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The chemistry of the carbon–transition metal double and triple bond: annual survey covering the year 1999☆

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Abstract

This survey is intended to be a comprehensive summary of articles that report on the synthesis, reactivity, or properties of compounds featuring a multiple bond between carbon and a transition metal. Reactions which employ metal carbene complexes as transient intermediates generated through well-established routes [Russ. Chem. Bull. 48 (1999) 16] 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 which are listed in or at the end of Organometallics section of *Chemical Abstracts* (Section 29) are included; patents which appeared in *Chemical Abstracts* in the year 1999 have been included. Only compounds which feature a multiple bond between one carbon atom and one transition metal are discussed in this survey, thus bridging carbene and carbyne complexes are not covered unless there is a multiple bond to at least one transition metal. The complexes of stable carbenes with transition metals have not been included; since the π-donation component of these complexes is minimal, there is no formal carbon–metal multiple bond [J. Chem. Soc., Chem. Commun. (1997) 1963; 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. The ionic model [R.H. Crabtree, The

Abbreviations (for other abbreviations see also the front of issue No. 1 in any year of the *Journal of Organic Chemistry*): ROMP, ring opening metathesis polymerization; RCM, ring closing metathesis; Grubbs catalyst, structure **1** (Fig. 1); Schrock catalyst, structure **2** (Fig. 1).

☆ See Ref. [1].

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Organometallic Chemistry of the Transition Metals, second ed., Wiley-Interscience, New York, 1994, pp. 25–31] has been employed for the discussion of oxidation states and ligand electron count throughout this survey. A special section focusing on alkene metathesis has been included prior to the discussion of carbene complexes of individual metals. The metal carbyne section has been organized according to reaction type.

Keywords: Annual survey; Carbon; Transition metals

1. Metal–carbene or metal–alkylidene complexes

1.1. Review articles

Several reviews covering aspects of metal–carbene complex chemistry appeared in 1999. Many reviews focusing on some aspect of olefin metathesis were published, including the following specific subjects: (1) applications of alkene metathesis in organic synthesis [2]; (2) RCM using molybdenum–carbene complexes [3]; (3) cross metathesis reactions of O- and C-alkenyl glycopyranosides [4]; (4) acyclic diene metathesis (ADMET) polymerization of 1,9-decadiene with ester-containing monoolefins using Grubbs catalyst [5]; (5) use of RCM for the synthesis of azasugars and alkaloids [6]; and (6) RCM of nitrogen-containing compounds [7]. Other specific subjects have been reviewed in which there is a heavy focus on carbene complexes, including: (1) use of metal vinylidenes in catalysis [8]; (2) annulation reactions involving α,β-unsaturated Fischer carbene complexes and alkynes [9]; (3) transfer of carbene ligands between transition elements [10]; (4) synthesis of cyclic Fischer carbene complexes from alkynols [11]; (5) use of nitrogen-stabilized Fischer carbene complexes for asymmetric organic synthesis [12]; (6) use of carbene complexes for organic synthesis [13]; (7) synthesis and reactivity of silylated titanium, zirconium, tantalum, and tungsten carbene complexes [14]; and (8) the annual survey of the carbon–transition metal double and triple bonds for 1997 [15]. 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) transition metal-catalyzed alkynol *endo* cycloisomerizations, which involve vinylidene–metal complexes [16]; (2) use of stoichiometric organotransition metal complexes in organic synthesis [17]; (3) metal–vinylketene complexes, which are often prepared from metal–carbene complexes [18]; (4) development of catalysts for use in natural products synthesis, which

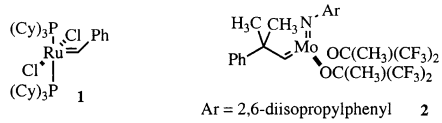
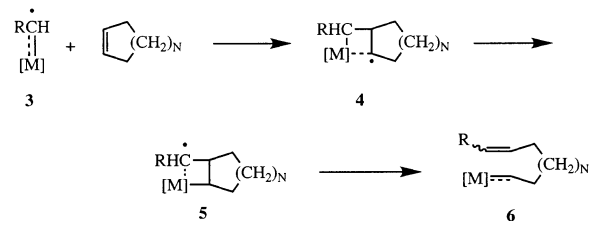


Fig. 1. Structures of alkene metathesis catalysts **1** and **2**.



Scheme 1.

includes a large discussion of metathesis reactions [19]; (5) palladium-catalyzed alkyne couplings, which include numerous examples of the synthesis of polyalkynylcarbene complexes [20]; (6) the effect of halide and related ligands on reactions of carbonylruthenium complexes, which includes many examples of ruthenium vinylidenes [21]; (7) synthesis of heterocyclic aromatics via tandem *ortho*-metallation and RCM [22]; (8) total synthesis of selected epothilones and related compounds [23,24]; (9) tris(pyrazolyl)borate–ruthenium complexes, which includes many examples of carbene complexes [25]; (10) calixarene-ligated organic groups, including carbene and carbyne complexes [26]; (11) use of desymmetrization reactions in organic synthesis [27]; (12) use of transition metal catalysts in organic synthesis [28]; (13) supramolecular topology [29]; and (14) reviews on transition metal–carbon σ bonds including carbene and carbyne complexes for Groups IV [30], V [31], VI [32], VII [33], and VIII–X [34] (Fig. 1).

1.2. Alkene metathesis

Alkene metathesis was the most common reaction process reported for metal–carbene complexes in 1999, and this special section is devoted to papers that focus on this process. Many examples of both polymerization (mostly ring opening metathesis polymerization (ROMP)) reactions and small-molecule syntheses appeared. Only metathesis reactions initiated by a discreet transition metal–carbene complex, or metathesis reactions that discuss the carbene complex intermediates of this reaction have been included here.

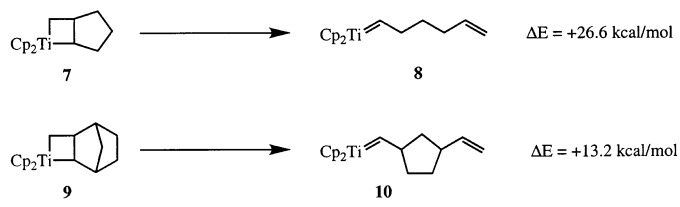
1.2.1. General studies of alkene metathesis catalysts

Several mechanistic studies related to alkene metathesis appeared in 1999. Persistent radicals were observed upon treatment of the Grubbs catalysts with benzophenone and various alkenes, including norbornene and norbornadiene [35]. A free radical mechanism was proposed for the initiation of metathesis reactions using the Grubbs catalyst (Scheme 1).

A probe for side reactions during metatheses using the Grubbs catalyst was reported [36]. This catalyst could be used at temperatures up to 70°C without loss of selectivity, and was observed to have no activity as an alkene isomerization catalyst. Slow decomposition of the catalyst to a noncarbene species was noted.

Titanium alkylidene-catalyzed olefin metathesis was studied by density functional theory [37]. Energies for exchange reactions of a variety of β-substituted titanacyclobutanes with 1,1-disubstituted alkenes were determined. Conversion of titanacyclobutanes to titanium–alkylidenes and alkenes was determined to be an endothermic process (Scheme 2). Conversion of norbornene-fused metallacyclobutanes (**9**) to 3-alkenylcyclopentyidene–titanium complexes (**10**) (as required for ROMP) was far less endothermic (+ 13.2 kcal/mol) than conversion of cyclopentane-fused metallacyclobutanes (**7**) to δ,ε-unsaturated alkylidene–titanium complexes (**8**) (+ 26.6 kcal/mol).

Numerous attempts to develop new catalysts for alkene metathesis were reported in 1999; some representative examples are depicted in Fig. 2. Several derivatives of



Scheme 2.

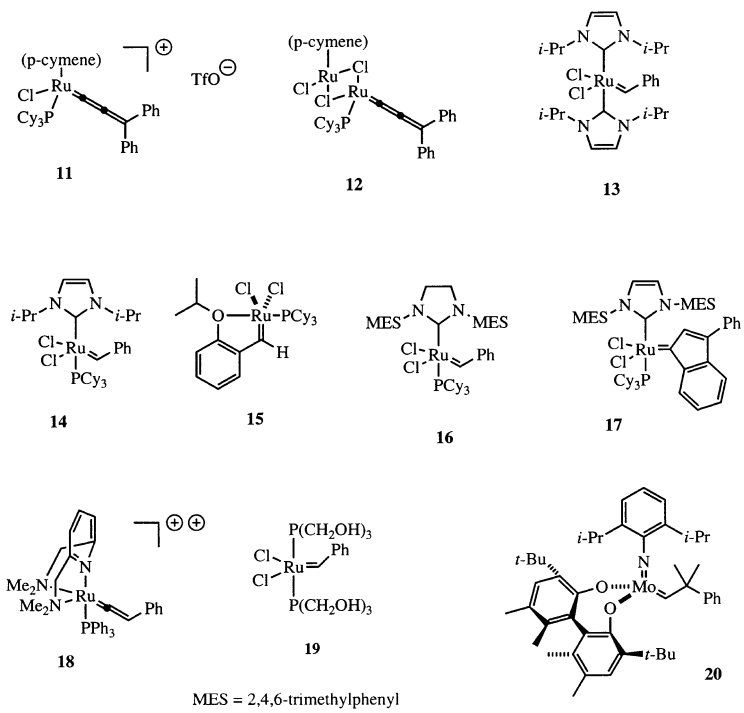
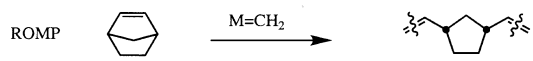


Fig. 2. Representative examples of new catalysts for alkene metathesis.

the Grubbs and Schrock catalysts were synthesized and tested in their ability to undergo either ROMP or RCM processes, including: (1) a dimeric ruthenium carbene complex, which was tested in the metathesis of unsaturated fatty acid esters [38]; (2) a cationic ruthenium allenylidene complex (**11**), which was effective in initiating the RCM and enyne metathesis reactions when the counterion was triflate [39]; (3) neutral allenylidene complexes (e.g. **12**) [40,41]; (4) neutral ruthenium complexes featuring *N*-heterocyclic carbene ligands and chlorine-bridged heterobimetallic derivatives [42]; (5) derivatives of the Grubbs catalyst featuring silicon-containing phosphine ligands [43]; (6) numerous reports of analogs featuring stable carbenes in place of phosphine ligands (e.g. **13**) [44–46] (analogs featuring one carbene and one tricyclohexylphosphine ligand (e.g. **14**) were significantly more reactive than the Grubbs catalyst) [47–49]; (7) a *cis* chelating phosphine analog of the Grubbs catalyst [50]; (8) a recoverable RCM catalyst (**15**) prepared from the coupling of *o*-methoxyphenyl diazomethane and ruthenium (II) complexes [51]; (9) ruthenium carbene complexes featuring one dihydroimidazol-2-ylidene ligand and one tricyclohexyphosphine ligand (e.g. **16**), which appear to be comparable in reactivity to the Schrock catalyst but considerably less air sensitive [52]; (10) indenylidene–ruthenium complex (**17**), which was generally successful for the RCM of monosubstituted alkenes at 40°C, but was ineffective for the RCM of more hindered systems [53]; (11) a dicationic ruthenium vinylidene complex (**18**), which was effective as a ROMP catalyst [54]; (12) a water-soluble analog of Grubbs catalyst (**19**) featuring tris(hydroxymethyl)phosphine ligands [55]; (13) a polymer-bound RCM catalyst (ROMP-Gel) generated in situ from Grubbs catalyst and polymer-bound monosubstituted alkenes [56]; (14) chloride-bridged dimeric ruthenium–carbene complexes [57]; and (15) various molybdenum–carbene complexes featuring homochiral binaphthyl-based ligands (e.g. **20**) which are effective in asymmetric RCM using kinetic resolution or desymmetrization approaches [58]. Catalysis of alkene metathesis reactions using non-alkylidene ruthenium and osmium complexes was also reported [59–61]. Several patents were issued for the synthesis and development of metal–carbene containing olefin metathesis catalysts [62–72].

A comparison of the rate of decomposition versus the rate of the RCM was conducted for a series of recently discovered RCM catalysts [73]. The investigators noted that many recently reported catalysts which have high activity are also prone to decomposition, thus requiring very high catalyst loading for successful RCM reaction. Based on the investigators' suggestion that catalyst utility is determined by the ratio of the rate of catalysis to the rate of decomposition, the Grubbs catalyst and monocarbene analogs were determined to be among the most generally useful RCM catalysts.

Other general studies of the alkene metathesis where carbene complexes were discussed include: (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; and (2) binding of the WCl_6/Et_2AlCl catalyst system to polystyrene supports [74]; a η^6-arene-tungsten carbene complex was proposed as the catalytically-active species.



Scheme 3.

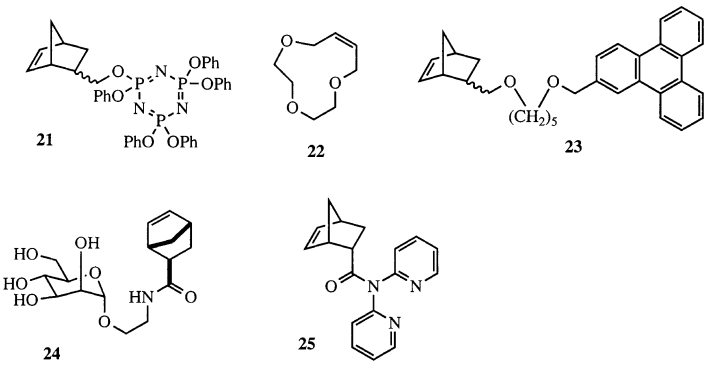


Fig. 3. Representative substrates for the ROMP reaction.

1.2.2. Polymerization reactions

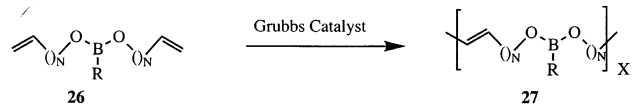
The ring opening metathesis polymerization (ROMP) (Scheme 3) reaction remains a very active area of investigation. The strained alkene norbornene, norbornene derivatives, and copolymerization involving a norbornene derivative and another alkene accounted for a large fraction of all reports of the ROMP reaction in 1998 (Fig. 3). Examples of ROMP using metal carbene complexes include: (1) ROMP of dicyclopentadiene using in situ-generated titanocene methylene complexes and various derivatives featuring substituted Cp rings [75]; (2) ROMP of phosphazene-functionalized norbornene derivatives (e.g. **21**) [76]; (3) ROMP of unsaturated crown ethers (e.g. **22**) [77]; (4) ROMP of norbornadiene derivatives using an in situ-generated ruthenium–carbene complex; very high *trans* selectivity was observed which diminished when tricyclohexylphosphine was added to the reaction mixture [78]; (5) formation of liquid crystalline material through ROMP of triphenylene-containing norbornene derivatives (e.g. **23**) [79]; (6) ROMP of peptide-linked norbornene derivatives [80]; (7) ROMP of *t*-butoxynorbornadiene derivatives using the Grubbs catalyst; unusual regeneration of the Grubbs catalyst was attributed to macrocycle formation [81]; (8) ROMP of norbornene derivatives substituted with carbohydrate recognition elements (e.g. **24**) for the synthesis of biologically active multivalent arrays [82]; (9) preparation of novel polymer-bound ligands for palladium [83] or zinc [84] through ROMP of pyridine-containing norbornene derivatives (e.g. **25**); (10) preparation of a polymer bound phosphonate ester useful for solid-phase Wittig chemistry via ROMP of phosphonate-substituted norbornene derivatives [85]; (11) preparation of a polymer-supported ROMP catalyst of limited stability by reaction of vinyl polystyrene with the Grubbs catalyst, which could successfully initiate the ROMP of norbornene derivatives [86];

(12) ROMP of norbornene derivatives using a ruthenium vinylidene catalyst and termination via reaction with electron-rich monosubstituted alkenes [87]; (13) ROMP of norbornenylmethyl ethers [88]; (14) ROMP of norbornene using an in situ-generated molybdenum– or tungsten–carbene complex [89]; (15) ROMP of vancomycin-bound norbornene derivatives [90]; (16) ROMP of chromophore-substituted norbornene derivatives for NLO studies [91]; (17) ROMP of norbornene derivatives substituted with highly conjugated aromatic rings [92]; and (18) ROMP of porphyrin-fused benzonorbornadiene derivatives [93].

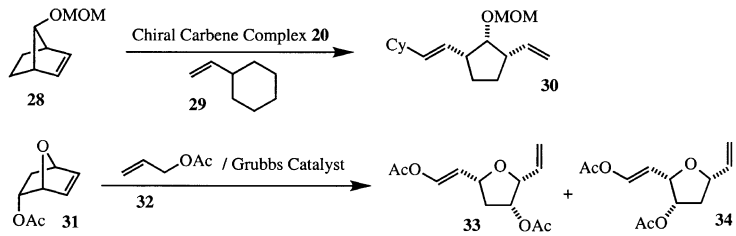
Acyclic diene metathesis (ADMET) polymerization was reported for boronate-linked dienes (**26**, Scheme 4) using either the Grubbs catalyst or the Schrock catalyst. ROMP polymerization was also reported for boronate-containing norbornene derivatives [94]. Similarly, germanium-containing polymers were prepared from the ADMET polymerization of bis(5-pentenyl)- and bis(4-butenyl)germanium compounds; higher molecular weight polymers were obtained using the Schrock catalyst [95].

1.2.3. Nonpolymer-forming ring opening metathesis reactions

A tandem asymmetric ring opening metathesis-cross metathesis reaction sequence was reported using 7-alkoxynorbornene derivatives (e.g. **28**, Scheme 5) and monosubstituted alkenes (e.g. **29**) in the presence of homochiral molybdenum carbene complex **20** (Fig. 2) [96]. A moderately regioselective tandem ring opening metathesis-cross metathesis (favoring **33** over **34**) was demonstrated for several 2-oxygenated-7-oxanorbornene derivatives (e.g. **31**) and allyl acetate and benzoate [97]. Solution and solid-phase cross metathesis of styrene derivatives with norbornene derivatives were demonstrated [98]. Ring opening-cross metathesis of 1,5-cycloctadiene and ethylene using a traditional catalyst system (molybdenum pentachloride/tetramethyltin) was reported [99]. Ring opening cross metathesis of ethylene and 8-oxabicyclo[3.2.1]octene systems was also demonstrated [100].



Scheme 4.



Scheme 5.

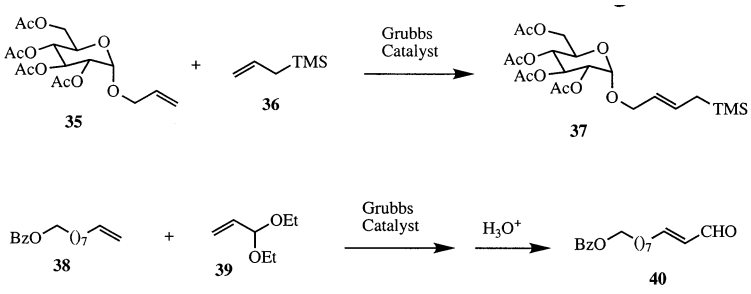
1.2.4. Cross metathesis and metathesis–dimerization reactions

The cross metathesis reaction of various dissimilar monosubstituted alkenes was investigated, including: (1) cross metathesis of C- or O-allyl glycosides (e.g. **35**, Scheme 6) with various monosubstituted alkenes [101,102] and metathesis–dimerization reactions for similar compounds [103]; (2) cross metathesis of monosubstituted alkenes (e.g. **38**) and acrolein acetal (**39**), resulting in α,β-unsaturated aldehydes (e.g. **40**) [104]; (3) cross metathesis of allylbenzene with several monosubstituted alkenes of diverse electronic properties [105]; (4) metathesis dimerization of allylsubstituted vitamin D derivatives [106]; (5) cross metathesis of various allylic and homoallylically-functionalized monosubstituted alkenes and allyltrimethylsilane [107]; (6) metathesis homo- and heterodimerization of allyl(amido)glycosides [108]; and (7) synthesis of trisubstituted alkenes via cross metathesis using the dihyroimidazolylidene ligated carbene complex **16** (Fig. 2) [109].

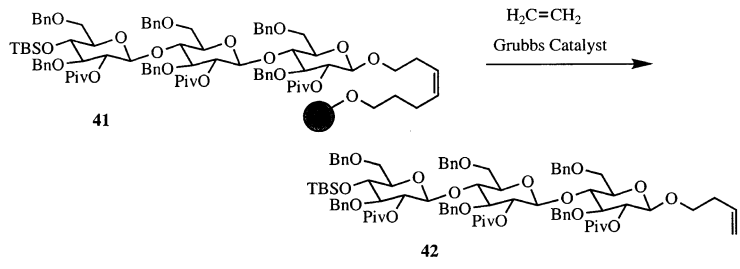
Carbohydrate derivatives linked to a resin though an alkene (e.g. **41**, Scheme 7) were cleaved by cross metathesis with ethylene, leaving a pentenyloxycarbohydrate derivative (**42**) [110]. Similarly, chelating auxiliary groups could be removed from stereoselectively-prepared 4-substituted-5-hexen-1-ol derivatives via cross metathesis with ethylene [111].

1.2.5. Ring closing metathesis

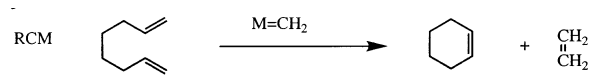
The ring-closing metathesis reaction (RCM) (Scheme 8) has emerged as a very important method for organic synthesis. Many examples forming diverse ring sizes



Scheme 6.



Scheme 7.



Scheme 8.

have been reported, including macrocylces and medium-size rings, as well as the traditional five- and six-membered ring-forming reactions.

Numerous examples of the formation of nitrogen heterocycles using the RCM reaction (Fig. 4) were reported in 1999, including: (1) use of the RCM reaction for the annulation of 6- to 8-membered rings onto the β-lactam nucleus [112]; (2) use of two RCM sequences for the synthesis of macrocyclic and 8-membered ring nitrogen heterocycles (**43**) in ircinal A [113]; (3) use of the RCM reaction for stereospecific construction of 2,5-disubstituted pyrrolines (**44**) [114]; (4) formation of the seven-membered ring system (**45**) present in balanol using the RCM reaction [115]; (5) formation of 6–8-membered ring trifluoroacetyl-protected nitrogen heterocycles in both the solution and solid phases [116]; (6) synthesis of bicyclic lactams (e.g. **46**) using RCM of *N*-allyl cyclic amide derivatives [117]; (7) synthesis of bicyclic lactams using RCM of unsaturated amide derivatives of proline [118]; (8) failed attempts to form 8-membered ring diamides from RCM of *N*-allyl tripeptide derivatives [119]; (9) synthesis of *N*-arylpyrrolidines (e.g. **47**) using RCM of *N*,*N*-diallylaniline derivatives [120]; (10) preferential *N*-heterocycle formation (e.g. **48**) in the reaction of *N*,*N*-diallyl allylsulfonamide derivatives and 6- and 7-membered ring forming homologues [121]; (11) synthesis of coniine using RCM to form a piperidine ring as a key step [122]; (12) synthesis of pyrrolines containing a trisubstituted alkene (e.g. **49**) via RCM of *N*-2-phenylallyl-substituted carbamate derivatives [123]; (13) synthesis of a key intermediate for halosaline synthesis (**50**) using RCM and cross metathesis as key steps [124]; (14) use of RCM for the synthesis of spirocyclic nitrogen heterocycles [125]; and (15) synthesis of Fredinger lactams using solid phase RCM [126].

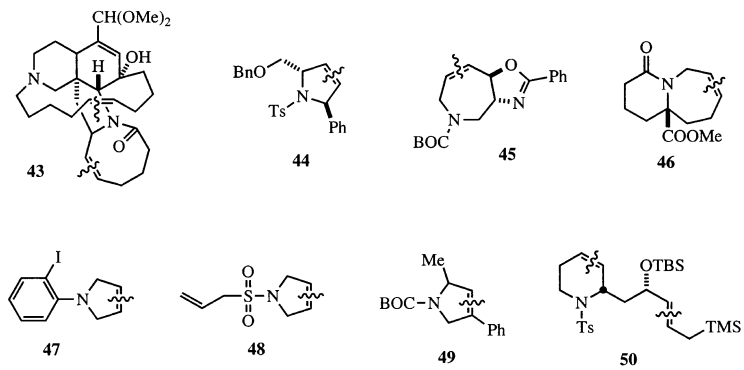


Fig. 4. Representative *N*-heterocycles produced through an RCM reaction (bond constructed through RCM indicated).

The RCM reaction has been employed for the synthesis of a variety of carbocyclic ring systems (Fig. 5, the indicated bond was formed via the RCM reaction). Examples include: (1) synthesis of polyoxygenated 6-membered rings (e.g. **51**) [127–132]; (2) formation of 5,6- and 6,6-fused carbocycles (e.g. **52**) via a double RCM procedure using tetraene precursors [133]; (3) formation of 5-aminocycloheptene derivative **53** for the synthesis of anatoxin A [134]; (4) synthesis of polyoxygenated 5-membered rings [135–137]; (5) synthesis of 7-membered ring carbocycle **54** for synthesis of the welwitindolinone ring system [138]; (6) preparation of spirocycles (e.g. **55**) through RCM of 4,4-diallyl-2-cyclohexen-1-one derivatives [139] and alkene-substituted piperazines [140]; (7) preparation of 6-membered rings containing two amino groups (e.g. **56**); which were protonated during the RCM event [141]; (8) formation of remote iodoalkene-containing cycloalkenes (e.g. **57**) in a selective RCM reaction favoring non-iodinated alkenes [142]; (9) RCM of 2,2-diallyl derivatives of cyclic 1,3-diones [143]; (10) formation of cycloalkenes as a byproduct while using the RCM as a method to cleave allyloxycarbohydrate derivatives from a solid support [144]; (11) synthesis of hydroxycycloheptenes [145]; and (12) synthesis of 3-cyclohexenecarboxylate esters using the RCM reaction [146].

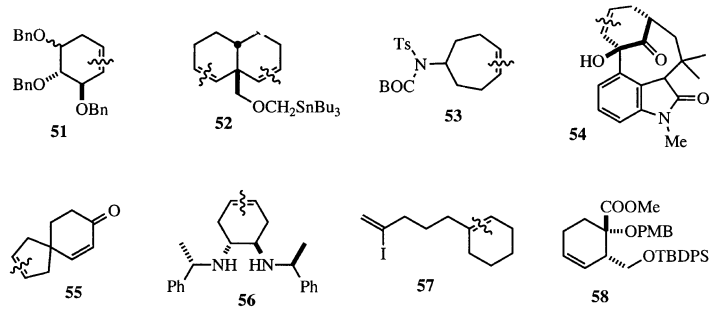


Fig. 5. Representative carbocycles produced through an RCM reaction (bond constructed through RCM indicated).

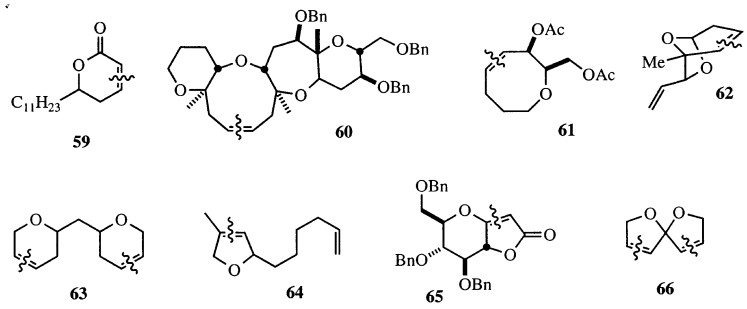
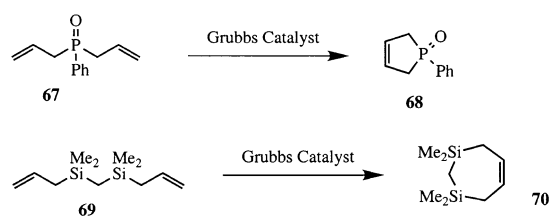


Fig. 6. Representative oxygen-heterocycles produced through an RCM reaction (bond constructed through RCM indicated).

Many examples of oxygen heterocycle synthesis using the RCM reaction were reported in 1999 (Fig. 6), including: (1) formation of remote iodoalkene-containing pyran derivatives in a selective RCM reaction favoring non-iodinated alkenes [147]; (2) formation of 6-membered ring lactones (e.g. **59**) through RCM processes involving α,β-unsaturated esters [148–150]; (3) formation of oxygen heterocycle substructures (e.g. **60**) related to ciguatoxin and brevitoxin [151–157] (4) formation of 8-membered ring oxygen heterocycles (e.g. **61**) for the total synthesis of laurencin [158,159] and laureatin [160]; (5) RCM of allylic homoallylic ethers [161]; (6) formation of the 6-membered ring system of *exo* brevicomin (e.g. **62**) through selective RCM of a trivinylketal derivative [162] and a related synthetic approach for the total synthesis of frontalin [163]; (7) selective formation of oxygen heterocycles (e.g. **63**) and not carbocycles in the RCM of dioxygen-containing tetraene derivatives [164]; (8) formation of homochiral 2-4-dihydrofuran derivatives (e.g. **64**) through RCM-isomerization of homochiral 3-alloxycycloalkenes [165]; (9) diastereoselective RCM reactions using substrates which contain diastereotopic vinyl groups [166]; (10) RCM reaction of various allylic homoallylic ether derivatives featuring one or fewer 1,1-disbstituted alkenes [167,168]; (11) synthesis of cyclic enol ethers (e.g. **65**) via RCM reactions involving enol ethers and unsaturated esters, including α,β-unsaturated esters [169]; (12) formation of 7-membered ring oxygen heterocycles containing various degrees of oxygen substitution [170,171]; (13) formation of dihydropyran rings fused to a furanose system through RCM and intramolecular enyne metathesis [172,173]; (14) formation of 2,4-dihydrofuran as a byproduct while using the RCM as a method to cleave an allyloxy protecting group [174]; (15) formation of highly oxygenated glycal derivatives through RCM of enol ethers [175,176]; and (16) selective formation of carbocyclic and oxacyclic spirocycles (e.g. **66**) over 1,1-divinylcycloalkanes by reaction of *gem* divinylcontaining tetraene derivatives with Grubbs catalyst [177].

Other heterocyclic compounds were also constructed via the RCM reaction. A variety of phosphorus heterocycles (e.g. **68**, Scheme 9) were prepared from the RCM reaction of alkene-containing phosphonates (e.g. **67**) [178] and phosphine oxides [179]. Cyclic phosphonates containing additional heteroatoms in the ring were prepared from the RCM reaction of alkene-containing phosphonamides and phosphonate esters [180]. Cyclic silanes, siloxanes, and disilanes (e.g. **70**) were prepared through RCM of various vinylsilane [181], allylsilane [182,183] and bis(alkenyloxy)silane derivatives [184]. A patent was issued for the preparation of polycyclic silicones through RCM of vinyl-substituted polycyclic silicones [185].



67 68 69 70

Scheme 9.

The RCM reaction was a key step in construction of the macrocyclic ring (**72**, Fig. 7) of the anticancer drug epothilone [186–188]. Numerous other examples of successful macrocyclic ring closure using the RCM reaction have also appeared, including: (1) the formation of conformationally-constrained peptide derivatives (e.g. **73**) [189] and other macocyclic peptides [190–192]; (2) the formation of analogues of the immunosuppressant compound sanglifehrin (e.g. **74**) [193]; (3) formation of macrocyclic rings present in trefoil knot compounds [194] and catenanes [195–197]; (4) formation of a double *p*-cyclophane ring system (**75**) for the total synthesis of cylindrocyclophane F [198]; (5) formation of macrocycle-bridged carbohydrate derivatives [199]; (6) synthesis of a macrocyclic ring (**76**) for the total synthesis of rosephilin [200,201]; (7) synthesis of the macrocyclic ring (**77**) of the tripyrrole pigment nonylprodigiosin [202]; (8) synthesis of macrocyclic ligands (e.g. **78**) through RCM of bis(alkene-containing phosphine)rhenium and platinum complexes [203]; (9) synthesis of palladium inclusion complexes through double RCM of bis[2,6-di(3-buten-1-yl)pyridine]–palladium complexes [204]; (10) synthesis of 10-membered ring lactones (e.g. **79**) [205]; (11) construction of 8- and 14-membered rings fused to the γ-lactone ring system [206]; (12) construction of 11-membered ring carbocycles for evaluation as epothilone analogs [207]; (13)

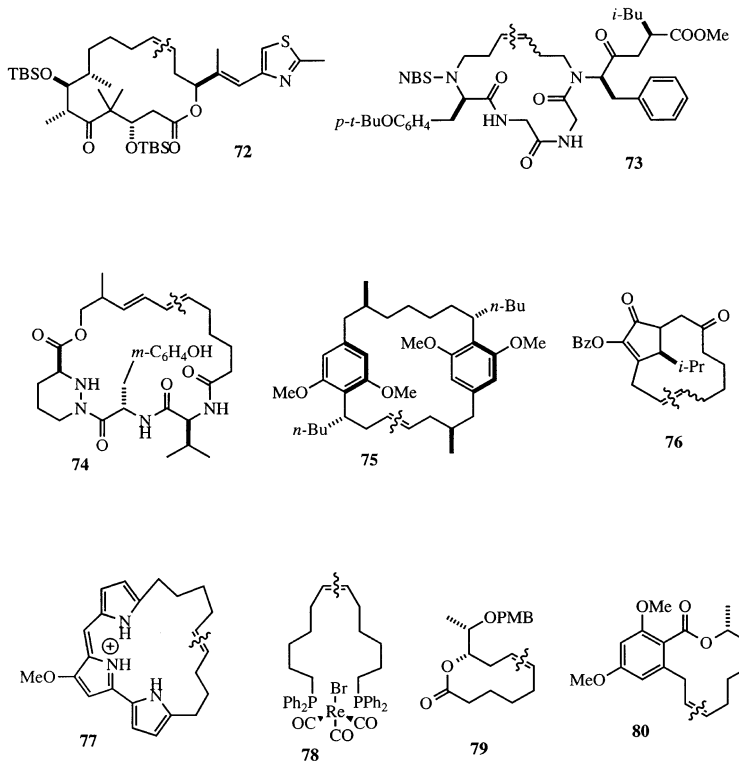
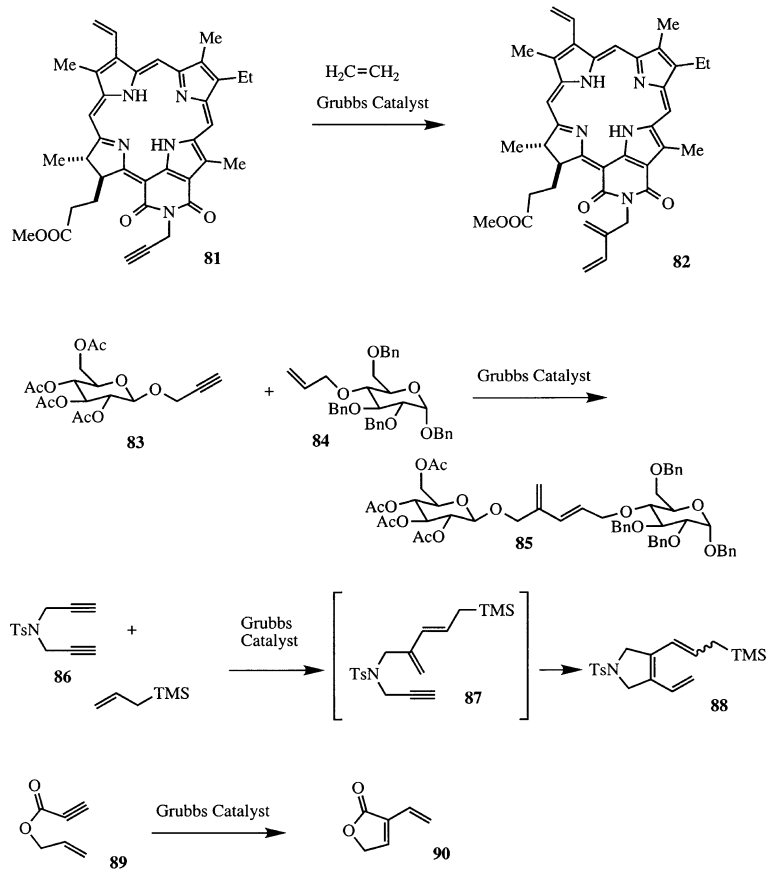


Fig. 7. Representative macrocycles (ring size > 10) prepared using the RCM reaction.

construction of 11-membered ring nitrogen heterocycles as part of a semibiomemetic approach to manzamine alkaloids [208]; (14) construction of the macrocyclic ring of sarain A [209]; (15) synthesis of cored dendrimers via macrocyclic RCM [210]; (16) formation of simple macrocyclic lactams [211] and lactones [212]; (17) formation of macrocyclic polyethers [213]; and (18) construction of the macrocyclic lactone rings (e.g. **80**) of macrocyclic lactones lasiodiplodin and zeranol [214].

1.2.6. Alkene metathesis involving alkyne components

Several examples of the synthesis of conjugated dienes through the intramolecular and intermolecular metathesis of enynes were reported in 1999. Examples of intermolecular enyne metathesis reactions include: (1) metathesis of of a propargylporphyrin (**81**, Scheme 10) and ethylene to afford diene **82**, which was a useful compound for the formation of porphyrin conjugates [215]; (2) intermolecular coupling of allyl- (e.g. **84**) and propargyl-substituted (e.g. **83**) carbohydrate deriva-



Scheme 10.

tives using the Grubbs catalyst [216]; (3) liquid and solid phase intermolecular enyne metathesis reactions [217]; (4) intermolecular enyne metathesis of allylic acetates and γ,δ-unsaturated esters [218]; (5) formation of trienynes (e.g. **88**) via tandem inter- and intramolecular enyne metathesis for the coupling of allyltrimethylsilane with various 1,6-diyne derivatives (e.g. **86**) [219]; (6) synthesis of dienes through enyne cross metathesis of ethylene with terminal and internal alkynes [220]; and (7) synthesis of 3-vinyl-3-furan-1-one (**90**) by intramolecular enyne metathesis of allyl propiolate (**89**) [221].

1.2.7. Non-metathesis reaction processes involving the Grubbs catalyst

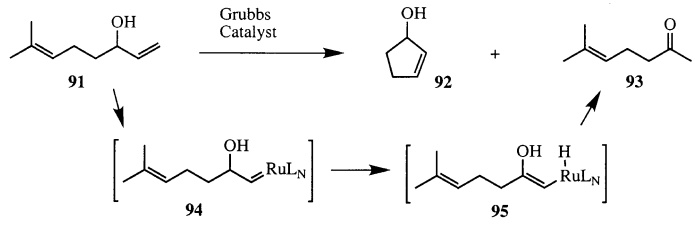
Attempted RCM of allylic alcohols (e.g. **91**, Scheme 11) led to the methyl ketone (e.g. **93**) and the expected RCM product **92** [222,223]. Reaction of other secondary allylic alcohols lacking the second alkene with Grubbs catalysts led to primarily the methyl ketone analogous to **93**. A tertiary allylic alcohol analog of **93** (linalool) underwent the RCM reaction efficiently. Formation of the methyl ketone is a stoichiometric process; the pathway in Scheme 11 was proposed for its formation.

The Grubbs catalyst was an effective promoter for other reaction processes, including: (1) the Kharasch addition of chloroform to monosubstituted and 1,1-disubstituted alkenes (Scheme 12) [224,225]; (2) the trimerization of propargyl glycosides, resulting in predominantly the 1,2,4-trisubstituted aromatic compound [226]; and (3) the polymerization of methyl methacrylate through a non-metathesis mechanism [227].

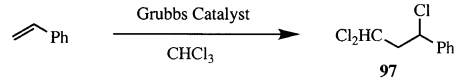
1.3. Individual carbene or alkylidene complexes classified according to metal

1.3.1. Group IV metal–carbene complexes

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



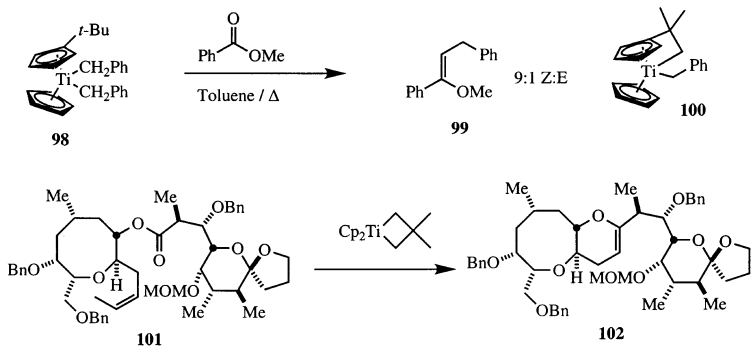
Scheme 11.



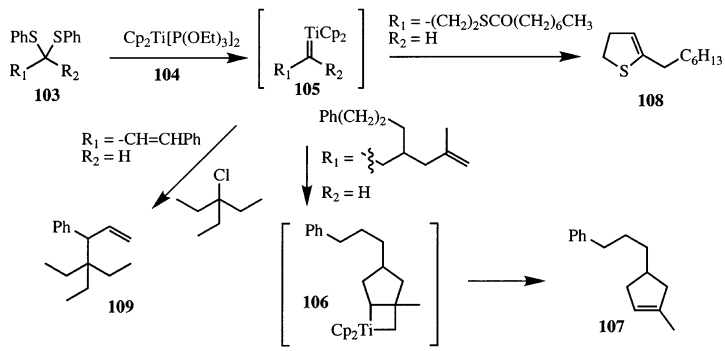
Scheme 12.

Decomposition of dibenzyltitanium complex **98** (Scheme 13) in the presence of carbonyl compounds affords carbonyl olefination products via a titanium carbene intermediate [228]. The stereochemistry for enol ether formation was more Z-selective than the complex featuring unsubstituted cyclopentadienyl ligands. Decomposition of **98** in the absence of a carbonyl trap led to C–H insertion product **100**. Formation of a carbonyl olefination reagent from reaction of $CH_2(ZnI)_2$ and titanium (II) chloride, presumably adding a titanium carbene complex, was reported [229]. A tandem metathesis-carbonyl olefination sequence was reported for alkene–ester **101** using the Tebbe reagent; the product (**102**) features the ring systems present in ciguatoxin [230].

Several examples of the generation of titanium alkylidene intermediates (**105**, Scheme 14) from dithioacetals (**103**) and low-valent titanium (**104**) were reported in 1999. A tandem titanium carbene generation-metathesis sequence was demonstrated for alkene-containing dithioacetals, resulting in metathesis products (e.g. **107**) [231]. Formation of S-heterocycles (e.g. **108**) was demonstrated for dithioacetals containing remote thioester groups [232]. Generation of alkenylcarbene–titanium complex intermediates from 1,3-bis(thiophenyl)-1-alkenes or from allylic thioacetals was also



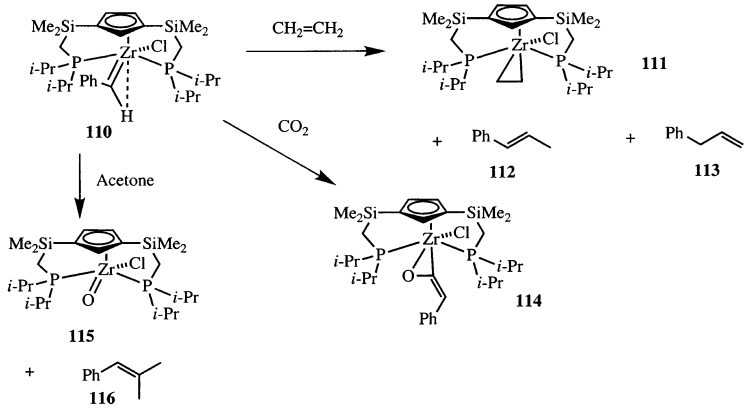
Scheme 13.



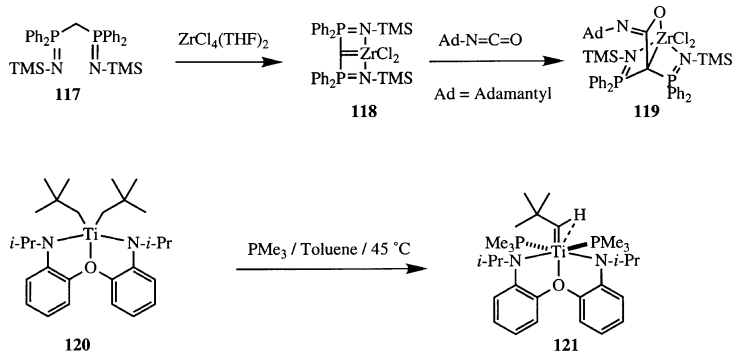
Scheme 14.

demonstrated; these complexes could led to alkylation products (e.g. **109**) with tertiary chlorides [233]. Dichloromethylenation of ketones using the same titanium complex and carbon tetrachloride was also reported [234].

Stable and isolable zirconium benzylidene complexes (e.g. **110**, Scheme 15) were synthesized from reaction of the corresponding methylzirconium complex with benzylpotassium [235] and tested in their reaction with a variety of unsaturated organic compounds [236]. Coupling with ethylene afforded the ethylene–zirconium complexes (**111**) and carbene–alkene coupling products (**112** and **113**). Zirconium–ketene complex (**114**) was obtained from reaction with carbon monoxide. Carbonyl olefination products (e.g. **116**) and zirconium-oxo complexes (e.g. **115**) were observed in coupling reactions with ketones and isocyanates. Stable titanium– and zirconium–carbene complexes (e.g. **118**, Scheme 16) featuring two phosporanimine substituents at the carbene carbon were also reported [237,238]. Reaction of these complexes with electrophiles (alcohols and isocyanates) afforded complexes (e.g. **119**) resulting from nucleophilic attack by the carbene carbon. A stable titanium–



Scheme 15.



Scheme 16.

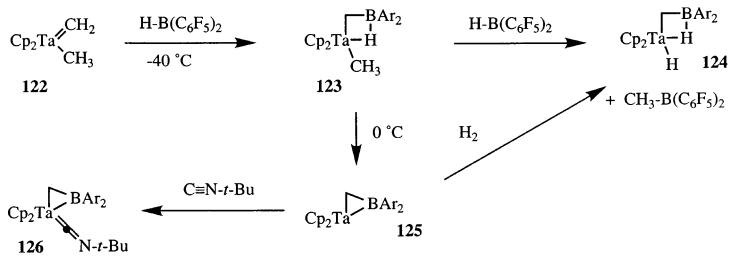
neopentylidene complex (**121**) was obtained via mild heating of the corresponding dineopentyl complex **120** [239].

Theoretical studies of thermal decomposition of titanium– and zirconium–alkyls have been reported [240]. Decomposition of tetraneopentyltitanium proceeded through α-hydride elimination followed by formation of the titanium–carbene complex and reductive elimination of neopentane. For the zirconium analog, oxidative addition into the γ C–H bond was the more favorable process. Ring opening processes for four-membered ring titanacycles featuring a 2-methylene group have been studied by restricted Hartree–Frock calculations [241]. Azatitanacyclobutanes undergo ring opening reactions due to a favorable interaction between the nitrogen lone pair and the LUMO at titanium.

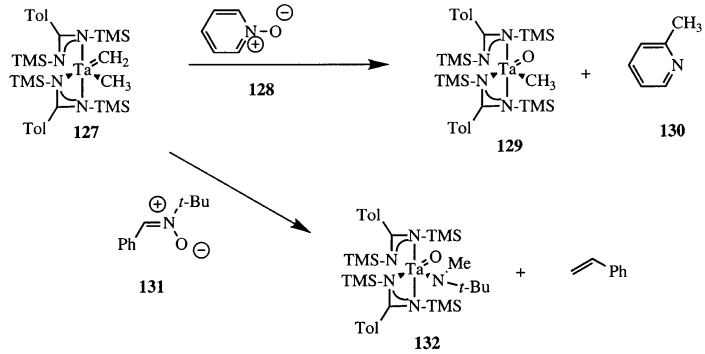
1.3.2. Group V metal–carbene complexes

Several papers emphasizing the synthesis and reactivity of Group V metal–carbene complexes appeared in 1999, and most of these papers focus on tantalum carbene complexes. Coupling of tantalum carbene complex **122** (Scheme 17) with triaryl borohydrides led to the complexes featuring hydride and bridging hydride ligands (e.g. **124**) [242]. The reaction initially produces a bridging hydride species **123**, which can be observed at low temperature. Above −40°C, reductive elimination of methane occurs, and the intermediate (**125**) can either be trapped by the borohydride reagent or by isocyanides. Synthesis of tantalum–methylene complexes through photochemical decomposition of trimethyltantalum species was also reported [243].

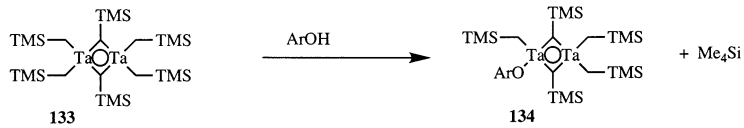
The reaction of tantalum–carbene complex **127** (Scheme 18) and unsaturated amine oxides (**128** or **131**) was investigated [244]. This reaction with pyridine *N*-oxide led to replacement of the carbene ligand by a metal-oxo species (**129**) and formation of methylated pyridine derivative **130**; a mechanism involving coordination of the oxygen to tantalum and formation of the 1,3-dipolar addition product followed by fragmentation and formation of the methylated pyridine derivative was proposed. A similar reaction pathway was observed for nitrones (**131**) except the *N*-methylated complex **132** and styrene were formed; initial imine olefination and formation of the η^2-nitrosobenzene complex was proposed, followed by rearrangement to the observed product.



Scheme 17.



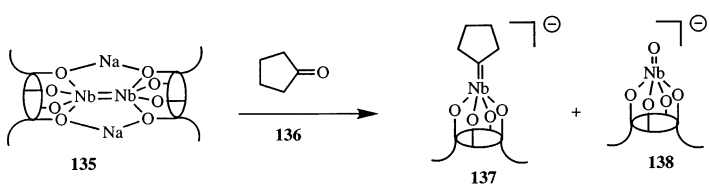
Scheme 18.



Scheme 19.

The reaction of μ-alkylidyne–tantalum complex **133** (Scheme 19) with various 2,6-disubstituted phenol derivatives, which afforded the analogous phenoxytantalum species **134**, was examined [245]. A dramatic rate decrease was noted for phenol derivatives which also have substituents at the 3- and 5-positions. Phenols featuring naphthyl groups at the 2- and 6-positions afforded diastereomeric complexes (*meso* vs. *d,l*).

Anionic calixarene-ligated niobium carbene complexes (e.g. **137**, Scheme 20) were synthesized through the coupling of calixerene-ligated niobium–niobium double-bond containing dimer **135** with ketones or aldehydes; this reaction also afforded one mole of the analogous niobium oxide **138** [246].

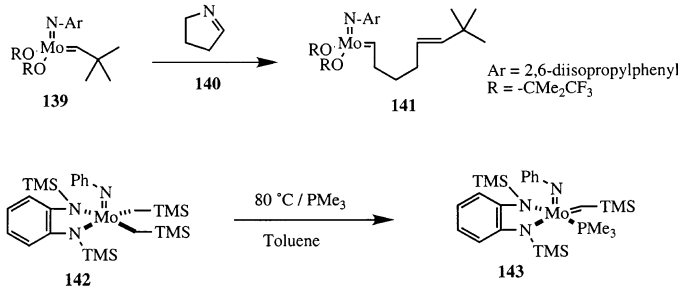


Scheme 20.

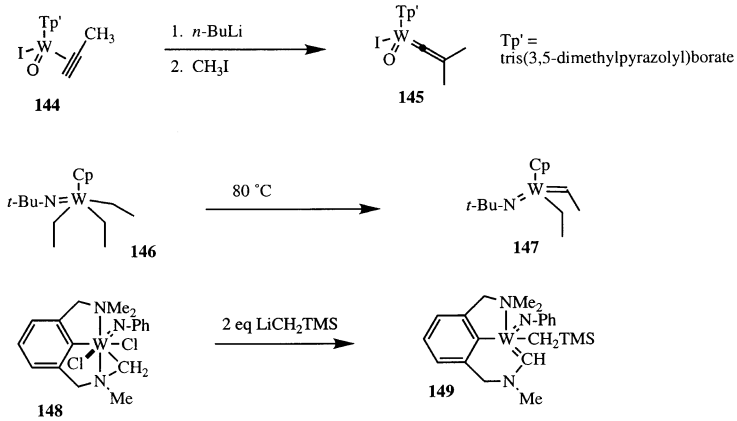
1.3.3. Group VI metal–carbene complexes (further classified according to structure and reaction type)

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. A mechanistic study of the reaction of cyclic imines (e.g. **140**, Scheme 21) with derivatives of the Schrock catalyst (**139**) were reported [247]. Reaction of molybdenum–carbene complex **139** with pyrroline (**140**) occurs by ligation of the imine nitrogen, which could be isolated and characterized, which subsequently undergoes conversion to the metathesis product **141**. Amino analogs of the Schrock catalyst (e.g. **143**) were generated from thermolysis of dialkylmolybdenum (VI) complexes (e.g. **142**) [248]. Derivatives of the Schrock catalyst were demonstrated as effective catalysts for the polymerization of 1-octyne and butyl propargyl ether [249]. Molybdenum–vinylidene complexes were proposed as intermediates in the polymerization of monosubstituted acetylenes [250]. Tungsten η^2-alkenyl complexes were proposed as intermediates in the isomerization of tungsten–alkyne complexes [251].

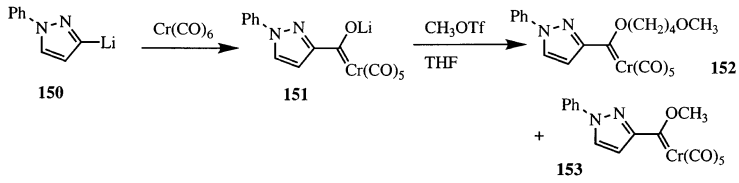
The tungsten (IV) alkyne complex (**144**, Scheme 22) was transformed to a vinylidene complex (e.g. **145**) by treatment with butyllithium followed by various



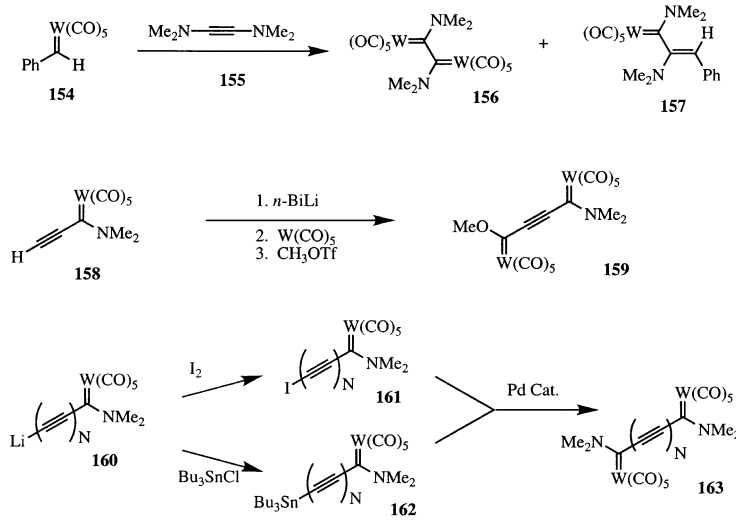
Scheme 21.



Scheme 22.



Scheme 23.



Scheme 24.

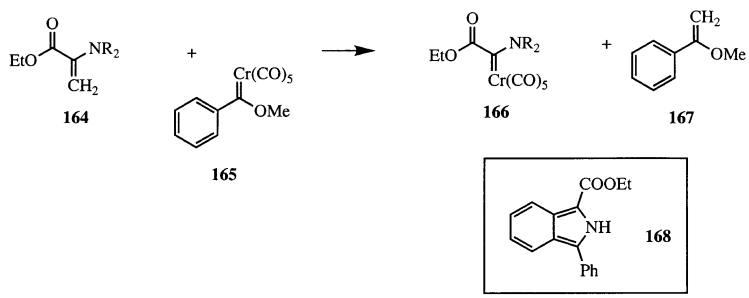
electrophiles (e.g. CH_3I) [252]. Presumably an alkynyltungsten species is generated, which reacts with electrophiles at the β-position. Thermolysis of trialkyltungsten (VI) imido complexes (e.g. **146**) at 80°C leads to the corresponding tungsten–carbene complexes (e.g. 1**47**) and an alkane fragment [253]; even complexes with β-hydrogens underwent this transformation. Coupling of alkyltungsten (VI) imido complex **148** with two equivalents of trimethylsilylmethyllithium led to carbene complex **149** [254].

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 (Scheme 23). A series of Fischer carbene complexes were prepared from lithiated heterocycle derivatives (e.g. **150**) using the Fischer method, or alternatively through the addition of lithiated heterocycles to Group VI metal pentacarbonyl–THF complexes, followed by addition of methyl triflate [255]. When the alkylation step was conducted in THF, the methoxycarbene complex (**153**) plus the THF-incorporated complex **152** were obtained.

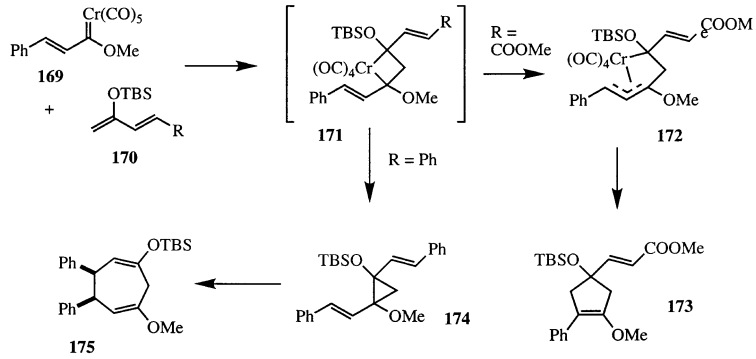
Bis carbene complexes bridged through all-carbon bridges (Scheme 24) were reported [256,257]. The 1,2-derivative (**156**) was prepared in low yield from the coupling of benzylidenetungsten complex **154** with bis(dimethylamino)acetylene (**155**). Other members of the series were prepared according to a general route involving deprotonation of the polyalkynylcarbene complexes **158** followed by the Fischer synthesis using the resulting organolithium reagent. Complexes featuring larger eight-carbon bridges could be prepared from the lithiated butadiynylcarbene complex **160** ($N = 2$); iodination or stannylation of complex **159** afforded the corresponding alkynyliodide (**161**) or alkynylstannane (**162**), which coupled using a palladium catalyst to afford bridged complexes of general structure **163**.

Carbene complexes of general structure **166** (Scheme 25) could be prepared from a metathesis reaction involving arylcarbene complexes and esters of dehydroamino acids (e.g. **164**) [258]. Reaction of the *N*-diphenylmethylene derivative with the arylcarbene complexes led to mixtures of the expected carbene complex **166** (R = Ph) and the isoindole derivative **168**. Another reported synthesis of carbene complexes was via photolysis of thymidene and uridine in the presence of tungsten hexacarbonyl; other nucleobases lead to tungsten–nitrogen complexes [259].

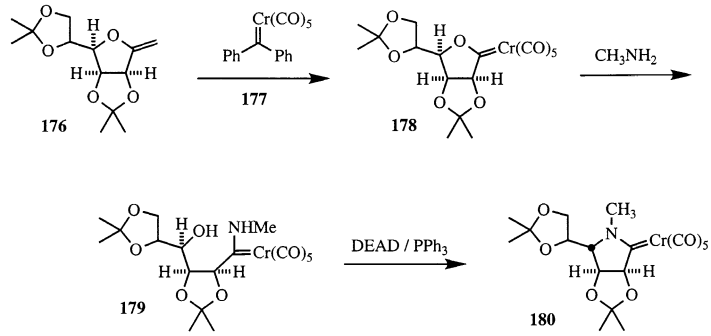
1.3.3.3. reaction of Group VI metal–carbene complexes with alkenes and dienes. This section focuses on reactions of Group VI metal–carbene complexes involving coupling with alkenes at the carbene-carbon. Other examples of the coupling of carbene complexes with alkenes where the reactive site is elsewhere can be found ahead under the heading: cycloaddition reactions occurring at the C–C π-bond of α,β-unsaturated metal–carbene complexes (Section 1.3.3.7). Cyclopropanation is a common reaction pathway for the coupling of Fischer carbene complexes with polarized alkenes. The coupling of α,β-unsaturated chromium carbene complexes (e.g. **169**, Scheme 26) with silyloxydiene derivatives (**170**) afforded either 5- or 7-membered ring products [260]. Competition between direct cyclopropanation followed by Cope rearrangement, resulting in the formation of cycloheptadiene (e.g. **175**), or direct 5-membered ring formation resulting in the formation of cyclopentenes (e.g. **173**), was noted. In the reaction with complex **169**, electron deficient silyloxydienes (e.g. **170**, R = COOMe) generally afforded 5-membered rings, whereas other derivatives led to cycloheptadienones. Analogs of carbene complex



Scheme 25.



Scheme 26.

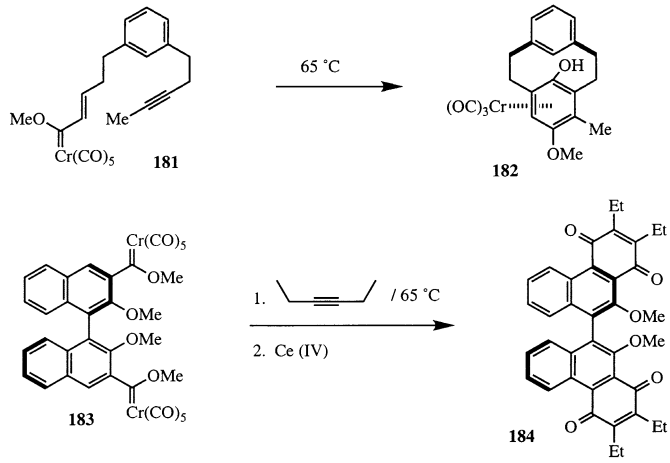


Scheme 27.

169 where a phenyl or methyl group replaces the alkenyl group generally afforded 5-membered rings upon reaction with both classes of silyloxydienes.

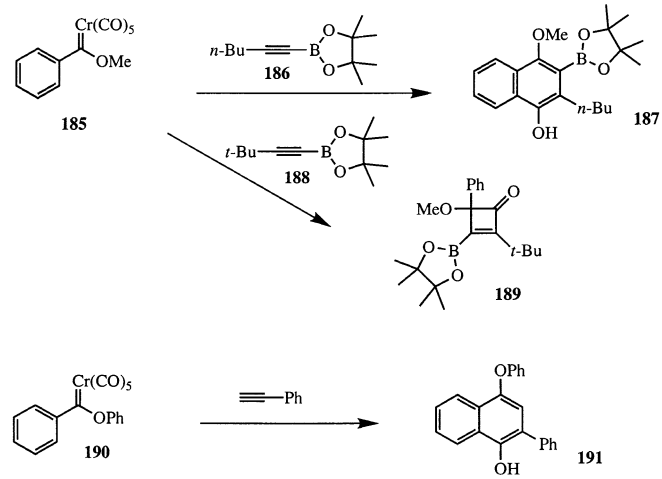
The coupling of diphenylcarbene complex **177** (Scheme 27) with 2-methylenecarbohydrate derivatives (e.g. **176**) let to the corresponding carbohydrate-containing carbene complexes (e.g. **178**) in good yield [261]. The oxacycles converted to the corresponding acyclic aminocarbene complexes (e.g. **179**) when treated with ammonia or methylamine, which would recyclize to the corresponding azacyclic carbene complexes (e.g. **180**) under Mitsunobu conditions.

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. **181**, Scheme 28) and alkynes (commonly known as the Dötz reaction) were reported in 1999. The intramolecular coupling of alkynes and α,β-unsaturated carbene complexes afforded the *anti* cyclophane **182** [262]. Related nonracemic and axial chiral bis carbene complexes of chromium (**183**) were prepared and treated with 3-hexyne [263]. Two diastereomeric benzannulation products were observed from the reaction, which were converted to a single quinone (e.g. **184**) upon

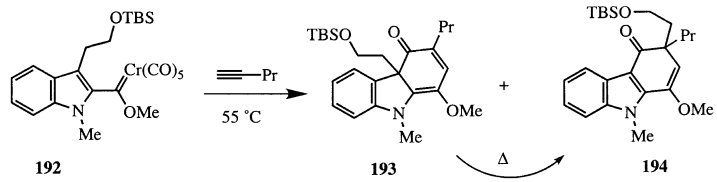


Scheme 28.

oxidation. Alkynylboranes (e.g. **186**, Scheme 29) were suitable substrates for benzannulation reactions, resulting in naphthylboronic esters (e.g. **187**) [264], however sterically hindered alkynylboranes (e.g. **188**) afforded cyclobutenones (**189**). The reactions provided products where the boron inserts β- to the carbene complex functionality; this regioselectivity preference was observed regardless of the steric bulk of the other alkyne substituent. Formation of diaryl ethers (e.g. **191**) from coupling of alkynes with aryloxy α,β-unsaturated carbene complexes (e.g. **190**) was demonstrated for a variety of aryl- and vinylcarbene complexes [265]. Coupling of 1,3-disubstituted-indol-1-ylcarbene–chromium complexes (e.g. **192**, Scheme 30) and alkynes led to the desired cyclohexadienone annulation products (e.g. **193**),



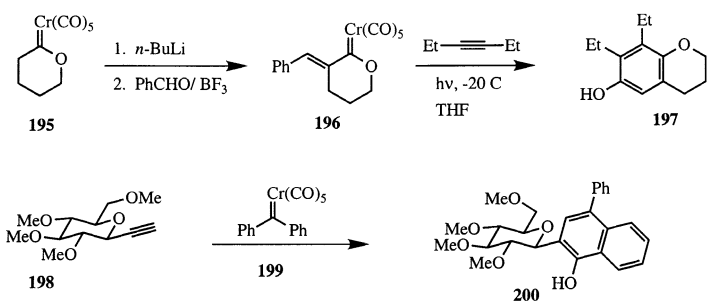
Scheme 29.



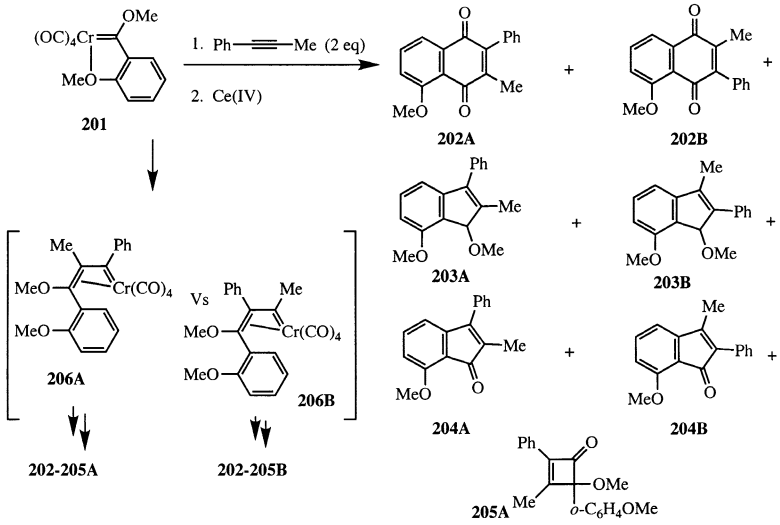
Scheme 30.

which underwent a secondary thermal rearrangement under the reaction conditions, affording cyclohexadienone **194**; similarly hindered 2,6-disubstituted arylcarbene complexes lead to mostly indenones except in a single case involving an intramolecular reaction [266]. Synthetic approaches to deoxyfrenolicin [267], menogaril [268], and olivin [269,270] which involve benzannulation of complex alkynes with arylcarbene–chromium complexes were also reported. Synthesis and benzannulation reactions were reported for cyclic carbene complexes which feature an alkylidene group in the exo position (e.g. **195**, Scheme 31); the optimal conditions for the benzannulation reaction involve photolysis at -20°C [271]. Low-temperature benzannulation reactions were also reported for 2-alkynylglucose derivatives (e.g. **198**) and diphenylcarbene–chromium complex (**199**), which occurred at 25°C [272].

A detailed mechanistic study of the relationship between regiochemistry and alkyne concentration in the coupling of arylcarbene complexes (e.g. **201**, Scheme 32) with alkynes was conducted [273]. The regiochemistry for reaction with 1-phenylpropyne was dependent on the concentration, and attributed to interconversion of the regioisomeric vinylcarbene intermediates (**206A** and **206B**) followed by ligation to the alkyne in a later step of the reaction. It was also noted that benzannulation products (**202**) were formed with a higher degree of regioselectivity than the corresponding indene products (**203**, **204**). Two hypothetical pathways for isomerization of **206A** and **B** were discussed but no preference was stated: (1) reversible insertion of the alkyne; and (2) isomerization through a cyclopropene intermediate. An unusual bimolecular mechanism was noted in the coupling of *o*-methoxyphenylcarbene complex **201** with alkynes at high concentration.



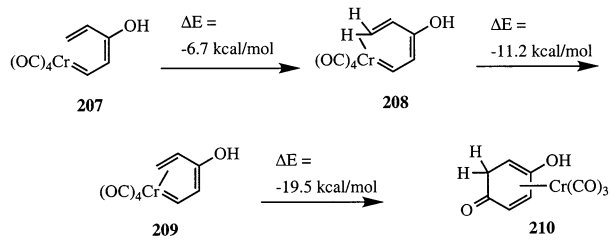
Scheme 31.



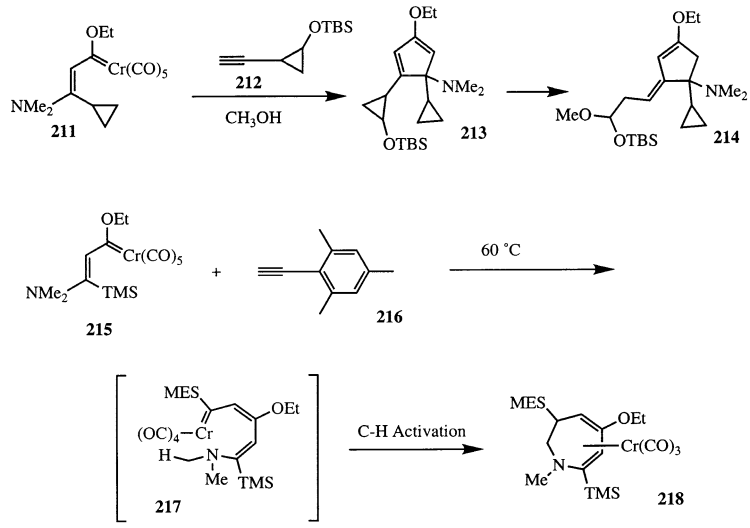
@ 45 °C, 0.5M **201**	@ 45 °C, 0.005M **201**	@ 90 °C, 0.05M **201**	@ 90 °C, 0.005M **201**
202A:B = 35:1 (73%)	**202A:B** = 49:1 (21%)	**202A:B** = 18.6:1 (36%)	**202A:B** = 19.9:1 (5%)
203A:B = 1:1 (11%)	**203A:B** = 1:1 (62%)	**203A:B** = 1.3:1 (57%)	**203A:B** = 1.4:1 (72%)
204A:B = 1:1 (3%)	**204A:B** = 1:1 (13%)	**204A:B** = 1:1 (4%)	**204A:B** = 1:1 (9%)
205A (7%)	**205A** (0%)	**205A** (0%)	**205A** (0%)
Σ **A:B** = 9.4:1	Σ **A:B** = 1.5:1	Σ **A:B** = 2.4:1	Σ **A:B** = 1.5:1

Scheme 32.

A theoretical study of the conversion of alkenylcarbene–chromium complexes to phenols (the Dötz benzannulation reaction) was undertaken using density functional theory [274]. The focus in this manuscript was on the conversion of γ-hydroxydienylcarbene complex **207** (Scheme 33) to the cyclohexadienone–chromium complex (**210**). The energy for each hypothetical step in the many proposed mechanisms for this reaction was calculated. Ultimately the energetically most reasonable pathway is that depicted in Scheme 33. An earlier mechanistic proposal by these authors, that alkyne complexation precedes CO dissociation in the Dötz reaction [275], was criticized based on the overwhelming amount of experimental evidence supporting CO-dissociation as a first step [276].



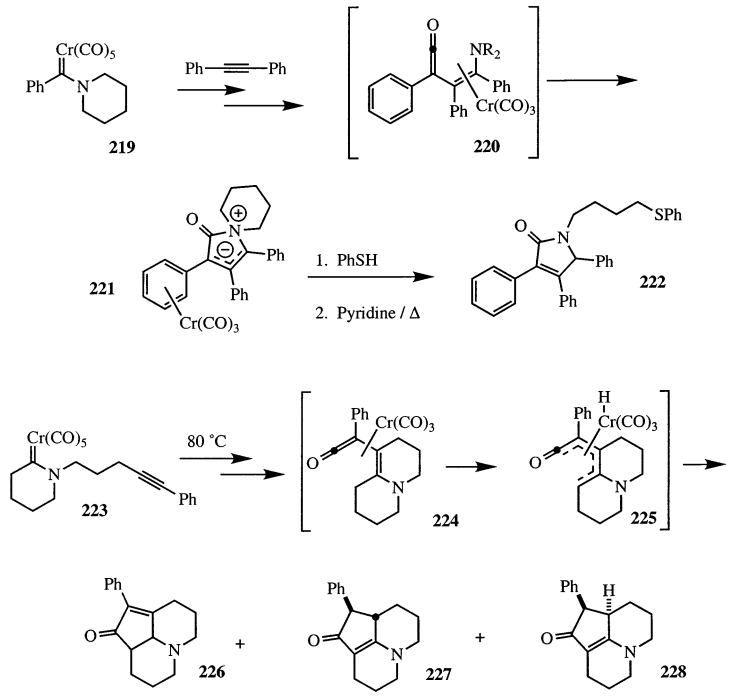
Scheme 33.



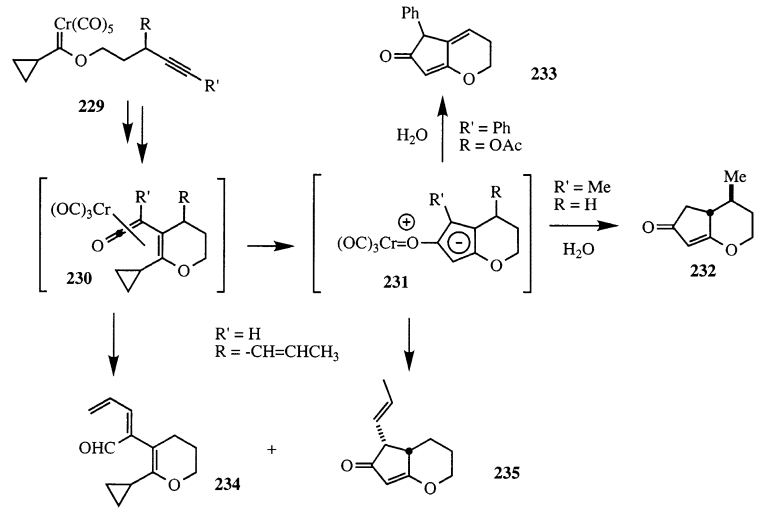
Scheme 34.

1.3.3.5. Nonbenzannulation reactions of Group VI metal–carbene complexes with alkynes. The coupling of β-amino-α,β-unsaturated carbene complexes (e.g. **211**, Scheme 34) with cyclopropylacetylene derivatives (e.g. **212**) leads to alkylidenecyclopentane derivatives (**214**) via ring opening of cyclopentadiene derivative **213** [277]. Initial formation of the cyclopentadiene followed by ring opening of the alkoxycyclopentenone afforded the observed products. Use of this reaction for the synthesis of fused 5-membered ring systems using alkynes containing remote ketone groups was also reported [278]. Coupling of these complexes with mesitylacetylene (**216**) affords the 7-membered ring heterocycle **218** [279]. Reaction with *t*-butylacetylene afforded predominantly 5-membered ring containing compounds accompanied by a low yield of the compound analogous to **218**. The mechanism for formation of the 7-membered ring involves oxidative addition into a C–H bond of the *N*-methyl groups in dienylcarbene complex intermediate **217**. Reaction of these carbene complexes with large excesses of phenylacetylene led to unusual spiro[4.4]nonatriene derivatives [280]. Coupling of alkynes and α-alkenyl analogs of complex **211** led to vinylcyclopentadiene derivatives of **213** [281].

Pyrrolidone derivatives (e.g. **222** and **226**–**228**, Scheme 35) were prepared from the coupling of aminocarbene–chromium complexes (e.g. **219** and **223**) with alkynes [282]. The coupling reaction initially produces a vinylketene (**220**) followed by *N*-ylide complex **221**, which can be captured through reaction with thiols or acetic acid/pyridine. An intramolecular variant of this reaction using alkyne–carbene complex **223** was also reported [283]. In this case, a C–H activation process occurs at the vinylketene stage (**224**) to produce the pentadienoyl complex **225**. Reductive elimination affords β-aminocyclopentanone derivatives fused to other ring systems (**226**–**228**). Capture of intermediate ketene complexes similar to **220** by intramolecular reaction with an alcohol led to β-lactone derivatives [284,285].



Scheme 35.



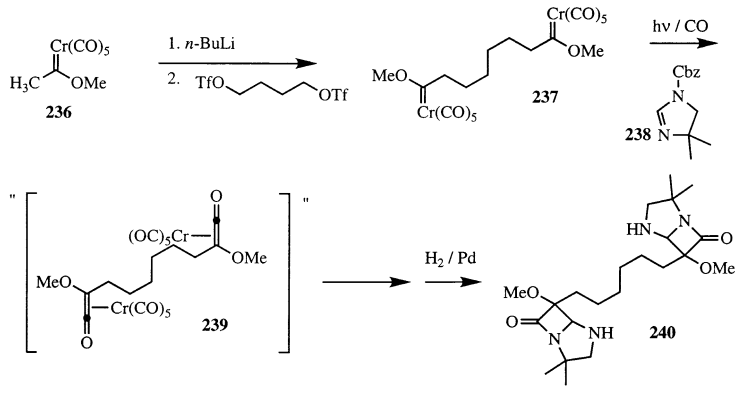
Scheme 36.

The intramolecular cyclopentannulation reaction (Scheme 36) of alkynes and cyclopropylcarbene–chromium complexes featuring a propargylic stereocenter, afforded cyclopentapyran derivatives (e.g. **232**) with a high degree of stereocontrol at the ring fusion [286]. The stereochemical control was proposed to arise through thermodynamic protonation of cyclopentadienide intermediates (e.g. **231**). Capture of the cyclopentadienide intermediates through β-elimination processes, resulting in the formation of 4-alkylidene-2-cyclopenten-1-ones (e.g. **233**), was also demonstrated [287]. Unanticipated reaction pathways resulting from allylic C–H activation were observed in intramolecular cyclopentannulation reactions involving conjugated enyne–cyclopropylcarbene complexes; the aldehyde **234** was the major product of this reaction, accompanied by the anticipated product **235** [288].

1.3.3.6. Photolysis reactions of Group VI metal–carbene complexes. Several publications concerning the formation of chromium ketene complexes (e.g. **239**, Scheme 37) through photolysis of Fischer carbene–chromium complexes appeared in 1999. Synthesis of carbon-linked β-lactams (e.g. **240**) from the reaction of bis carbene complexes (e.g. **237**) with imines (e.g. **238**) was reported using both achiral and homochiral imines [289]. Synthesis of cyclobutenones was reported using the photolytic coupling of alkenes and chromium carbene complexes [290]. Photochemical conversion of cyclic aminocarbene complexes to the corresponding α-aminoesters via ketene intermediates and methanol was also reported [291].

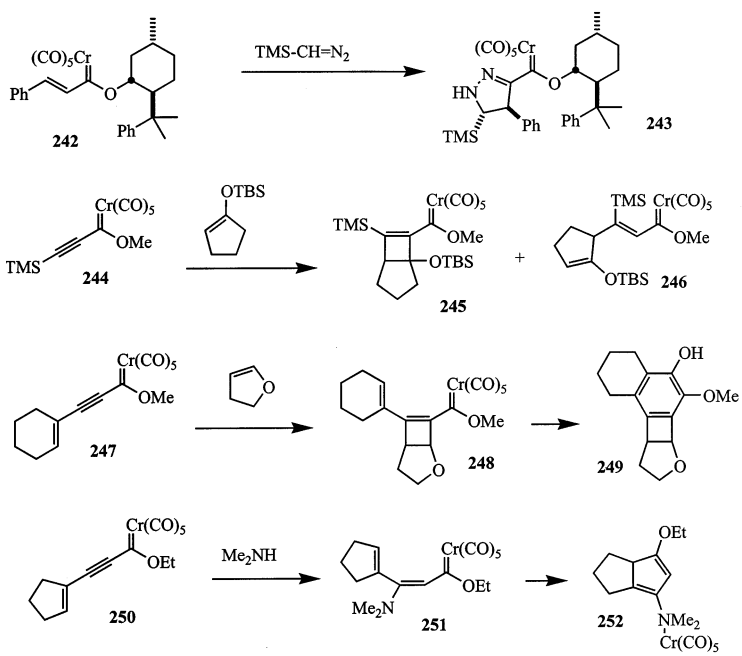
1.3.3.7. Reactions occurring at the conjugated C–C π-bond of α,β-unsaturated Group VI metal–carbene complexes. Numerous reaction processes where a carbene complex activates a π-bond for nucleophilic addition or cycloaddition reactions (i.e. the carbene complex is a surrogate for an 'activated ester') were reported in 1999.

Representative examples of $[N+2]$ cycloaddition processes involving α,β-unsaturated carbene complexes as 2π components are depicted in Scheme 38. Diels–Alder reactions were observed for the reaction of 1,3-diazadienes with alkynylcarbene complexes, resulting in pyrimidine derivatives [292]. The $[3+2]$ cycloaddition of



Scheme 37.

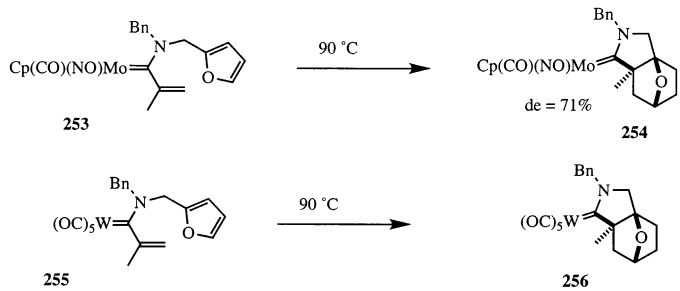
diazomethane derivatives and chiral nonracemic α,β-unsaturated chromium–carbene complexes (e.g. **242**) was reported [293]. The diastereoselectivity was very high when the phenylmenthoxycarbene complexes were employed. The reaction rates and diastereoselectivity were considerably greater for the carbene complex than for the analogous ester. A comprehensive study of the [2 + 2] cycloaddition reaction involving alkynylcarbene complexes (e.g. **244**) and various enol ethers was reported [294]. This reaction featured a competition between ene reaction (product **246**) and [2 + 2] cycloaddition (product **245**). The ene reaction was favored for trimethylsilylalkynylcarbene complexes reacting with acyclic enol ethers and cyclic enol ethers featuring an exocyclic oxygen. In many cases the [2 + 2] cycloadducts underwent an electrocyclic ring opening reaction at or below room temperature. The coupling of cyclic enol ethers with enynylcarbene complexes (e.g. **247**) afforded cyclobutenylcarbene complexes (e.g. **248**), which underwent cyclization in refluxing THF to afford the corresponding benzocyclobutane derivatives (e.g. **249**) [295]. Observation of benzannulation instead of the expected cyclopentannulation was attributed to the greater distance between C1 and C5 in analogs fused to a less strained ring system. Michael addition of amines to enynylcarbene complexes (e.g. **250**) afforded dienylcarbene complexes (e.g. **251**), which cyclized at room temperature without CO insertion to provide cyclopentadiene derivatives (e.g. **252**) [296]. Stereoselective Diels–Alder reactions were reported for cyclic carbene complexes featuring an exo-methylene group and a carbohydrate substituent [297].



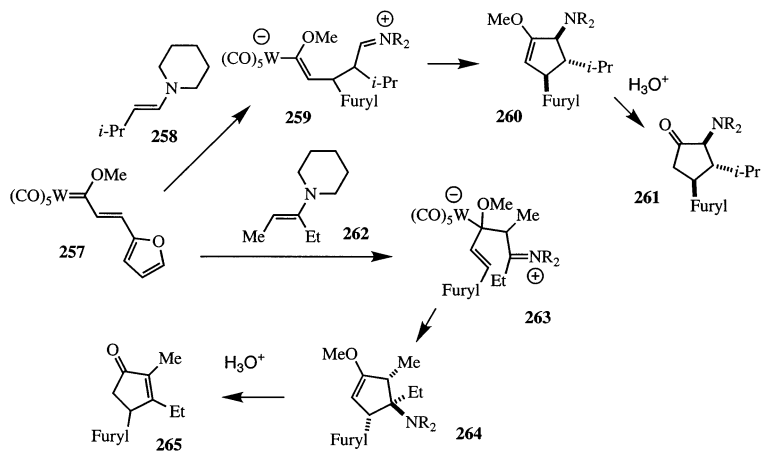
Scheme 38.

Chiral-at-molybdenum α,β-unsaturated carbene complexes were prepared (e.g. **253**, Scheme 39) and their intramolecular Diels–Alder reactions with appended furan rings examined [298]; comparison with analogous achiral tungsten– and manganese–carbene complexes was also tested as well as simple ester analogs. The diastereoselectivity in the Diels–Alder step was moderate, however it was better than that observed for achiral-at-metal carbene complexes featuring chiral nitrogen substituents. The molybdenum complexes were less reactive than the $(CO)_5W$- and $Cp(CO)_2Mn$-complexes and provided the lowest yields of Diels–Alder products.

Cyclopentannulation reactions were reported for the coupling of alkenylcarbene complexes (e.g. **257**, Scheme 40) with enamines [299]. Different types of products were obtained, depending upon whether the imine is derived from an aldehyde (e.g. **258**) or a ketone (e.g.**262**). Aldehyde-derived imine **258** led to cyclopentenone **261** through Michael addition of the imine followed by attack of the vinyl anionic equivalent at the iminium salt followed by hydrolysis. Ketone-derived imine **262** afforded cyclopentenone **265** through reaction of the imine at the carbene carbon followed by intermolecular addition of the resulting allyl–tungsten species (**263**) to



Scheme 39.



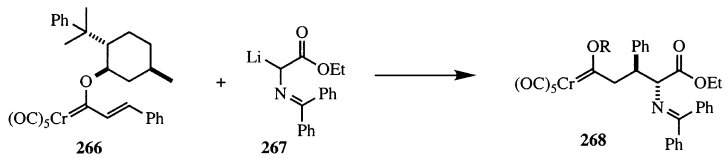
Scheme 40.

the iminium salt, followed by hydrolysis. Both processes occurred with a high degree of diastereoselectivity, and homochiral products were produced if chiral analogs of **258** or **262** were employed.

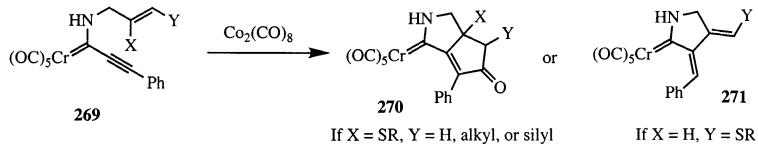
The Michael addition of glycine-derived carbanions (e.g. **267**, Scheme 41) to homochiral α,β-unsaturated alkoxycarbene complexes featuring a chiral alkoxy substituent (e.g. **266**) was reported [300]. Reactions involving diphenylmethylidene-protected amines were highly selective for formation of the anti diastereomer, while reactions involving dibenzyl-protected or disilyl-protected nitrogens were selective for formation of the *syn* diastereomer. In all cases involving the 8-phenylmenthyl chiral auxiliary, the addition was completely face selective.

The Pauson–Khand reaction involving allylamino(alkynyl)carbene complexes (e.g. **269**, Scheme 42) was studied, with emphasis on heteroatom-substituted alkene derivatives [301]. Alkene–carbene complexes where X is a thio group and Y is a nonheteroatom afforded mostly Pauson–Khand products (**270**), while derivatives of **269** where Y is a heteroatom afforded mostly diene derivative **271**.

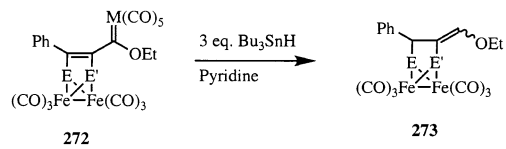
Further studies of trimetallic carbene complexes (e.g. **272**, Scheme 43), derived from the cycloaddition reaction between iron-bridging chalcogenide complexes and alkynylcarbene–chromium and –tungsten complexes were reported. The reaction of tungsten– and chromium–carbene derivatives of **272** with tributyltin hydride afforded the E- and Z-reduced enol ether derivatives **273**. In the cases examined E′ = tellurium or selenium and E = sulfur or tellurium [302].



Scheme 41.



Scheme 42.



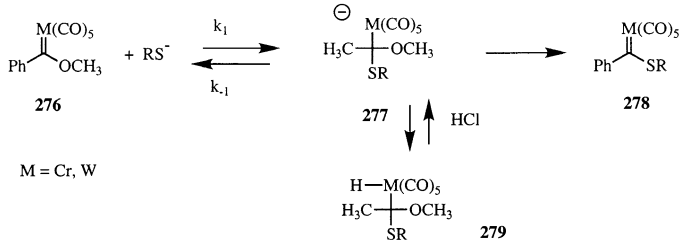
Scheme 43.

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).

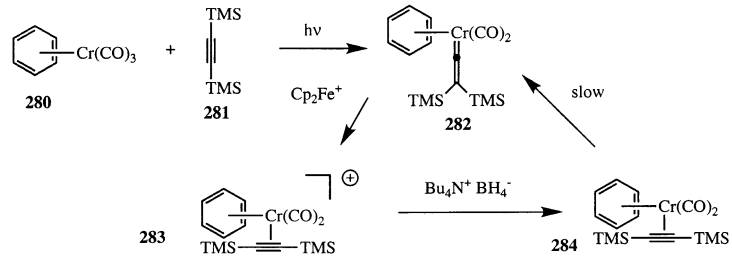
1.3.3.8. Physical organic chemistry of Group VI Fischer carbene complexes. A detailed study of the thermodynamic and kinetic acidity of various Fischer carbene complexes was determined in 50:50 water acetonitrile and in pure acetonitrile. Thiocarbene complexes (**274**, **275**, Fig. 8) were thermodynamically more acidic than alkoxycarbene complexes (pK_a 12–13), however their kinetic acidity was reduced relative to alkoxycarbene complexes [303]. The corresponding anions were considerably more stable than the analogous alkoxycarbene complex-derived anions.

Kinetic parameters for the conversion of alkoxycarbene–metal complexes to thiocarbene complexes (Scheme 44) were determined using stopped-flow techniques [304]. The tetrahedral intermediate in this process (**277**) was observable, and several conclusions about the transformation were reached. At low [RS^-] and relatively low pH, no intermediate is observable during the transformation of the alkoxycarbene complexes to thiocarbene complexes, however the tetrahedral intermediate is observable at high [RS^-] and high pH and rapidly converts to the thiocarbene complex upon treatment with acid. Rate constants for k_1, k_{-1}, and k_2, and equilibrium constants for the thiolate addition step were determined for a variety of thiolate ions. The pK_a of the metal-protonated tetrahedral intermediate (**279**) from addition of thiolate anions to thiocarbene and alkoxycarbene complexes has been determined to be ~ 0.5 [305].

1.3.3.9. Synthesis and reactivity of Group VI metal–vinylidene complexes, and reactions which involve vinylidene–metal complexes as intermediates. Photolytic coupling of arene–$M(CO)_3$ complexes (e.g. **280**, Scheme 45) with bis(trimethylsilyl)acetylene led to the bis(trimethylsilyl)vinylidene complexes (e.g. **282**) [306]. The complexes were studied by electrochemistry and through chemical redox reactions. One-electron oxidation afforded the observable cationic alkyne complexes (e.g. **283**), which afforded the neutral alkyne complexes (e.g. **284**) upon reduction; the



Scheme 44.



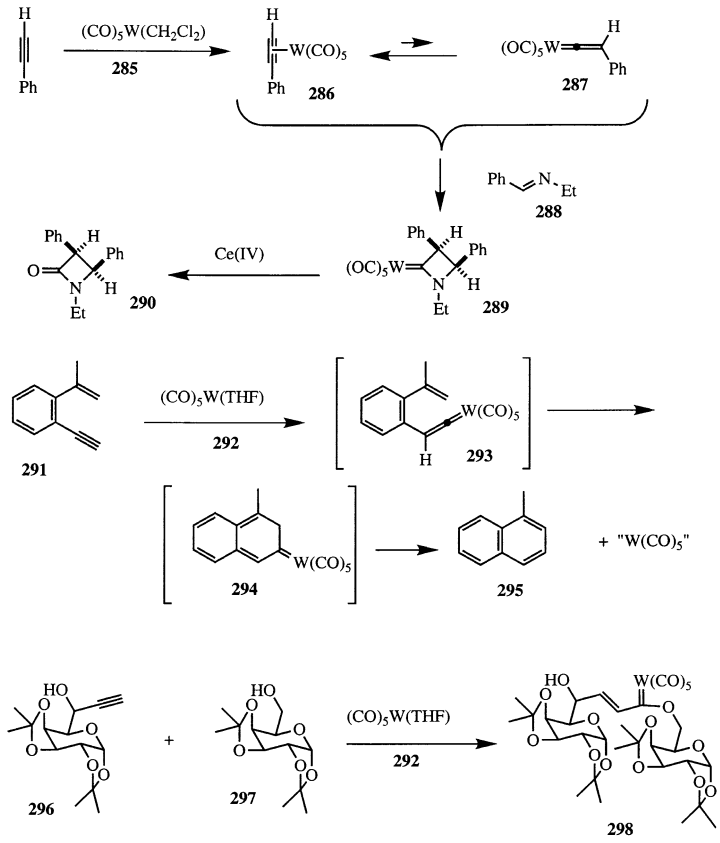
280 281 282 283 284

Scheme 45.

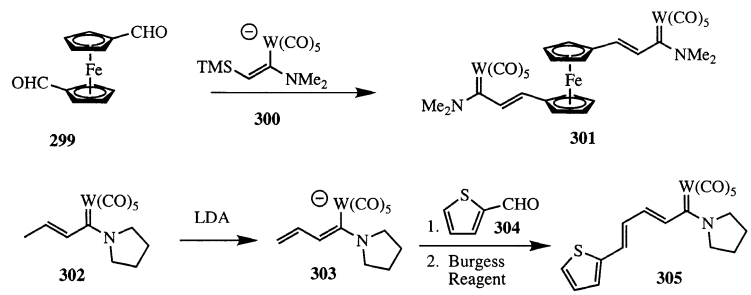
alkyne complexes (**284**) slowly isomerized to the vinylidene complexes (**282**) at room temperature. For molybdenum analogs of **282** and **284**, the neutral vinylidene complexes were in equilibrium with alkyne complexes.

Many examples of the coupling of alkynes with Group VI metal pentacarbonyl sources, which afford unstable metal–vinylidene intermediates, were reported in 1999 (Scheme 46). Coupling of in situ-generated dichloromethane–metal pentacarbonyl complexes (e.g. **285**) with phenylacetylene, followed by reaction with imines (e.g. **288**) or carbodiimides led to carbene complex analogs of β-lactams (e.g. **289**) [307]; the proposed mechanism involved [2 + 2]-cycloaddition of the metal vinylidene complex (e.g. **287**) and phenylacetylene. Oxidation of the cycloadducts afforded β-lactam derivatives (e.g. **290**) upon oxidation. The cyclization of *o*-alkenylphenylacetylene derivatives (e.g. **291**) to naphthalenes (e.g. **295**) was catalyzed by $(THF)W(CO)_5$ (**292**) [308]. The proposed mechanism involves conversion of the terminal alkyne to the tungsten–vinylidene complex (**293**), followed by electrocyclic ring closure and conversion of the resulting carbene complex (**294**) to the corresponding naphthalene (**295**). The coupling of carbohydrate-derived propargyl alcohols (e.g. **296**) with $(THF)W(CO)_5$ led to the α,β-unsaturated carbene complexes (e.g. **298**) in moderate yield [309]. If this reaction was conducted in the presence of a second carbohydrate with an active OH group (e.g. **297**), tungsten carbene-linked saccharide units (e.g. **298**) could be obtained. The resulting carbene complexes underwent Diels–Alder and Michael addition reactions with moderate diastereoselectivity.

1.3.3.10. Reactions involving carbanions derived from Group VI metal–carbene complexes. Several examples of reactions that involve deprotonation of a Group VI Fischer carbene complex at the α-position, followed by reaction with an electrophile were reported in 1999. Hydrocarbon- and ferrocene-bridged carbene complexes (e.g. **301**, Scheme 47) were prepared using the Peterson olefination involving dialdehydes (e.g. **299**) and anions derived from α-silylcarbene–tungsten complexes (**300**) [310]. Dienylcarbene complexes (e.g. **305**) were prepared by γ-deprotonation of α,β-unsaturated carbene complexes **302**, followed by treatment with an aromatic aldehyde (e.g. **304**) and dehydration [311]; the nonlinear optical properties of these and related complexes were tested. Alkylation and carbonyl addition reactions for anions derived from carbene–phosphine chelate complexes of chromium were



Scheme 46.



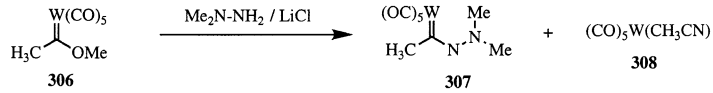
Scheme 47.

reported [312]. Carbonyl addition reactions of these anions proceeded with a moderate degree of diastereoselectivity. A similar carbene–aldol strategy was also employed for the synthesis of ϕ-ferrocenylhexatrienylcarbene–tungsten complexes from 5-ferrocenyl-2,4-pentadienal [313].

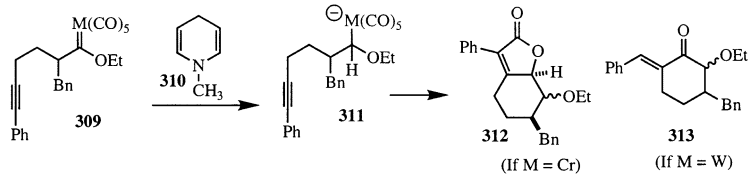
1.3.3.11. Reactions involving the addition of nucleophiles to the carbene carbon. Coupling of carbene complexes with 1,1-disubstituted hydrazine derivatives (Scheme 48) in the presence of lithium chloride led to Z-hydrazinocarbene complexes (e.g. **307**) in good–moderate yields [314]. The reaction was much faster in the presence of lithium chloride, which allowed the exchange reaction to be conducted at a lower temperature where a competing fragmentation to the nitrile complex (**308**) was less competitive. Reaction with 1,2-disubstituted hydrazine derivatives afforded mixtures of the expected hydrazinocarbene complex accompanied by the simple aminocarbene complex resulting from reductive cleavage of the N–N bond. Other studies involving aminolysis of carbene complexes include: (1) conversion of tetrahydrofuranylidene–chromium and tungsten complexes to the corresponding pyrrolidinylidene complex by aminolysis followed by the Mitsunobu reaction [315]; and (2) aminolysis of polymer-bound alkoxycarbene complexes and reaction of soluble alkoxycarbene complexes with polymer-bound amino acid derivatives [316].

The coupling of dihydropyridine derivatives (e.g. **310**, Scheme 49) with alkyne–carbene chromium or tungsten complexes (e.g. **309**) led to 6-membered ring products **312** or **313**, depending upon whether the metal was chromium or tungsten [317]. A mechanism involving carbonyl insertion into the ylide **311** followed by coupling of the resulting acylate complex with the alkyne was proposed. Further support for this mechanism came from examination of inter- and intramolecular couplings with alkenes.

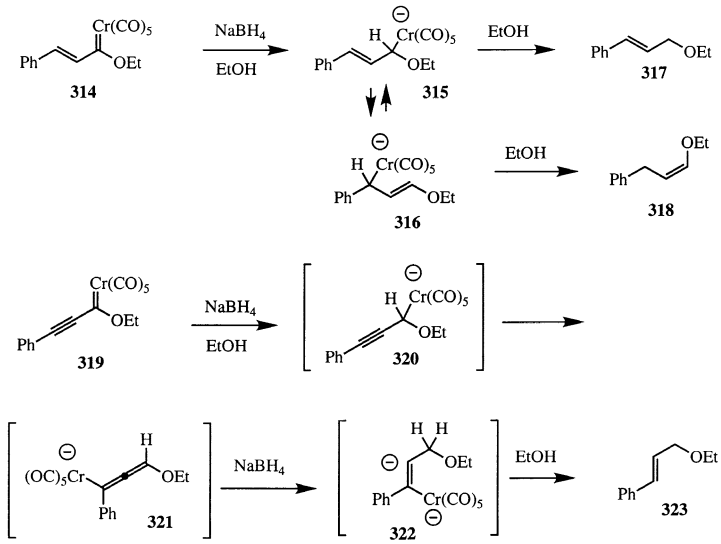
The addition of hydride nucleophiles to α,β-unsaturated carbene complexes (e.g. **314**, Scheme 50) has been studied [318]. Addition to alkenylcarbene complexes led to alkenes **317** and **318**, which arise via initial addition of hydride to the carbene carbon, followed by reversible 1,3-rearrangement of the allylmetal and protonation. Addition to the alkynylcarbene complex **319** led to allylic ether derivative **323** by a mechanism involving addition of hydride to the carbene carbon, followed by rearrangement to an allenylmetal system (**321**) followed by addition of a second hydride (resulting in dianion **322**) and protonation. The proposed mechanistic processes were supported through deuterium labeling studies. The high Z selectivity



Scheme 48.



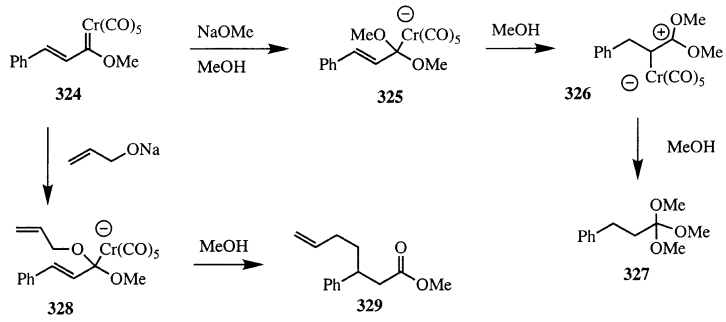
Scheme 49.



Scheme 50.

in the formation of enol ethers **318** was attributed to coordination of the oxygen in the metal in the 1,3-rearranged intermediate. Reaction of transition metal hydrides with non heteroatom-stabilized tungsten carbene complexes led to products resulting from insertion of the carbene ligand into the M–H bond [319].

The coupling of alkoxide derivatives with α,β-unsaturated carbene complexes (e.g. **324**, Scheme 51) was studied [320]. Reaction with sodium methoxide–methanol afforded orthoester derivatives (e.g. **327**, Scheme 51) after reaction at the carbene carbon, followed by 1,2-shift of the metal, followed by addition of methanol. Reaction with allylic alkoxides led to γ-substituted ester derivatives (e.g. **329**). A mechanism involving addition to the carbene carbon, followed by an unusual rearrangement involving simultaneous metal migration and C–C bond formation, followed by protonation of the resultant carbon–metal bond was proposed.

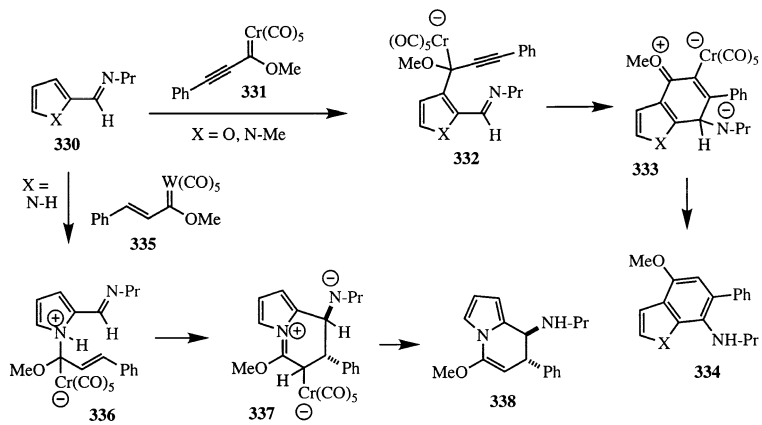


Scheme 51.

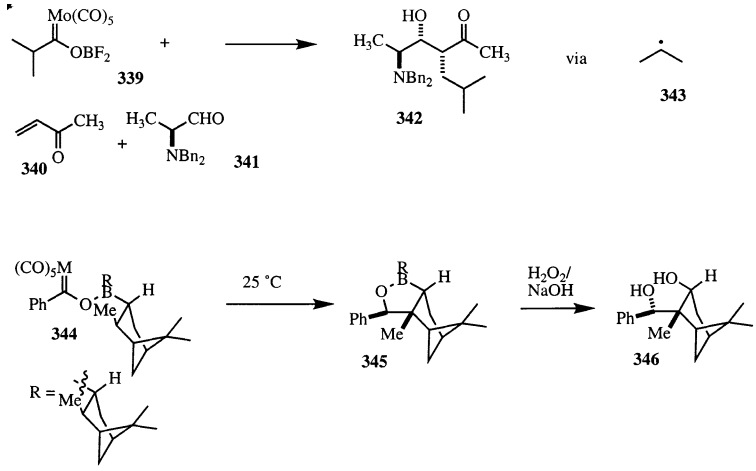
A novel benzannulation process was reported for the coupling of alkynylcarbene complexes (e.g. **331**, Scheme 52) with heteroaromatic aldehyde-derived imines (e.g. **330**) [321]. Furan, benzofuran, and *N*-substituted indole derivatives led to the carbocyclic benzannulation products (e.g. **334**); a mechanism involving nucleophilic addition to the carbene carbon at the 3-position of the heterocyclic ring, followed by simultaneous 1,2-shift of the metal and attack on the imine was proposed. A heterocyclic benzannulation product (e.g. **338**) was formed from the coupling of N–H pyrrole (e.g. **331**, X = N–H) and indole derivatives with α,β-unsaturated carbene complexes; a similar mechanism was proposed except that the initial attack occurs at the heterocyclic N atom. Coupling of N–H pyrroles and indoles with alkynylcarbene complexes afforded 7-membered ring annulation products which result from initial Michael addition of the imine N atom to the alkyne carbon followed by a 1,3-shift of the metal.

A new procedure for the conversion of carbene complexes to the corresponding esters was reported using dimethyl dioxirane as the oxidant, which presumably involves nucleophilic addition of oxygen to the carbene carbon as an initial step [322].

1.3.3.12. Other reactions of Group VI metal–carbene complexes. The unusual three-component coupling of boryloxycarbene–molybdenum complexes (e.g. **339**, Scheme 53), α,β-unsaturated ketones (e.g. **340**), and aldehydes was reported [323]. The reaction afforded α-substituted-β-hydroxyketones in moderate yield (e.g. **342**) with a very high degree of diastereoselectivity. Reactions employing chiral aldehydes (e.g. **341**) afforded the products with a high degree of diastereoselectivity with respect to the original stereocenter. A mechanism involving fragmentation of the starting carbene complex to the alkyl radical (**343**), followed by addition of the radical to the double bond of the enone were proposed as key steps in the coupling reaction. Treatment of chloroborane derivatives with molybdenum carbene acylates



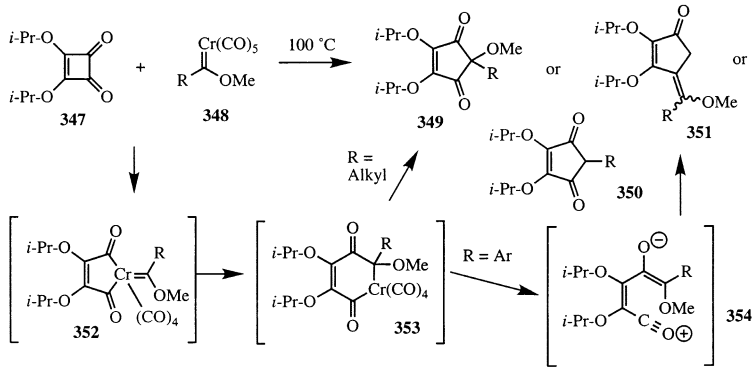
Scheme 52.



Scheme 53.

leads to generation of boryloxycarbene complexes (e.g. **344**) [324], which undergo a highly selective intramolecular C–H insertion process below room temperature. The corresponding diols (e.g. **346**) were obtained stereoselectively after treatment of the crude borane (e.g. **345**) with basic hydrogen peroxide.

The coupling of Fischer carbene complexes with cyclobutenediones (e.g. **347**, Scheme 54) was reported [325]. The reaction afforded ring expansion products (**348**–**350**). Reaction of cyclobutenedione **347** with alkylcarbene complexes led to simple cyclopentenediones (**348** and **349**) while reaction with arylcarbene complexes led to alkylidenefuranones (**351**). A mechanism involving oxidative addition of the acyl–acyl bond followed by migration and reductive elimination was proposed to explain the formation of cyclopentenedione derivatives. Ionization of the C–Cr bond in intermediate **353** followed by *O*-acylation was proposed to account for the formation of alkylidenecyclopentenones. Reaction of less oxygenated cyclobutene-



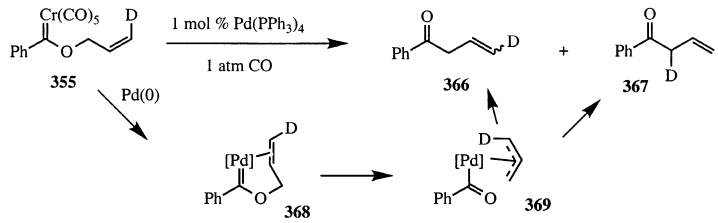
Scheme 54.

dione derivatives with arylcarbene complexes led to mixtures of cyclopentenediones and alkylidenefuranones.

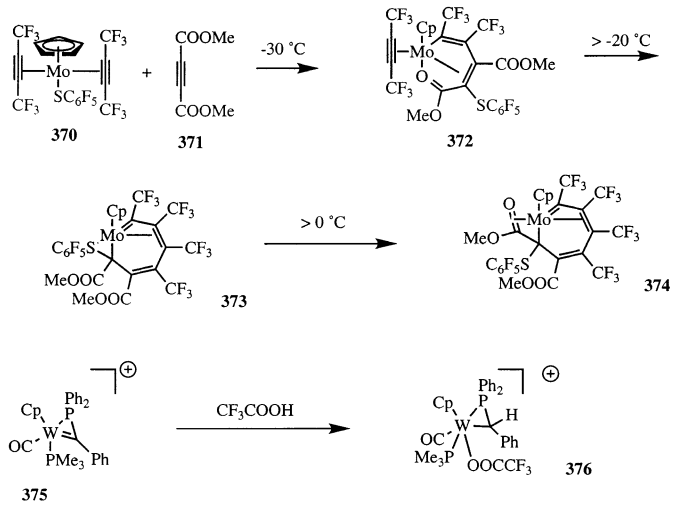
A palladium-catalyzed rearrangement of allyloxycarbene–chromium complexes (e.g. **355**, Scheme 55) to allylketone derivatives (e.g. **356**, **357**) was reported [326]. Transmetallation to form a palladium–carbene complex (e.g. **358**) followed by formation of a π-allyl complex (e.g. **359**) and reductive elimination were proposed as key steps. Transmetallation reactions of diaminocarbene–tungsten complexes led to stable platinum, palladium, ruthenium, and gold–carbene complexes upon treatment with the appropriate transition metal salt [327].

Molybdenum– and tungsten–carbene complexes (e.g. **373**, **374**, Scheme 56) were prepared from the coupling of bis(hexafluoro-2-butyne)metal complexes (e.g. **370**) with alkynes [328]. The reaction of tungsten carbene complex **375** with trihalogenated acetic acid derivatives led to complexes which appear to be derived from electrophilic addition to the carbene carbon (e.g. **376**) [329].

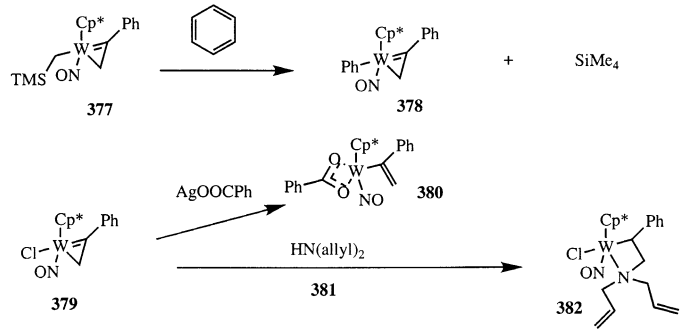
Thermal decomposition of η^2-alkenyltungsten complexes (e.g. **377**, Scheme 57) in benzene or toluene leads to the corresponding C–H activation products (e.g. **378**)



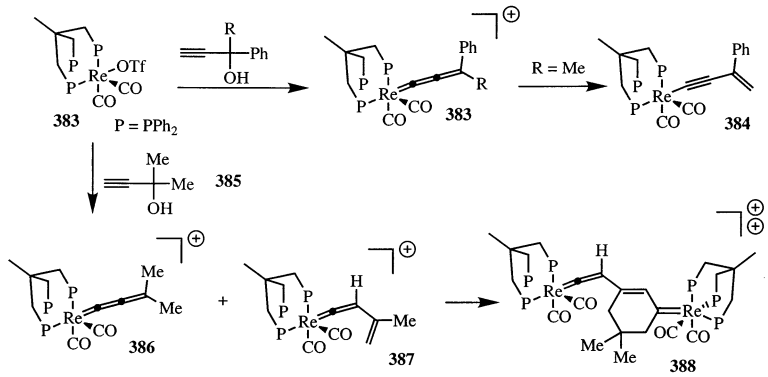
Scheme 55.



Scheme 56.



Scheme 57.



Scheme 58.

accompanied by tetramethylsilane [330]. A mechanism involving conversion to the η^2-alkenyl complex to a (hydrido)alkyne complex, followed by loss of tetramethylsilane, followed by C–H activation and hydride insertion to reform the η^2-alkenyl complex was proposed; this mechanism was supported through deuterium labeling studies. Double C–H activation processes were observed for various saturated hydrocarbons. Ligand exchange processes and the subsequent effect of various ligands on the structure of η^2-alkenyl-tungsten complex **379** were studied [331]. When X is a two-electron donor ligand, the alkenyl ligand exists in the η^2-form, while the alkenyl complex exists in the η^1-form when X is a four-electron donor ligand (e.g. as in **380**). Diallylamine underwent a unique reaction pathway to afford the nucleophilic ring-opening product **382**. Theoretical studies and structural preferences were determined for a variety of η^2-alkenyl-Group VI and VII transition metal complexes [332]. Octahedral (ML_5) and pseudotetrahedral ($CpML_2$) complexes were studied.

1.3.4. Group VII metal–carbene complexes

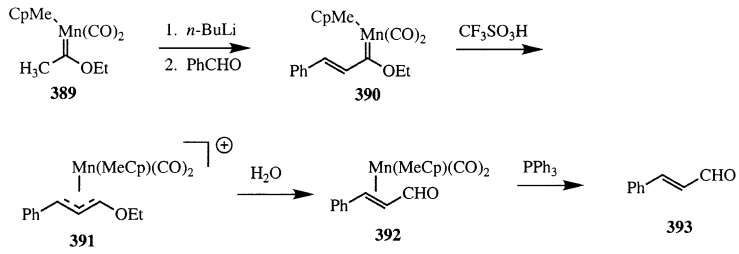
Rhenium–cumulene complexes (e.g. **383**, Scheme 58) were prepared from the reaction of propargyl alcohol derivatives with rhenium triflate **382** [333]. The methylallenylidene complex was readily deprotonated to form the enynylrhenium species **384**. Reaction with 2-methyl-3-butyn-2-ol led (**385**) to the unusual [3 + 3] cycloadduct (**388**), which was proposed to arise from the coupling of allenylidene **386** and alkenylvinylidene **387**. Reaction with propargyl alcohol also led to a dimeric complex. Carboranyl-substituted rhenium carbene complexes were prepared from carboranyl-substituted rhenium carbonyls using the Fischer (see initial comment on Group VI metal–carbenes, Section 1.3.3.2) synthetic route [334].

The reactivity of Fischer carbene–manganese complexes (e.g. **389** and **390**, Scheme 59) has been studied [335]. The methylcarbene complex **389** could be converted to the α,β-unsaturated complex (e.g. **390**) by deprotonation and reaction with an aldehyde. This same reaction leads to the α,β-unsaturated aldehyde (e.g. **393**) if the crude reaction mixture is treated with HCl and then refluxed in acetonitrile. A stable π-allyl complex (e.g. **391**) can be obtained by protonation of the α,β-unsaturated carbene complex, which transforms the unsaturated aldehyde complex (e.g. **392**) upon exposure to water.

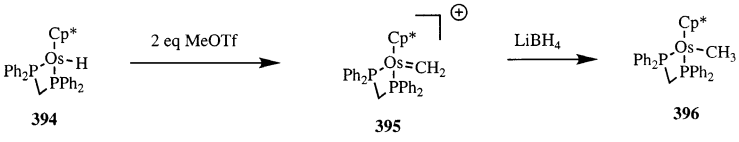
Reaction of cationic rhenium carbonyls with diazocyclopentadiene in the presence of nucleophiles led to substituted cyclopentadienyl–$Re(CO)_3$ complexes; a mechanism involving rhenium carbenes was discussed but not favored by the authors [336].

1.3.5. Group VIII metal–carbene complexes

1.3.5.1. Cationic metal–carbene complexes which are not cumulenes. Cationic osmium methylene complex **395** (Scheme 60) was generated from the reaction of



Scheme 59.



Scheme 60.

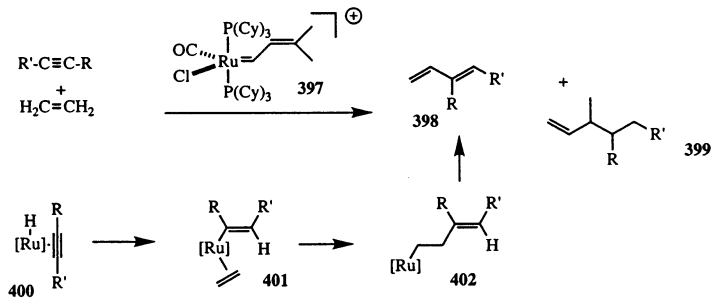
osmium–hydride complex **394** with two equivalents of methyl triflate [337]. A mechanism involving alkylation of osmium, followed by reductive elimination of methane, followed by alkylation to form the dication and deprotonation was proposed. This mechanism was proposed based on confirmation of the presence of methane. Carbene complex **395** afforded methyl–osmium complex **396** upon treatment with lithium borohydride.

Use of cationic ruthenium–carbene complex **397** (Scheme 61) as a catalyst for the hydrovinylation of acetylenes was reported [338]. Reaction of alkynes with ethylene in the presence of complex **397** afforded the alkene derivatives **398** and **399**. The same reaction using dimethyl acetylenedicarboxylate led to the [2 + 2] cycloadduct. A ruthenium hydride was proposed as the active catalyst; formation of **398** occurs via hydrometallation of the alkyne followed by alkene insertion and β-hydride elimination. A neutral analog of complex **397** was prepared by addition of a ruthenium hydride to the alkyne of a propargylic alcohol followed by treatment with acid [339].

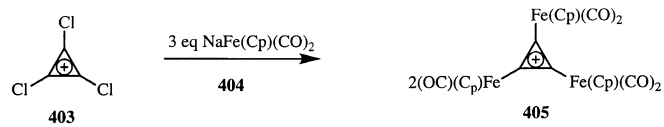
The synthesis of triiron cyclopropenium complexes (e.g. **405**, Scheme 62) was reported; significant iron–carbon double bond character was noted for these complexes [340].

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

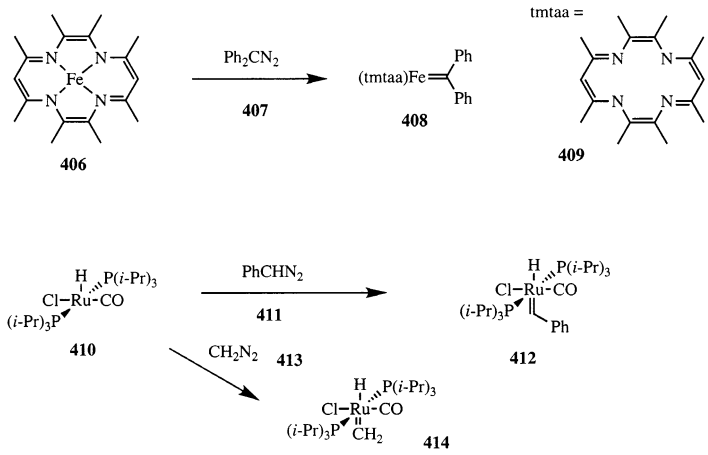
Several reports of the preparation of Group VIII metal–carbene complexes directly from diazo compounds appeared in 1999. Iron–carbene complex **408** (Scheme 63) was prepared through the coupling of diphenyldiazomethane with iron



Scheme 61.



Scheme 62.

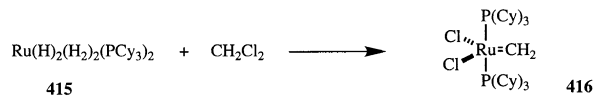


Scheme 63.

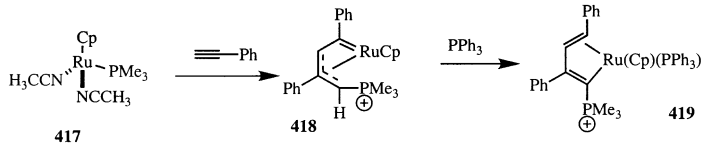
(II)-tmtaa complex **406** [341]. A similar route was employed for the analogous ruthenium complex [342]. The electronic and magnetic properties of carbene complexes were studied by Extended Hückel Calculations; complex **408** was determined to be intermediate between a Fischer carbene complex and a Schrock carbene complex. Ruthenium–carbene complexes (e.g. **412**) were prepared from the coupling of ruthenium hydride complex **410** with phenyldiazomethane [343]. The diazomethane adduct **414** was stable below $-50°C$; in this case the carbene ligand could be displaced by pyridine. Analogous osmium carbene complexes were similarly prepared [344], and ligand exchange processes examined. The use of a homochiral ruthenium complexes as a catalyst for cyclopropanation of styrene by ethyl diazoacetate was reported [345]. A stable ruthenium carbene complex could be isolated from the reaction in the absence of an alkene trap. Cyclopropanation of styrene proceeded with a low ee.

Ruthenium–carbene complexes (e.g. **416**, Scheme 64) were prepared from the coupling of ruthenium hydride complexes (e.g. **415**) with *gem* dichloro compounds [346]. A mechanism involving oxidative addition into the C–Cl bond followed by α-elimination of chloride was proposed. The reaction with 1,2-dichloroethylene afforded the ethylidene complex, which was produced via hydrogenation of the C–C double bond of an unobserved vinylidene intermediate.

Coupling of two equivalents of a terminal alkyne with ruthenium complex **417** (Scheme 65) led to the π-allylcarbene–ruthenium complex (e.g. **418**) [347]. The complex is reactive to both nucleophiles (PPh_3) and electrophiles (H^+). Reaction



Scheme 64.



Scheme 65.

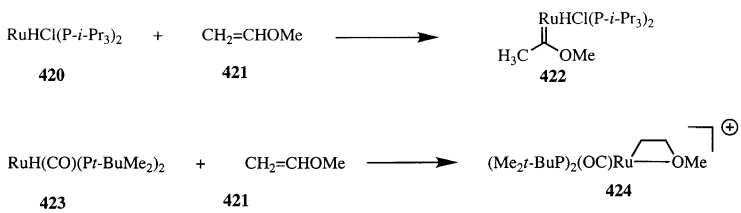
with triphenylphosphine led to the η^3-dienyl complex **419**. Reaction with trifluoroacetic acid led to the analogous η^4-diene complex.

Ruthenium bis(carbene) complexes were proposed as an intermediate in the ruthenium-catalyzed synthesis of 1-acyloxy-1,4-disubstituted butadiene derivatives from two moles of a terminal alkyne and one mole of a carboxylic acid [348]. Iron carbene complexes were suggested as intermediates in the synthesis of stilbene derivatives via dimerization of α,α-dichlorotoluene derivatives using disodium tetracarbonylferrate (Collman's reagent) [349].

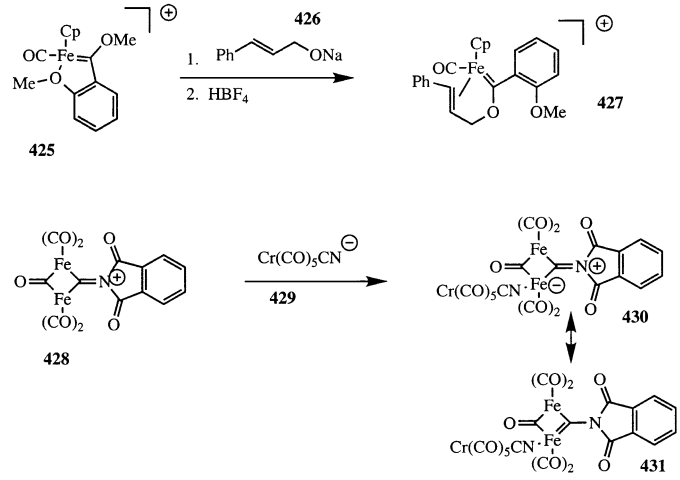
1.3.5.3. Heteroatom-substituted Group VIII metal–carbene complexes. A comparison of the reaction of complexes **420** and **423** (Scheme 66) with methyl vinyl ether (**421**) was conducted [350]. Reaction of the neutral chloride complex **420** with **421** affords carbene complex **422** while reaction with cationic carbonyl complex **423** leads to β-methoxyethyl–ruthenium complex **424**. Theoretical studies show that ligand (Cl^- vs. CO) had no effect on the relative stability of the η^2-vinyl ether complex versus carbene complex, however the transformation of η^2-vinyl ether to the alkyl complex is more favorable for the CO complex than the Cl complex.

The reaction of the cinnamyl alcohol-derived anion **426** (Scheme 67) with cationic alkoxycarbene–iron complex **425** led to chelated allyloxycarbene complex **427** [351]. A trimetallic aminocarbene–iron complex (**431**) was prepared by reaction of iron complex **428** with $[(CO)_5CrCN]^-$ (**429**) [352].

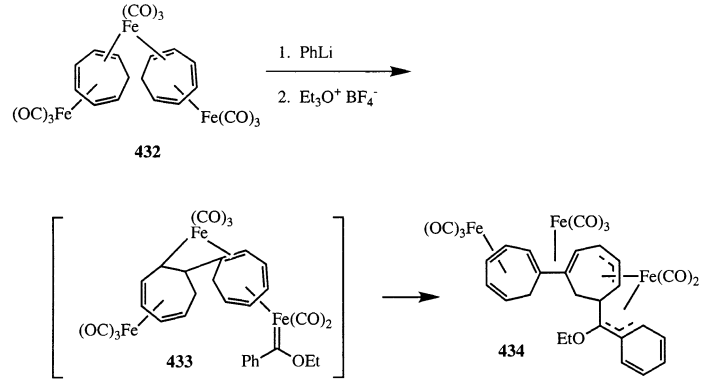
Heteroatom-stabilized iron carbene complexes were suggested as intermediates in several reaction processes. Attempted synthesis of a Fischer carbene complex from iron–carbonyl complex **432** (Scheme 68) using the Fischer synthesis led to the cycloheptadienyl ring-substituted complex **434** [353]. The mechanism proposed for the formation of **434** involves generation of a Fischer carbene complex (**433**) followed by carbene insertion process. A phosphoroxycarbene–iron complex was proposed as an intermediate in the synthesis of acylphosphine–iron complexes from iron acylates and chlorodiphenylphosphine [354].



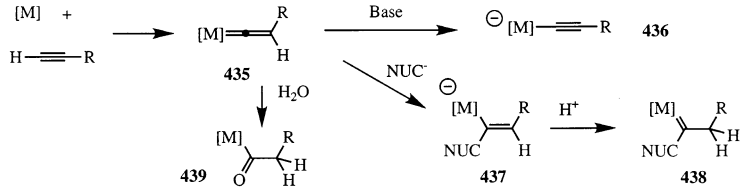
Scheme 66.



Scheme 67.



Scheme 68.



Scheme 69.

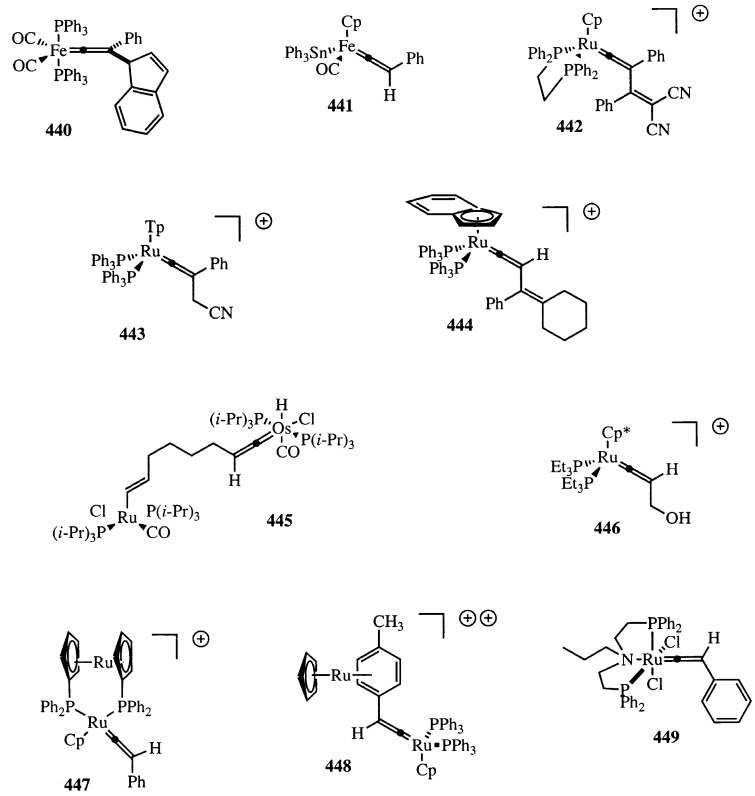


Fig. 9. Representative Group VIII metal–vinylidene complexes reported in 1999.

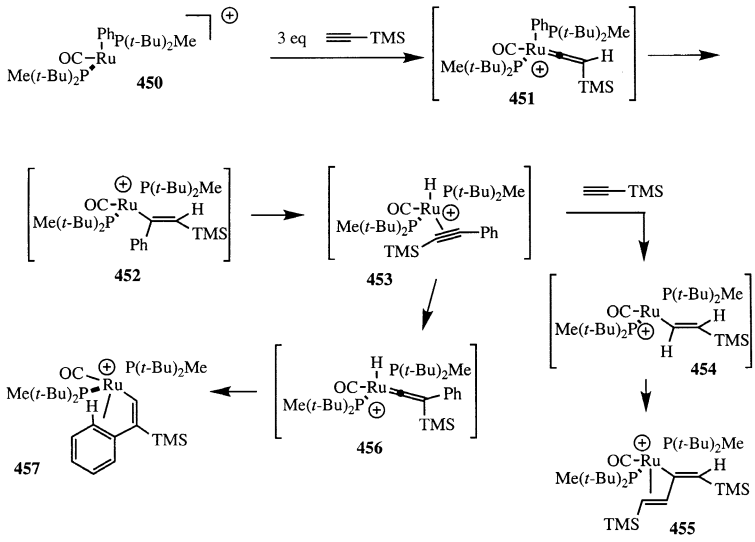
1.3.5.4. Group VIII metal–vinylidene complexes. Many examples of the formation of metal vinylidene complexes (**435**, Scheme 69) via coupling of coordinatively unsaturated Group VIII metal complexes with terminal or silylated alkynes were reported in 1999. Representative examples are depicted in Fig. 9. Common reaction pathways for these complexes include reaction with alcohols to form Fischer carbene complexes (**438**) or water to form metal acyls (**439**), and deprotonation at the β-position to form alkynylmetal complexes (**436**). Other common synthetic routes to metal vinylidenes included addition of electrophiles to metal acetylide complexes (e.g. the reverse of the reaction synthesizing **436**), and treatment of acylmetal complexes with dehydrating agents (i.e. the reverse of the reaction synthesizing **439**).

Specific reports which highlight the reaction pathways depicted in Scheme 69 include: (1) synthesis of iron indenylvinylidene complexes (e.g. **440**) from (alkynyl)(η^5-indenyl)iron complexes through phosphine-induced migration of the indenyl ligand to the β-carbon of the acetylide ligand [355]; (2) synthesis of neutral iron– and ruthenium–vinylidene (e.g. **441**) complexes through reaction of anionic acyl complexes with acetyl chloride [356]; (3) synthesis of cationic ruthenium

vinylidene complexes (e.g. **442**, **443**) by the reaction of ruthenium acetylide complexes with benzylidenemalononitrile derivatives [357], iodoacetonitrile [358], or isothiocyanates–alkyl halides [359] and subsequent base-induced cyclization reactions of the vinylidene complexes to cyclic vinylruthenium complexes; (4) synthesis of cationic vinylvinylidene complexes (e.g. **444**) via regioselective β-protonation of enynylruthenium complexes [360]; reaction of these complexes with nitriles affords the uncomplexed vinylacetylene derivative corresponding to the vinylidene ligand [361]; (5) synthesis and deprotonation of cationic indenylruthenium complexes featuring an electron-deficient aromatic ring at the β-position of the vinylidene ligand [362]; (6) synthesis of a complex featuring vinylruthenium and vinylideneosmium substituents (**445**) by sequential coupling of a ruthenium hydride and the analogous osmium hydride with 1,7-octadiyne [363]; (7) synthesis and deprotonation of cationic ruthenium–vinylidene complexes featuring bridging phosphine ligands [364]; (8) synthesis of cationic γ-hydroxyvinylidene–ruthenium complexes (e.g. **446**) from propargyl alcohols and observation of an alkynylruthenium hydride intermediate [365] and subsequent dehydration processes [366]; (9) synthesis of cationic ruthenium vinylidene complexes by protonation of neutral arylethynylruthenium complexes [367]; (10) synthesis of a cationic ruthenium–vinylidene complex featuring a chelating bis(diphenylphosphino)ruthenocene ligand (e.g. **447**) [368]; (11) synthesis of a dicationic vinylidene–ruthenium complex (**448**) featuring a ruthenium-complexed aromatic ring at the β-position through addition of electrophiles to cationic alkynylruthenium complexes [369]; (12) synthesis of cationic ruthenium vinylidene complexes through electrophilic attack on alkyne complexes derived from 1,4-diethynylbenzene [370]; (13) synthesis of ruthenium vinylidene complexes featuring 2,6-bis(dimethylaminomethyl)pyridine (pincer) ligands [371]; and (14) preparation of Fischer carbene–ruthenium complexes by reaction of neutral ruthenium vinylidene complexes (**449**) with primary amines [372], which proceeds via an observable anionic amine-coordinated alkynyl–ruthenium complex which is transformed to the carbene complex at room temperature.

The reaction of phenylruthenium complex **450** (Scheme 70) with $>$ two equivalents of trimethylsilylacetylene led to η^3-dienylcomplex **455**, vinylruthenium complex **457**, and phenyl(trimethylsilyl)acetylene [373]. All of these compounds arise from the initially-anticipated ruthenium–vinylidene complex **451**, which is transformed to alkenylruthenium complex **452** after migration of the phenyl group and to phenyl(trimethylsilyl)acetylene complex **453** after β-hydride elimination. Insertion of a second equivalent of trimethylsilylacetylene affords η^3-dienyl complex **455**. Formation of a vinylidene complex from alkyne complex **453** followed by hydride migration leads to vinylruthenium complex **457**. Vinylruthenium intermediate **452** can also be generated from the reaction of a ruthenium hydride analog of complex **450** with phenyl(trimethylsilyl)acetylene [374].

Numerous processes suggest metal vinylidene complexes as intermediates (Scheme 71, including: (1) synthesis of ruthenium–diene complexes **459** and **460**, and η^3-dienyl complex **461** via coupling of terminal alkynes with ruthenium-coordinated alkene complex **458** [375]; (2) synthesis of ruthenium diene complexes through protonation of alkynylruthenium complexes featuring a coordinated allyl ether

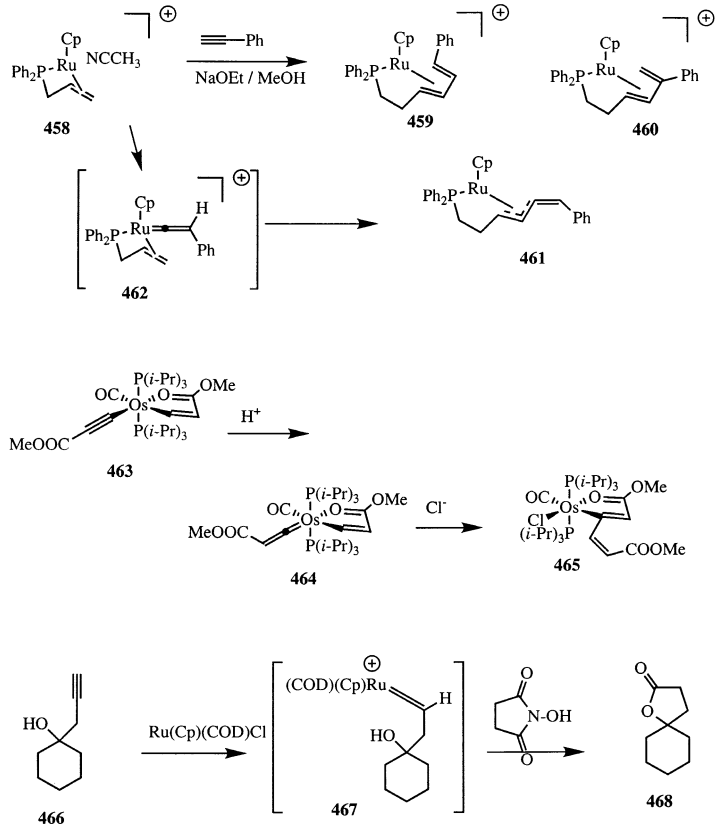


Scheme 70.

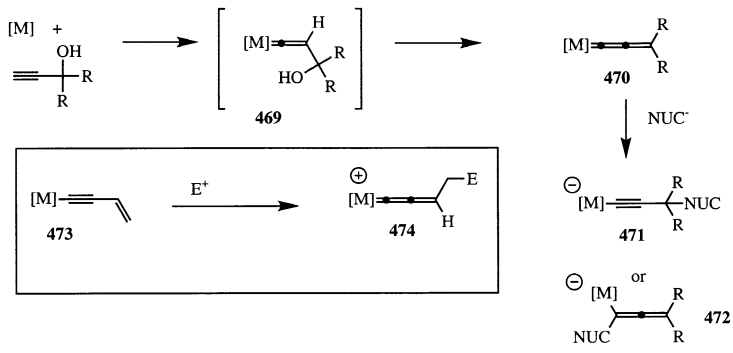
group [376]; (3) proton-induced coupling of the alkenyl and alkynyl ligands of osmium complex **463**; the osmium–vinylidene complex **464** can be isolated and characterized [377]; (4) conversion of homopropargyl alcohols (e.g. **466**) to γ-butyrolactones (e.g. **468**) using a ruthenium catalyst and an *N*-hydroxyimide oxidant, where nucleophilic addition of an alcohol to a ruthenium vinylidene complex (e.g. **467**) is a key step [378]; and (5) synthesis of a mixture of allyloxycarbene complexes and allylketone complexes via coupling of terminal alkynes with allyl alcohols in the presence of a $Ru(Tp)(DMSO)_2Cl$ complex [379].

1.3.5.5. Group VIII metal complexes of higher cumulenes. Metal-higher cumulene complexes (**470**, **474**, Scheme 72) are produced from the coupling of coordinatively unsaturated Group VIII metal complexes with propargyl alcohols which contain no hydrogens β- to the OH group (Scheme 72), or by addition of electrophiles to the δ-carbon of alkynylethynyl–metal complexes (**473**). A variety of reaction processes of Group VIII metal–cumulene complexes were reported in 1999. A common reaction pathway for these complexes is reaction with nucleophiles at the γ-position, resulting in alkynylmetal complexes (**471**), or attack at the γ-position, resulting in allenylmetal complexes (**472**). Representative examples of this class of compounds are depicted in Fig. 10.

Specific reports which highlight the reaction pathways depicted in Scheme 72 include: (1) preparation of neutral bimetallic chloride-bridged allenylidene–ruthenium complexes (e.g. **475**) and synthesis of a variety of additional ruthenium–allenylidene complexes through ligand exchange processes of this complex [380]; (2) synthesis of cationic homobimetallic complexes of the Group VIII metals bridged by a C_5H ligand (e.g. **476**) via coupling of 1,4-pentadiyn-3-ol with two equivalents



Scheme 71.



Scheme 72.

of a metal halide in the presence of silver tetrafluoroborate [381]; (3) synthesis of diiron complexes featuring a butatrienylidene bridge (e.g. **477**) by electrophilic addition to butadiynyl-linked diiron complexes [382]; (4) preparation of a variety of neutral alkynylruthenium complexes by addition of nucleophiles to the γ-carbon of cationic ruthenium–allenylidene complex **478** [383]; (5) coupling of dithiocarbamate ligands with either vinylidene or allenylidene–ruthenium complexes (e.g. **479**), which afforded sulfur chelate complexes through attack of the sulfur at the α-carbon of the cumulene ligand [384]; (6) reaction of primary and secondary amines at the α-carbon of cationic ruthenium–allenylidene complex **480** [385]; (7) generation of cationic ruthenium trienylidene complex **481** and trapping by reaction with pyridine at the γ-position of the butatrienylidene ligand [386]; and (8) generation of dicationic ruthenium allenylidene complexes (e.g. **482**) by oxidation of a ruthenocenylacetylene–ruthenium complex [387].

Additional reactions of butatrienylidene complexes (e.g. **481**, **487**) were reported (Scheme 73). Reaction of cationic butatrienylidene–ruthenium complex **481** with sulfur nucleophiles occurred at the γ-position, resulting in γ-thioallenylidene complexes (e.g. **483**) [388]. Sulfonium salts derived from allylic sulfides undergo a rapid Cope rearrangement at room temperature to afford C-allylated allenylidene complexes (**485** and **486**). The cycloaddition reaction of in situ-generated cationic ruthenium–butatrienylidene complex **487** (Scheme 74) and benzylideneaniline derivatives (e.g. **488**) afforded quinolinoacetylene complex **490** [389]. The phosphite analog **491** led to azabutadiene complex **494**. A mechanism involving either initial [4 + 2] or [2 + 2]-cycloaddition at the distal carbon–carbon double bond of the allenylidene complex was proposed. Similar [2 + 2] cycloaddition reactions using carbodiimides also occured of at the distal double bond of cationic ruthenium allenylidene complex **480** of Fig. 10 [390].

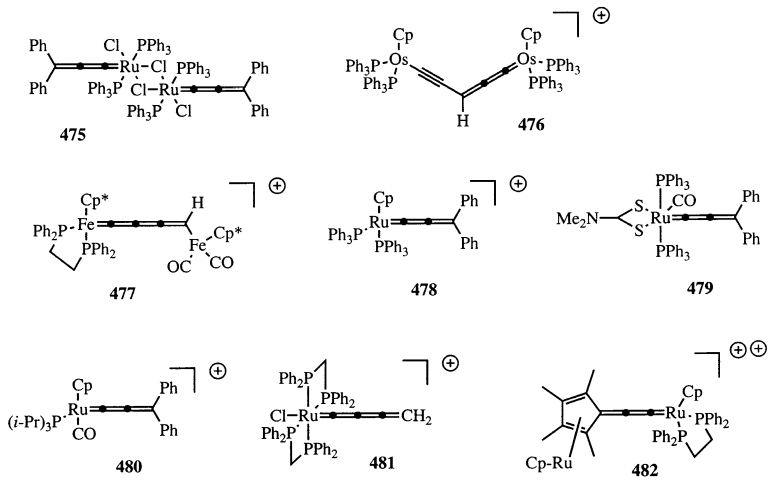
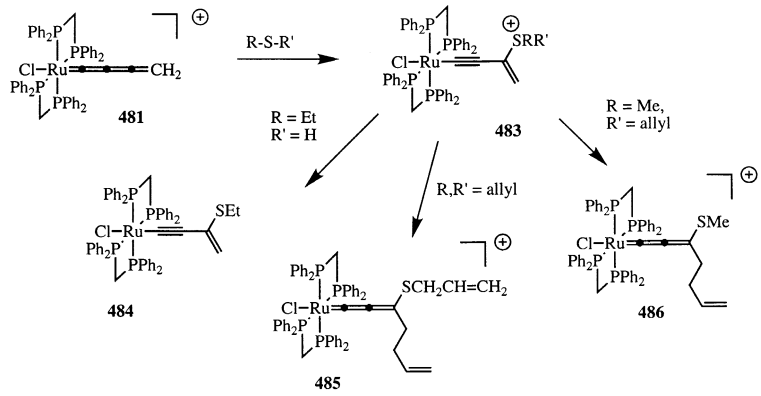
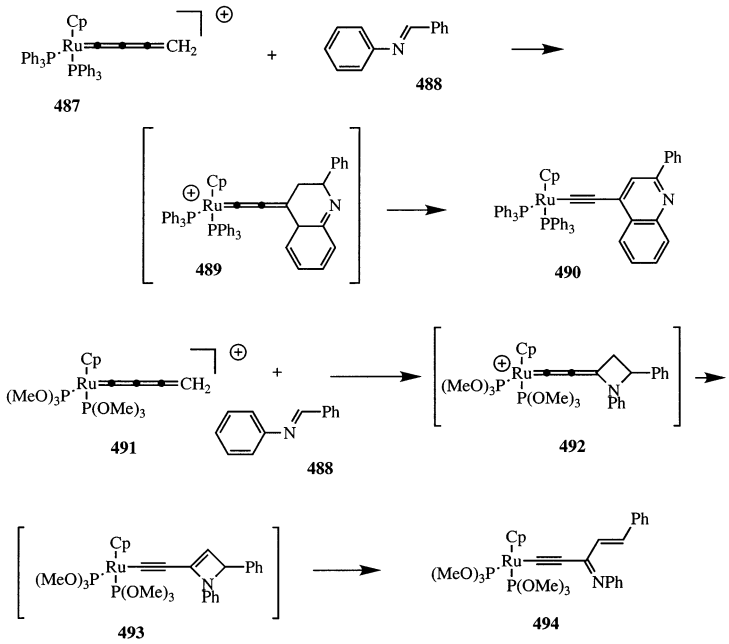


Fig. 10.



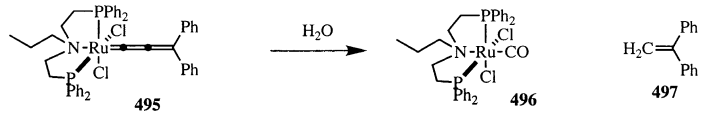
Scheme 73.



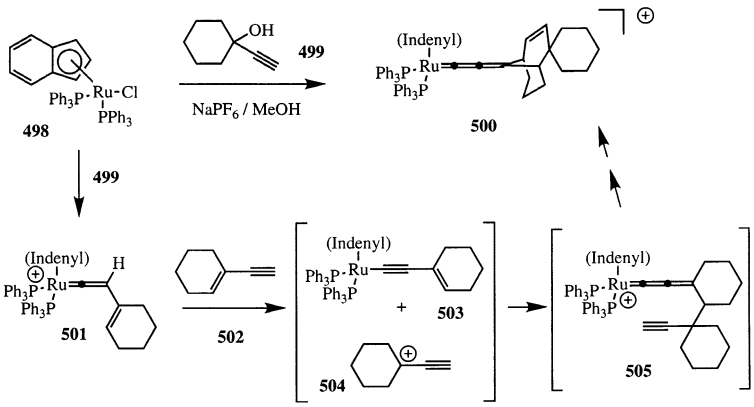
Scheme 74.

The reaction of allenylidene– or alkenylvinylidene–ruthenium complexes (e.g. **495**, Scheme 75) with water led to the ruthenium carbonyl complex **496** and the corresponding alkene (e.g. **497**) [391]. A mechanism was not proposed, however deuterium and oxygen-18 labeling studies verify that the oxygen of the carbonyl and the hydrogens of the alkene come from water.

The unusual cationic ruthenium allenylidene complex (**500**, Scheme 76) was obtained from the coupling of one mole of the ruthenium salt **498** with two moles



Scheme 75.



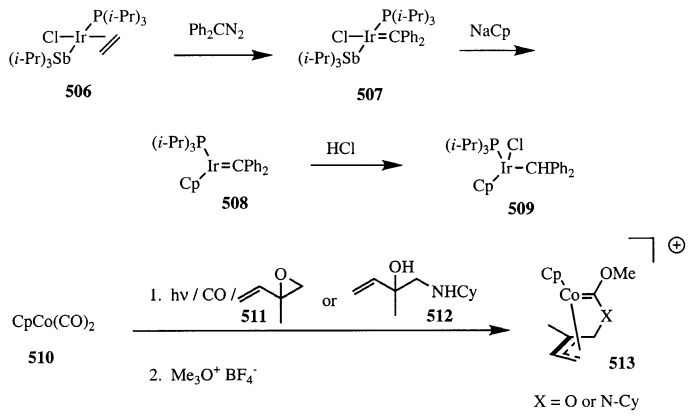
Scheme 76.

of 1-ethynylcyclohexanol (**499**) [392]. The proposed mechanism for the combination of ethynylcyclohexane units involves formation of the cyclohexenylvinylidene complex **501**. Subsequent deprotonation by enthynylcyclohexene (**502**) afford enynyl complex (**503**) and propargylic cation **504**; the key C–C bond forming event involves electrophilic attack of the propargyl cation on the alkene of complex **503**. This reactivity pattern was unique to ethynylcyclohexanol; the analogous 5- and 7-membered ring systems led to simple formation of the stable alkenylvinylidene complexes analogous to **501**.

In numerous examples, carbene resonance forms have been suggested as major contributors to the structure of alkynylreuthenium [393,394] and alkynyliron complexes [395]. Ruthenium allenylidene complexes were considered as intermediates in the ruthenium-catalyzed cyclopropanation of norbornene with propargyl alcohols, but their involvement was not consistent with the labeling studies [396].

1.3.6. Group IX metal–carbene complexes

1.3.6.1. Simple carbene complexes. Iridium–carbene complexes (e.g. **507**, Scheme 77) were prepared from the coupling of iridium–ethylene complexes (e.g. **506**) with diaryldiazomethane derivatives [397]. A variety of ligand exchange processes for these complexes were demonstrated. Reaction of the Cp complex **508** with HCl led to the alkyliridium chloride complex **509**. Reaction of a (η^5-indenyl)rhodium diphenylcarbene complex with CO led to the corresponding carbonyl complex and diphenylketene [398]. A cationic cobalt carbene complex featuring a π-allyl ligand

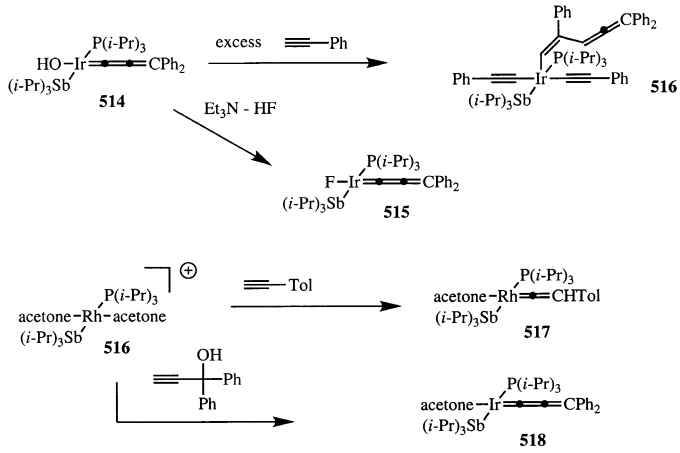


Scheme 77.

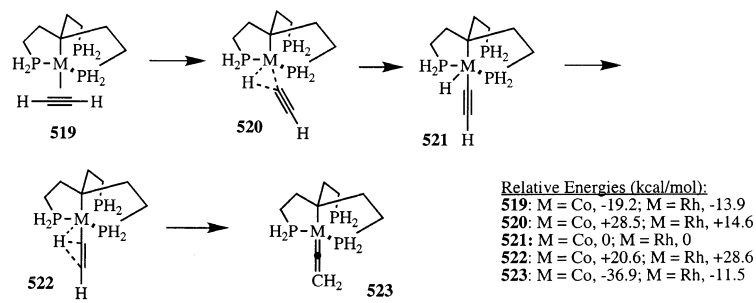
(**514**) was prepared from $CpCo(CO)_2$ via reaction with vinyl epoxide **511** (resulting in the acyl complex) followed by alkylation [399]. The aminocarbene complex was synthesized in a similar manner using an amino alcohol (e.g. **512**) as the starting material. Attempts to generate similar complexes of chromium or manganese failed. A cationic rhodium–carbene complex was prepared by protonation of a hetero-bimetallic complex featuring a vinylrhodium group [400]. An iridium oxametallacyclopentadiene complex, obtained from the coupling of an iridium–acetylide complex with dimethyl acetylenedicarboxylate, was found by X-ray to have significant carbon–metal double bond character [401].

1.3.6.2. Cumulene complexes. Similar synthetic procedures and reactivity patterns were generally observed for Group IX and VIII (Schemes 69 and 72) metal–cumulene complexes. Ligand exchange processes for allenylidene–iridium hydroxide complex **514** (Scheme 78) were examined [402]. Reaction of complex **514** with a fluoride source led to the fluoro complex **515**. Reaction with excess phenylacetylene led to allenylalkenyliridium complex **516**–alkyne insertion into the Ir–C double bond was the key carbon–carbon bond-forming step. A similar process was employed for the conversion of rhodium cumulene hydroxide complexes to the corresponding fluoride [403], azide, and μ-azide [404] complexes. Synthesis and ligand exchange processes were demonstrated for cationic rhodium vinylidene (e.g. **517**) and allenylidene (e.g. **518**) complexes featuring easily replaced ligands [405]. Iridium vinylidene complexes were suggested as intermediates in the formation of allenes during the protonation of methyl(alkynyl)iridium complexes [406].

The energy of various intermediates and transition states for the conversion of η^2-alkyne–cobalt or rhodium complexes (**519**, Scheme 79) to vinylidene complexes (**523**) was calculated for the reaction pathway involving oxidative addition into the acetylene C–H bond [407]. Conversion of the alkynyl–metal hydride complex (**521**) to the vinylidene was more exothermic for the cobalt series than the rhodium series. The exothermic conversion of the alkynyl–rhodium hydride to the rhodium–vinyl-



Scheme 78.

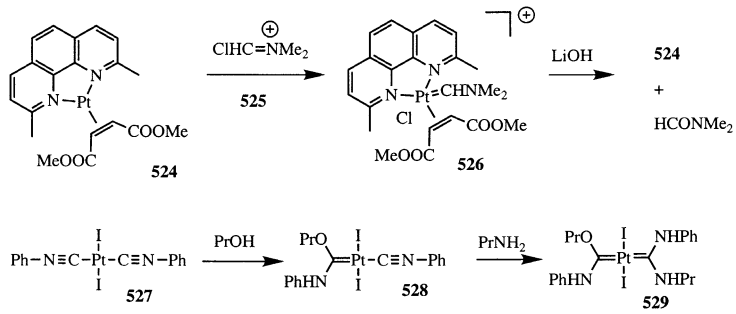


Scheme 79.

idene complex is in disagreement with experimental results, where the alkynyl–rhodium hydride structure is favored.

1.3.7. Group X metal–carbene complexes

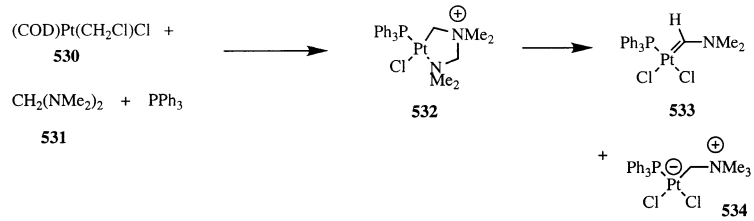
Platinum–carbene complexes (e.g. **526**, Scheme 80) were prepared from the reaction of chloroiminium salt **525** with platinum(0)–alkene complexes (e.g. **524**) [408]. Reaction of the carbene complex with a variety of nucleophiles led to DMF and the original platinum complex **524**. Unsymmetrical platinum bis(carbene) complexes (e.g. **529**) were generated from the reaction of bis(phenylisocyanide)–platinum complexes (**527**) with alcohols and amines [409]. The complexes were synthesized either by reaction of one equivalent of an alcohol followed by one equivalent of an amine, or by reaction with two equivalents of an alcohol followed by an exchange reaction with an amine. Related luminescent diaminocarbene–platinum complexes were generated from the reaction of platinum isocyanide complexes with amines [410]. Bridging aminocarbyne complexes of platinum and tungsten were generated by protonation of isocyanide-bridged heterobimetallic systems [411].



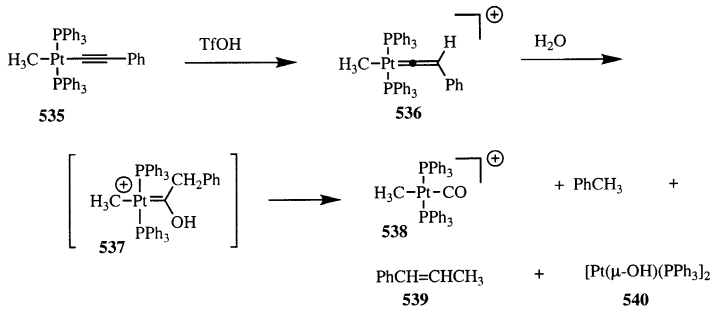
Scheme 80.

Aminocarbene-platinum complexes (e.g. **533**, Scheme 81) were prepared from the reaction of chloromethylplatinum complex **530** with bis(dimethylamino)methane (**531**) in the presence of a phosphine ligand [412]. A cyclic complex (e.g. **532**) was generated initially which slowly converted to the carbene complex at room temperature; ylide complexes (e.g. **534**) were obtained as a byproduct. The proposed mechanism for formation of the cyclic complex involves complexation of one amine at platinum followed by an intramolecular nucleophilic displacement of the chloride.

Cationic platinum–vinylidene complexes (e.g. **536**, Scheme 82) were generated from protonation of neutral alkynylplatinum complexes (e.g. **535**) below -20°C



Scheme 81.



Scheme 82.

[413]. Reaction of the vinylidene complexes with water led to carbonyl complex **538** and hydroxy-bridged dimer **539**, accompanied by alkane and alkene fragments. The decomposition products were proposed to arise from an unobservable hydroxycarbene complex (e.g. **537**).

2. Metal–carbyne or metal–alkylidyne complexes

2.1. Review articles

A review focusing on alkyne metathesis as a synthetic tool, which metal–carbyne complexes often initiate, was reported in 1999 [414].

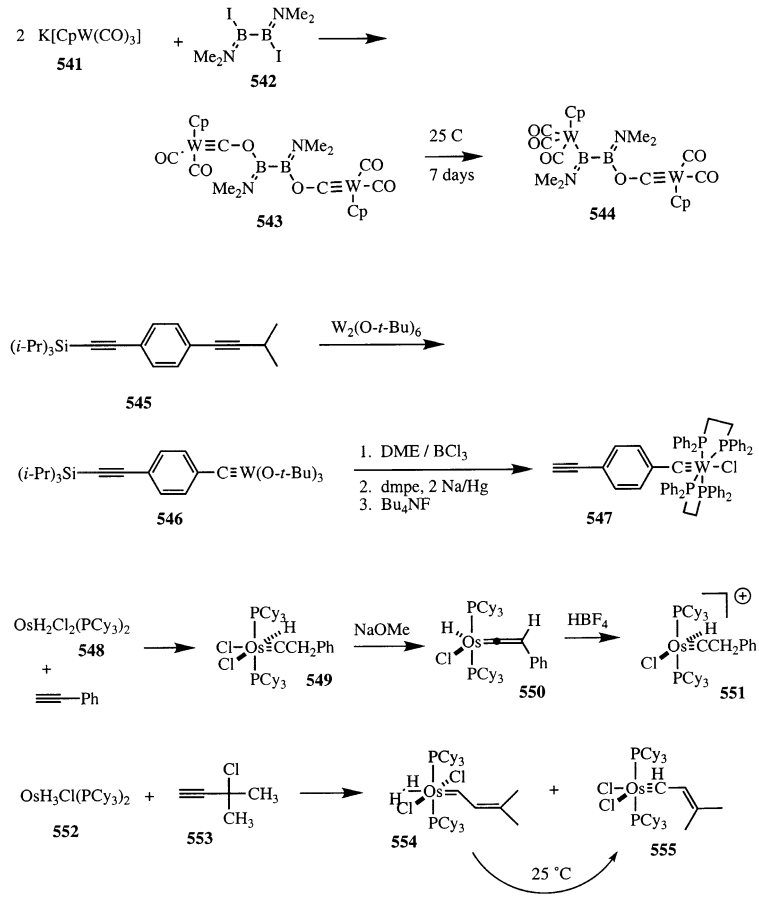
2.2. Synthesis and/or generation

Molybdenum and tungsten bis-oxycarbyne complexes (e.g. **543**, Scheme 83) were generated through the coupling of $[CpM(CO)_3]^-$ derivatives with borane reagent **542** [415]. Upon standing for 7 days, a shift of one boron from oxygen to the metal occured, affording monocarbyne complex **544**. A *p*-ethylnylphenylcarbyne–tungsten complex (**547**) was prepared by reaction of a *p*-diethynylbenzene derivative with $W_2(O\text{-}t\text{-}Bu)_6$ followed by ligand exchange processes [416]. Hydridosmium–carbyne complexes (e.g. **549**) were prepared via the coupling of terminal alkynes with osmium–hydride complexes [417]. Complex **549** was converted to vinylidene complex **550** by treatment with base, which converted to the cationic coordinatively unsaturated complex **551** upon treatment with HBF_4. A mixture of vinylcarbene complex **554** and vinylcarbyne complex **555** was obtained from the coupling of osmium–hydride complex **552** with propargyl chloride derivative **553**; carbene complex **554** converted to carbyne complex **555** at room temperature. Dicationic manganese-bimetallic complexes featuring a bridging carbyne ligand (e.g. **559**, Scheme 84) were prepared from the oxidation of vinylidene-bridged complex **558**, which arises via reductive dimerization of cationic alkynylmanganese complex **556** [418]. These complexes were reduced to the corresponding neutral bridging vinylidene–manganese complexes treatment with Cp_2CoCH_3, which were reoxidized to the bridging carbyne complex with ferrocenium salts.

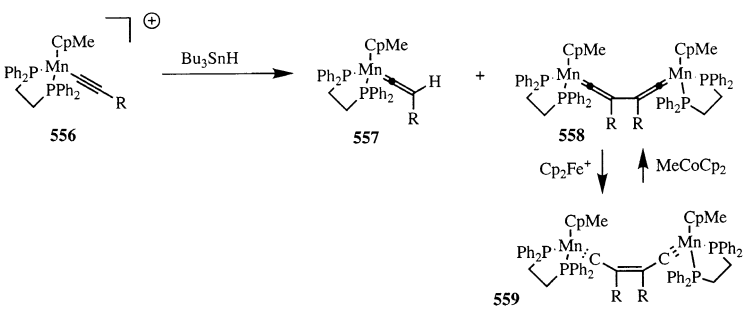
2.3. Reactivity

2.3.1. Addition reactions of metal–carbyne complexes

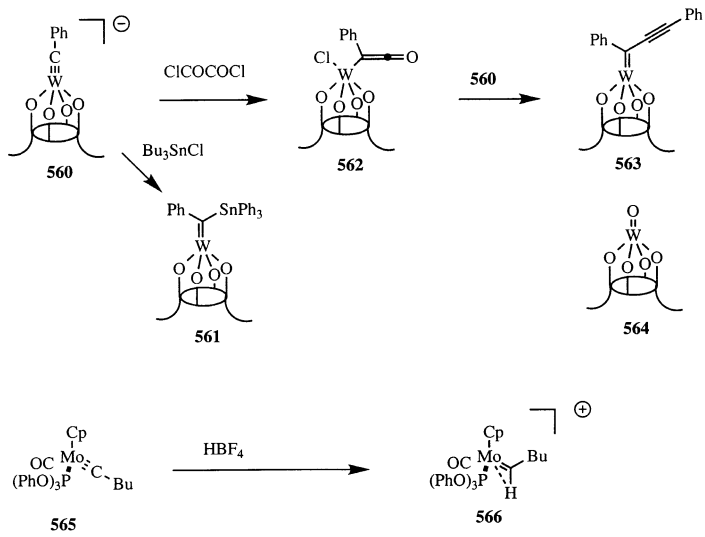
Addition of electrophiles to anionic calixarene-ligated tungsten carbyne complexes (e.g. **560**, Scheme 85) resulted in formation of the analogous neutral tungsten carbene complexes (e.g. **561**) [419–421]. The reaction with oxallyl chloride led to ketene complex **562**, which afforded alkynylcarbene complex **563** and tungsten oxo species **564** upon coupling with excess **560**. Protonation of various molybdenum–carbyne complexes (e.g. **565**) afforded products from protonation at the carbyne carbon (e.g. **566**) or the metal depending upon the electron donating ability of the



Scheme 83.



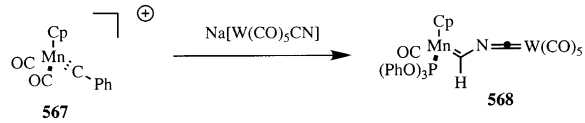
Scheme 84.



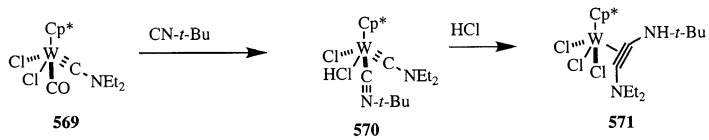
Scheme 85.

ligands at molybdenum [422]. Nucleophilic addition of various anionic transition metal complexes to cationic manganese– and rhenium–carbyne complexes (e.g. **567**, Scheme 86) in most cases results in heterobimetallic complexes (e.g. **568**) featuring a manganese–carbene group [423,424]. An arsenocarbyne tungsten complex was prepared by substitution of chlorine in a chlorocarbyne complex [425].

Ligand exchange, oxidation, and electrophile addition reactions were demonstrated for aminocarbyne–tungsten complexes (e.g. **569**, Scheme 87) [426]. Reaction of isocyanide–carbyne complex **570** with HCl led to the carbyne-isocyanide coupling product, alkyne complex **571**.



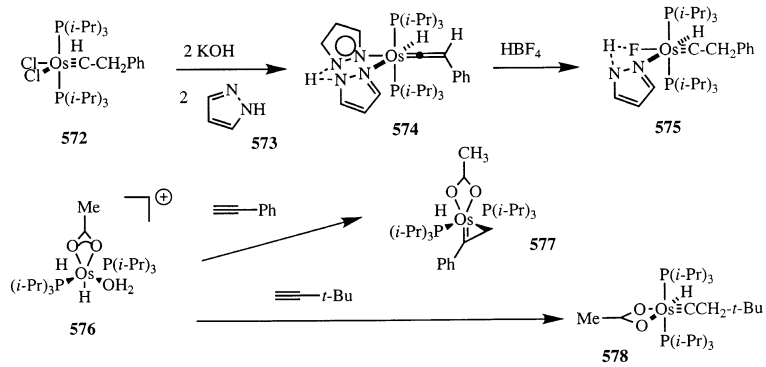
Scheme 86.



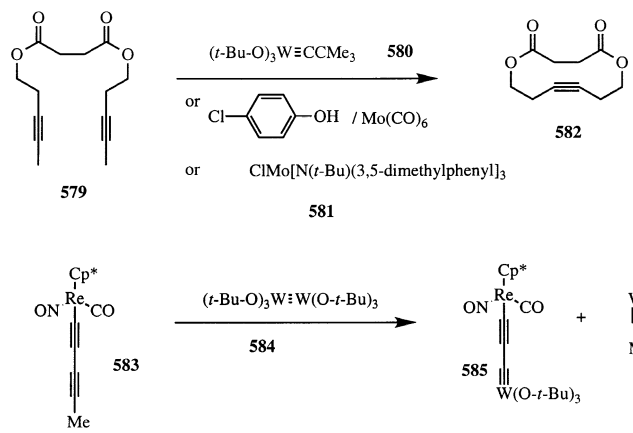
Scheme 87.

2.3.2. Reactions involving carbanions derived from metal–carbyne complexes

Reaction of osmium–carbyne complex **572** (Scheme 88) with two equivalents of pyrazole (**573**) and two equivalents of KOH leads to the osmium–vinylidene complex **574** [427]. Reaction of the vinylidene complex with HBF_4 regenerates a carbyne ligand, resulting in the osmium–fluoride complex **575**. The reaction of osmium–hydride complex **576** with a series of acetylenes was reported [428]. Reaction with phenylacetylene or diphenylpropargyl alcohol resulted in the η^2-alkenyl complex (e.g. **577**), while reaction with trimethylsilylacetylene or 3,3-dimethyl-1-butyne led to the carbyne complex (e.g. **578**). Subsequent deprotonation of the carbyne complexes with KOH led to the vinylidene complexes. The observed structural preferences are agreement with DFT calculations.



Scheme 88.



Scheme 89.

2.3.3. Alkyne metathesis

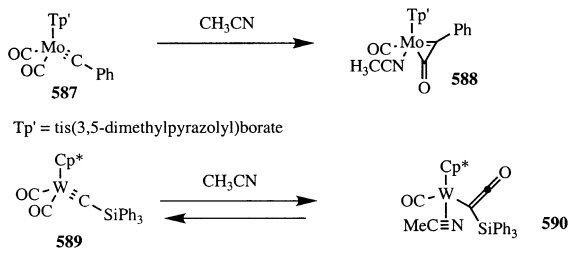
Ring closing alkyne metathesis of series of diyne derivatives (e.g. **579**, Scheme 89) was demonstrated using either the tungsten alkylidene complex **580**, the molybdenum hexacarbonyl–*p*-chlorophenol systems [429], or molybdenum complex **581** [430]. The tungsten systems were found to be more general for this process. Ring closing alkyne metathesis followed by Lindlar hydrogenation led to macrocyclic cis alkenes. The analogous approach using RCM of alkenes typically affords mixtures of alkene stereoisomers. Heterobimetallic complexes bridged through one alkynyl and one carbyne ligand (e.g. **585**, Scheme 89) were prepared by cross metathesis of butadiynylrhenium complexes and tungsten complex **584** [431]. An equal amount of tungsten carbyne complex **586** was also produced in this metathesis reaction.

Several reports on the initiation of alkyne metathesis using complexes that are not carbyne complexes appeared in 1999, however the involvement of metal carbyne intermediates was noted. High molecular weight alkyne-containing polymers were prepared through metathesis polymerization of acyclic diynes (ADIMET) using molybdenum hexacarbonyl and *p*-chlorophenol; presumably a metal–carbyne complex is an intermediate in this process [432]. Non-polymer forming metathesis of 1-phenylpropyne was also reported using this catalyst system [433].

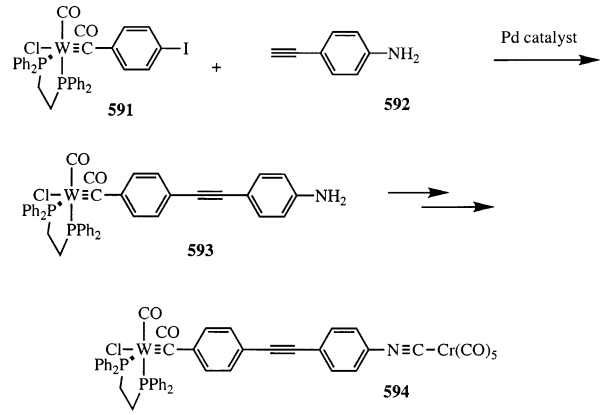
2.3.4. Other processes involving metal–carbyne complexes

Synthesis and acetonitrile-induced CO insertion reactions were reported for tungsten– and molybdenum–carbyne complexes (e.g. **587**, **589**, Scheme 90) [434]. Reaction of the tris(dimethylpyrazolyl)borate complexes with acetonitrile led to the η^2-ketenyl complex (i.e. **588**) containing an *N*-bound acetonitrile ligand, while reaction with pentamethylcyclopentadienyl complex **589** with acetonitrile led to the η^1-ketenyl complex **590** containing a side-on bound nitrile ligand as a four-electron donor.

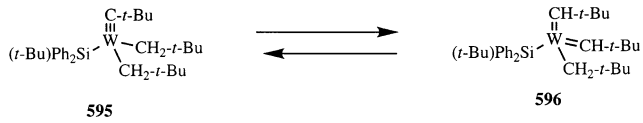
A series of studies on the functionalization of arylcarbyne–tungsten complexes (e.g. **591**, **593**, Scheme 91) was reported in 1999. Reaction of the *p*-iodophenylcarbyne complex **591** with *p*-aminophenylacetylene (**592**) was reported, followed by subsequent conversion of the amine group to the corresponding isocyanide [435]. Further complexation of the isocyanide with Group VI metal carbonyls led to donor–acceptor complexes (e.g. **594**) [436].



Scheme 90.



Scheme 91.



Scheme 92.

Mechanistically-oriented studies of the reactions of metal–carbyne complexes include: (1) studies of the excited state properties of tungsten–carbyne complexes and observation of electron-transfer processes occurring from the excited state [437]; (2) studies of the reaction of compounds containing either a Mo≡Mo or W≡W bond with excess benzonitrile, which affords acetylenes and metal nitrides via the intermediacy of the carbyne complex [438]; and (3) comparison of the thermodynamic stabilities of metal–alkylidyne (e.g. **595**, Scheme 92) versus bis-carbene complexes (e.g. **596**) for a variety of metal–ligand-combinations [439].

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