other processes involving metal–carbyne complexes

Several papers have reported of the coupling of cationic manganese carbyne complex **388** (Scheme 74) (and the rhenium analog) with metal carbonyl derivatives. Bridging ketene–bimetallic complexes (**389**) and bridging carbene–bimetallic complexes (**390**) were prepared from manganese (or rhenium) carbyne complexes and anionic metal carbonyls [368]. A reductive dimerization of **388** occurred upon treatment with the cobalt carbonyl anion, while a heterobimetallic (**390**) was produced upon reaction with the tungsten pentacarbonyl dianion. Other related studies of the formation of bimetallics from **388** and the rhenium analog include: (1) reaction with binuclear iron sulfides [369], (2) reaction with binuclear anionic iron–cobalt and tungsten–cobalt complexes [370], (3) reaction with tetracarbonyl-(hydrido)iron [371]. Heterobimetallic carbene complexes were also prepared from the reaction of neutral carbyne–Group VI metal complexes and carboranyl–substituted ruthenium complexes [372].



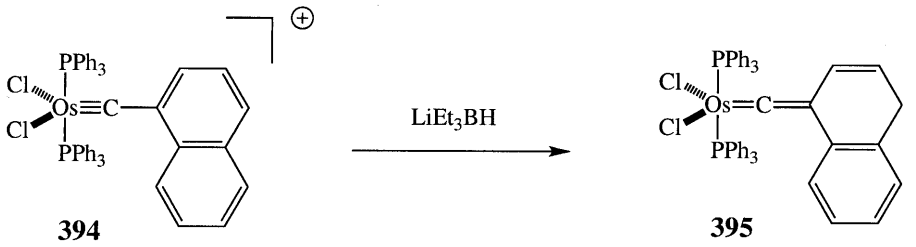
Scheme 74.

Tungsten–carbyne complexes featuring the fluorinated triamidoamine ligand (**393**, Scheme 75) were prepared by treatment of tungsten halides (**391**) with alkyllithium reagents; the intermediate alkyltungsten complex **392** underwent elimination of two hydrogens to afford the carbyne complex [373]. Deuterium labeling studies revealed that both α- and β-hydride elimination processes were occurring in the initially formed alkyltungsten complexes. The hydridocarbene complex (**393**, R=H) could be prepared by treatment of complex **391** with cyclopropyllithium.



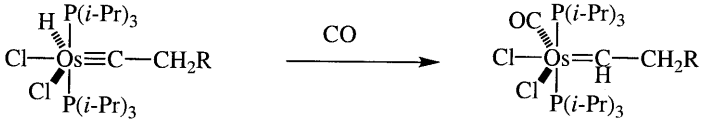
Scheme 75.

The addition of hydride to cationic naphthylcarbene–osmium complexes (e.g. **394**, Scheme 76) was studied [374]. Addition to the 1-naphthylcarbyne complex proceeded by ε-attack, affording the alkenylvinylidene complex **395**. Similar conjugate addition reactions were investigated for the corresponding 2-naphthylcarbyne complexes.



Scheme 76.

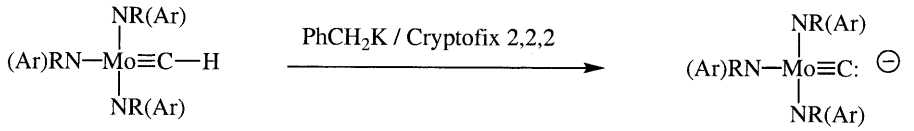
A theoretical study of (hydrido)carbyne–osmium complexes [H–Os≡C–CH_2R] was conducted [375]. The major question addressed in these studies concerns the observation that the osmium complex exists as the hydrido–carbyne complex [H–Os≡C–CH_2R] while the corresponding ruthenium complex converts to the corresponding carbene complex {[H–Ru≡C–CH_2R]→[Ru=$CHCH_2R$]} (the product of migrating the hydride ligand to the carbyne carbon). The calculations suggests that the higher oxidation state is more stable in the 5d metal (osmium) than the 4d metal (ruthenium). As noted in Scheme 77, the carbene complex structure of osmium is preferred in some ligand environments. Treatment of (hydrido)carbyne–osmium complex **396** with carbon monoxide led to carbene complex **397** [376]. Additional ligand substitution/dissociation processes for complexes **396** and **397** were also reported.



396 **397**

Scheme 77.

A complex containing a carbide ligand (**399**, Scheme 78) was generated by deprotonation of a methylidyne–molybdenum complex **398**) with benzylpotassium [377].



398 **399**

Scheme 78.

Other experimental studies of metal–carbyne complexes include: (1) the synthesis and luminescent properties of rhenium–carbyne complexes [378], (2) gas-phase decomposition–chemical vapor deposition for tungsten carbyne complexes [379,380], and (3) synthesis and reactivity of phosphaalkenylcarbyne–Group VI metal complexes [381]. A theoretical study comparing structural aspects of Fischer carbyne and Schrock carbyne complexes of tungsten [382] was reported. The Fischer carbyne complexes feature a lower bond order in the tungsten–carbon bond, resulting a weaker and longer tungsten carbon bond.

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