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Coordination Chemistry Reviews 249 (2005) 999–1084

COORDINATION CHEMISTRY REVIEWS

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Review

# The chemistry of the carbon-transition metal double and triple bond: annual survey covering the year 2003☆

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Received 12 October 2004
Available online 19 March 2005

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☆ For 2002, see J.W. Herndon, Coord. Chem. Rev. 248 (2004) 3.

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doi:10.1016/j.ccr.2004.10.009

## Abstract

This is a review of papers published in the year 2003 that focus on the synthesis, reactivity, or properties of compounds containing a carbon-transition metal double or triple bond.

*Keywords:* Carbon-transition metal; Chemistry; Double and triple bond

## 1. Introduction

This survey is intended to be a comprehensive summary of articles that report on the synthesis, reactivity, or properties of compounds featuring a multiple bond between carbon and a transition metal. Reactions that employ metal carbene complexes as transient intermediates generated through well-established routes are not covered, unless there is some effort to characterize the carbene complex intermediate. This area was reviewed in 2003 [1,2]. Although a determined effort has been made to include patents, in general only patents that focus on the metal–carbene or metal–carbyne complex are 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 *N*-heterocyclic (or Arduengo) 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 [3–5]. This area was reviewed several times in 2003 [6–8]. 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 [9] has been employed for the discussion of oxidation states and ligand electron count throughout this survey. A special section focusing on alkene metathesis has been included prior to the discussion of carbene complexes of individual metals. The metal carbyne section has been organized according to reaction type.

Abbreviations (see also the front of issue #1 of the *Journal of Organic Chemistry* [10]):

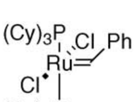
| | |
|---|---|
| DFT | density functional theory |
| Grubbs Catalyst I | structure 1 (Fig. 1) |
| Grubbs Catalyst II | structure 2 (Fig. 1) |
| Schrock Catalyst | structure 3 (Fig. 1) |

See also Scheme 1 for abbreviations of distinct modes of metathesis.

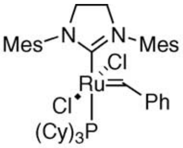
## 2. Metal–carbene or metal–alkylidene complexes

### 2.1. Review articles and comments

Several reviews/comments covering aspects of metal–carbene complex chemistry appeared in 2003. Many articles focusing on some aspect of carbene complex-initiated olefin metathesis were published, including the following specific subjects: (1) use of tungsten and molybdenum imido complexes as catalysts for alkene metathesis [11]; (2) transition metal carbene complexes in olefin metathesis [12]; (3) ruthenium–carbene complexes as metathesis catalysts [13,14]; (4) the utility of Grubbs Catalyst II [15]; (5) well-defined metathesis polymerization catalysts [16]; (6) dual activity of ruthenium catalysts for controlled radical reactions and alkene metathesis [17]; (7) ring closing metathesis [18]; (8) alkene cross metathesis [19]; (9) enyne metathesis [20]; (10) catalytic asymmetric alkene metathesis [21]; (11) catalysis in acyclic diene metathesis polymerization [22]; (12) sequential metathesis in oxa- and azanorbornene derivatives [23]; (13) synthesis of piperidine and pyrrolidine alkaloids using ring closing metathesis as a key step [24]; (14) synthesis of coumarins by ring closing metathesis [25]; (15) cross metathesis in nitrogen-containing systems [26]; (16) synthesis of organosilicon compounds using alkene metathesis [27]; (17) acyclic diene metathesis of 1,2-divinylferrocene [28]; (18) synthesis of vinylsilicon reagents by metathesis [29,30]; (19) competitive isomerization and ring closure in the reaction of 1,6-dienes with ruthenium allenylidene complexes [31]; (20) industrial applications of alkene metathesis [32]; (21) olefin metathesis



**1**

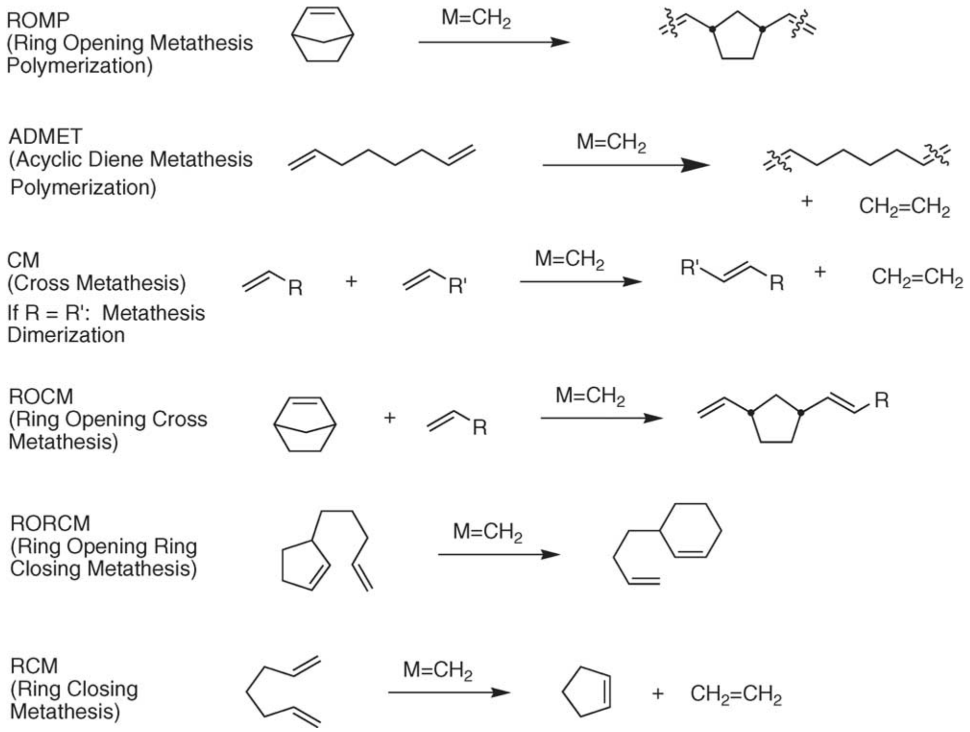


**2**

Ar = 2,6-diisopropylphenyl

**3**

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



Scheme 1.

in glycobiology [33]; and (22) attachment of metathesis catalysts to cadmium selenide nanoparticles [34]. Several review articles report on synthesis of various compound classes where olefin metathesis is a commonly-employed synthetic route. Specific compound classes represented include: (1) roseophilin and prodigiosin alkaloids [35]; (2) ciguatoxins and related marine toxins [36]; (3) epothilones [37]; (4) biologically important nitrogen heterocycles [38]; (5) styrylactone natural products [39]; (6) dendrimers [40]; (7) macrocyclic natural products containing E alkenes [41]; (8) rotaxanes [42]; (9) carbohydrate derivatives [43]; (10) synthetic oils and oleochemicals [44,45]; (11) phosphines [46]; (12) cyclic compounds prepared through tandem allyltitanation followed by ring closing metathesis [47]; and (13) combinatorial libraries designed to modulate protein–protein or protein–DNA interactions [48]. Additional review articles include some metathesis segments. Articles in this category focus on the following subjects: (1) catalysis through surface organometallic chemistry [49]; (2) immobilized catalysts [50,51]; (3) electron rich phosphine ligands in synthesis [52]; (4) asymmetric C–C and C–heteroatom bond-forming catalysts featuring partially hydrogenated binaphthyl ligands [53]; (5) transition metal carbene complexes in homogeneous catalysis [54]; (6) catalytic applications of transition metals in organic synthesis [55]; (7) polymerizations in aqueous media [56]; (8) synthesis of cyclobutane hydrocarbons by cycloaddition and alkene metathesis [57]; and (9) organosilicon reactions in palladium-catalyzed cross coupling [58]. Several reviews on carbene complex chemistry featuring some aspect other that metathesis appeared in 2003, including the following subjects: (1) solvent-controlled selectivity in the synthesis of five-membered ring carbocycles [59]; (2) copper carbene complexes [60]; (3) iridium carbene complexes directly prepared from amines or ethers [61]; (4) nonmetathesis behavior of ruthenium–carbene complexes [62]; (5) asymmetric propargyl substitution reactions mediated by optically active ruthenium allenylidene complexes [63]; (6) porphyrin carbene complexes [64]; and (7) design of new reaction processes based on cyclopropylcarbene complexes [65]. Although not specifically focusing on metal–carbene complexes, some review articles place a heavy emphasis on this subject. Subjects reviewed in this category include: (1) cyclizations initiated by ruthenium alkene metathesis catalysts and other ruthenium complexes [66]; (2) acetylide-bridged metal complexes [67]; (3) metal–alkyne complexes, which are often easily transformed to or from metal–vinylidene complexes [68]; (4) the ambivalent behavior of aryl-functionalized phosphine ligands [69]; (5) metal–imido complexes [70]; (6) attempts to prepare isophosphaalkynes [71]; (7) anionic triazacyclononane complexes [72]; (8) coordinatively unsaturated organoruthenium amidinates in homogeneous catalysis [73]; (9) relativistic effects in gas-phase ion chemistry, with a large section devoted to platinum–carbene complexes [74]; (10) carbon–carbon bond cleavage reactions [75]; (11) thermal activation of hydrocarbon C–H bonds by $Cp^{*}W(NO)$ (and molybdenum analogs) complexes [76]; (12) labeling of proteins with transition metals [77]; and (13) complexes featuring pincer ligands and other abnormal binding modes [78].

### 2.2. Alkene metathesis

Alkene metathesis was the most common reaction process reported for metal–carbene complexes in 2003, 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 offer significant discussion of the carbene complex intermediates in this reaction have been included here. Distinct modes of alkene metathesis are depicted in Scheme 1.

#### 2.2.1. General studies of alkene metathesis catalysts

Numerous attempts to develop new catalysts for alkene metathesis were reported in 2003; some representative examples are depicted in Fig. 2. Several derivatives of the Grubbs and Schrock catalysts were synthesized and tested in their ability to undergo either ROMP or RCM processes, including: (1) analogs of Grubbs Catalysts I and II where the chlorides have been replaced by alkoxides (e.g. **5**) [79]; (2) a low activity analog of Grubbs Catalyst II where the mesityl groups have been replaced by adamantly groups [80]; (3) indenylidene–ruthenium complexes (e.g. **6**) generated in situ from ruthenium allenylidene complexes [81]; (4) allenylidene–ruthenium complexes that feature a chelating arene/stable carbene ligand [82]; (5) the fast initiating 3-bromopyridylcarbene–ruthenium complex **7** [83]; (6) paraffin-dispersed Grubbs Catalyst II [84]; (7) a tethered analog of Grubbs Catalyst II (**8**) that is especially effective for the preparation of cyclic ROMP polymers [85]; (8) ferrocene-tethered analogs of Grubbs Catalyst I [86]; (9) silica-bound analogs of Grubbs Catalyst II [87]; (10) a readily-available *o*-isopropoxyphenylcarbene–ruthenium complex catalyst (**9**) [88]; (11) aromatic ring-substituted *o*-isopropoxyphenylcarbene–ruthenium complexes [89]; (12) a hindered *o*-isopropoxyphenylcarbene complex catalyst [90,91]; (13) vinylidene–ruthenium complexes featuring a salicylimide ligand [92]; (14) ruthenium catalysts containing an imidazolium ring (e.g. **10**) that are useful for metathesis in ionic liquids [93,94]; (15) an indenylidene complex (**11**) useful for ROMP and free-radical-based polymerizations [95]; (16) a chiral ruthenium–carbene complex catalyst (**12**) featuring a chelating chiral dihydroimidazolylidene ligand [96]; (17) analogs of the Schrock carbene complex that feature an imine–carbene tether [97]; (18) phosphine-chelated molybdenum–carbene complex **13**, which becomes a highly activated ROMP catalyst upon treatment with thallium(I) salts [98]; (19) immobilized chiral analogs of the Schrock carbene complex [99]; (20) polyethylene glycol-bound ruthenium–carbene complex catalysts [100]; (21) ruthenium–carbene complexes attached to a zeolite through a salicylimide ligand [101]; and (22) a silica-bound rhenium–carbyne–carbene complex [102]. Several patents were issued for the synthesis and development of metal–carbene containing olefin metathesis catalysts [103–111]. A new synthetic route to ruthenium metathesis

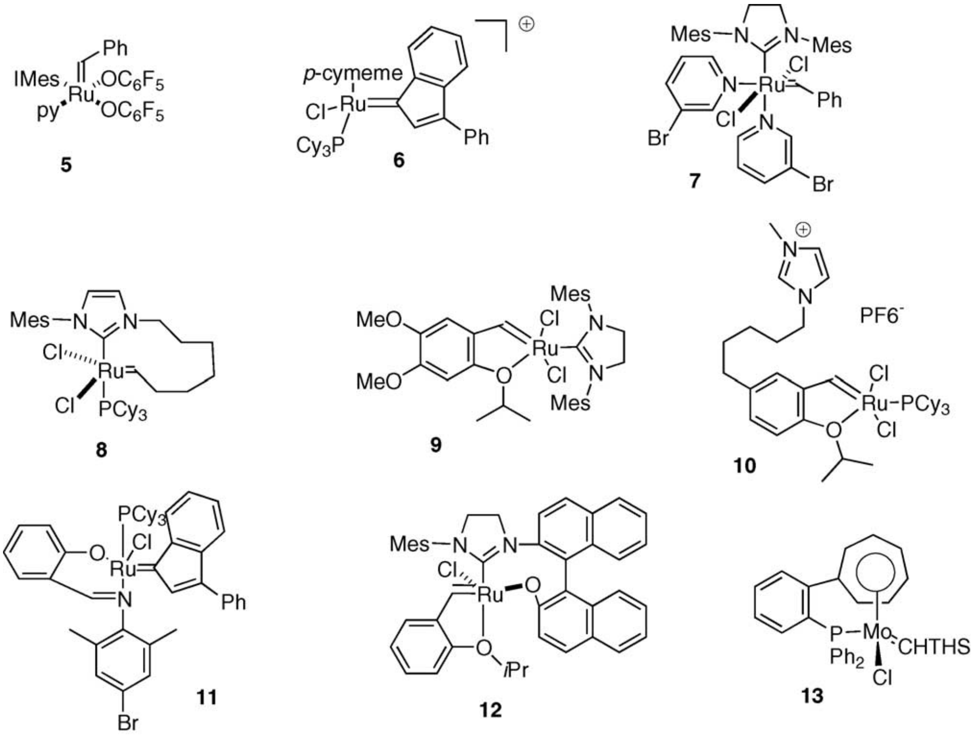
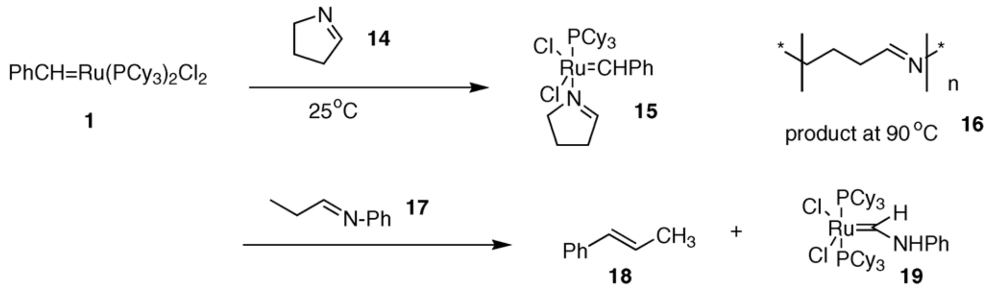


Fig. 2. Representative examples of new catalysts for alkene metathesis.



Scheme 2.

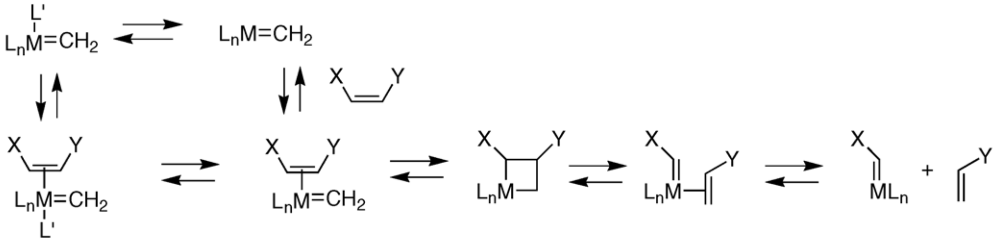
catalysts featuring one heterocyclic ring and one labile donor ligand was reported [112].

Other general studies of alkene metathesis where carbene complexes were discussed include: (1) improved methods for the preparation of a variety of analogs of Grubbs Catalyst II (substitution in the *N*-heterocyclic carbene ligand) and examination of their relative rates of metathesis [113]; (2) a study of electronic effects on the rate of metathesis reactions induced by derivatives of Grubbs Catalyst II (variation of the phosphine ligand)—all of the catalysts under study were more active than Grubbs Catalysts II in ROMP and RCM reactions [114]; (3) comparison of various ruthenium–carbene complexes for ROMP of norbornene diesters [115]; (4) studies of the rate and mechanism for metathesis reactions catalyzed by cationic ruthenium allenylidene complexes, which convert to indenylidene ruthenium complexes during the reaction cycle [116]; (5) comparison of 7-coordinate tungsten/molybdenum complexes with Grubbs Catalyst I for ROMP reactions [117]; (6) microwave-induced RCM reactions [118,119]; (7) studies that show microwave acceleration of RCM is due to thermal effects [120]; (8) RCM reactions in the air and in protic solvents [121]; (9) reaction of ruthenium metathesis catalysts with imines (Scheme 2), which lead to either oligomeric materials (e.g. **16**) from cyclic imines or to stoichiometric metathesis products (e.g. **18** and **19**) from enamine tautomers of acyclic imines [122]; (10) an experimental comparison of gas-phase metathesis reactivity of the 14-electron intermediates derived from Grubbs Catalysts I and II [123]; (11) a new method for removal of ruthenium impurities from metathesis reactions using activated carbon and silica [124]; (12) use of TLC for analysis of metathesis reactions employing combinatorial catalyst mixtures [125]; (13) use of a noncarbene–ruthenium complex to initiate ROMP polymerization and identification of ruthenium–carbene complex intermediate by $^1$H NMR [126]; and (14) generation of alkene metathesis catalysts from $WCl_6$ through reductive, oxidative, and pulse electrolysis methods; carbene complex intermediates were not detected [127].

Several theoretical studies of ruthenium–carbene-catalyzed alkene metathesis appeared in 2003. A theoretical study of alkene metathesis using ruthenium–methylene complexes $Cl_2(PMe_3)_2Ru{=}CH_2$ and $Cl_2(PCy_3)_2Ru{=}CH_2$ was reported (Scheme 3) [128]. Metathesis of propylene was studied. The dissociative mechanism was more favorable for both complexes when the free energy is considered, however the associative mechanism was more reasonable when only total electronic energies were employed. The dissociative pathway becomes even more favorable relative to the associative pathway when a sterically more bulky complex was employed. In another theoretical study of ruthenium-induced metathesis, a low energy novel reaction pathway was identified involving a chloromethylruthenium complex instead of a methyleneruthenium complex [129]. Although the chloromethyl complex was unstable relative to the methylene complex, the chloromethyl complex becomes more stable after coordination of the alkene. Molybdenum–carbene metathesis reactions were also studied theoretically [130].

### 2.2.2. Polymerization reactions

Initiation of the ring opening metathesis polymerization (ROMP) (see Scheme 1) reaction using carbene complexes remains a very active area of investigation. The strained alkene norbornene, norbornene derivatives, and copolymerization involving a norbornene derivative and another alkene accounted for a large fraction of all reports of the ROMP re-



Scheme 3.

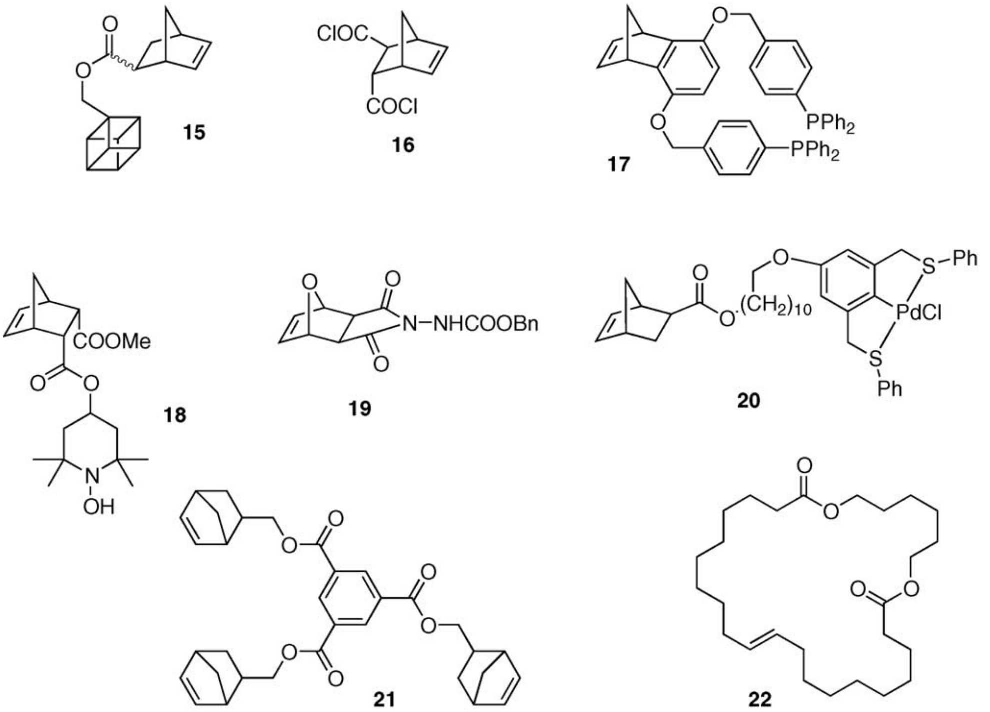


Fig. 3. Representative substrates for the ROMP reaction.

action in 2003 (Fig. 3). Numerous cycloalkenes have been subjected to ROMP using metal carbene complexes, including: (1) norbornene-fused cyclic sulfonamides (the resulting polymer was used as a support for solid phase RCM [131] or sulfonation [132]); (2) norbornenes containing a cubane ring system (e.g. **15**) [133]; (3) 2,2,2-trifluoroethyl esters of norbornenecarboxylic acid [134]; (4) chloromethylnorbornenes [135]; (5) acid chloride-substituted norbornenes (e.g. **16**) for preparation of a solid phase nucleophile scavenger [136]; (6) 8-hydroxyquinoline containing norbornenes [137]; (7) peptide-bound norbornenes [138]; (8) diphosphine-substituted norbornenes (e.g. **17**) [139]; (9) norbornenes bound to TEMPO radical precursors (e.g. **18**) [140]; (10) phosphine and imidazolium-containing norbornenes [141]; (11) *N*-aminosuccimide derivatives of oxanorbornene (e.g. **19**) [142]; (12) norbornenes containing a palladium-ligated system (e.g. **20**) [143,144]; (13) norbornenes connected to *p*-cyanobiphenyls for preparation of liquid crystal polymers [145]; (14) norbornenes attached to hydrogen-bonding motifs [146]; (15) dicyclopentadiene [147]; and (16) cyclooctatetraene in the presence of 1,4-difunctionalized-2-butene derivatives [148]. Other studies related to carbene complex-induced ROMP include: (1) ROMP of norbornene using dendrimeric ruthenium–carbene complexes [149]; (2) star polymers through co-ROMP of (tris)norbornene monomers (e.g. **21**) and simpler norbornenes [150]; (3) entropically-driven ROMP of macrocyclic alkenes (e.g. **22**) [151]; and (4) correlation of reaction temperature with carbene complex formation for molybdenum trihalide–methylaluminoxane catalyzed ROMP reactions [152].

Several examples using carbene complexes to initiate acyclic diene metathesis (ADMET, see Scheme 1) polymerization reactions were reported in 2003. Substrates subjected to ADMET polymerization are depicted in Fig. 4, and include: (1) amino acid substituted 1,*n*-dienes[1] (e.g. **23**) [153]; (2) 1,4-divinyl-2,5-bis(heptyloxy)benzene (**24**) [154]; (3) copolymerization of branched and unbranched acyclic 1,*n*-dienes [155]; (4) copolymerization of silicon-tethered dienes (e.g. **25**) and *p*-divinylbenzene [156]; and (5) solid state ADMET polymerization [157]. A study of alkene isomerization during ADMET polymerization was also reported [158].

### 2.2.3. Nonpolymer-forming ring opening metathesis reactions

Several examples of the tandem RORCM (see Scheme 1) reaction were reported in 2003. Representative reaction equations are presented in (Scheme 4). RORCM was employed for the conversion of monocyclic compound **26** into the bicyclic ring-expanded product **27**, which was employed in the total synthesis of astrophylline [159]. RORCM of allyloxymethylcyclobutenes (e.g. **28**) followed by oxy-Cope rearrangement was used as a method for medium-sized ring synthesis [160]. RORCM was employed for tricyclic alkene derivatives [161]. An unusual ring contraction process was reported using RORCM to excise two carbons from a cyclic diene **30** [162]. A sequence involving RO-CM to generate

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[1] The term 1,*n*-diene refers to an open-chain system where there are alkene groups at each end of the chain.

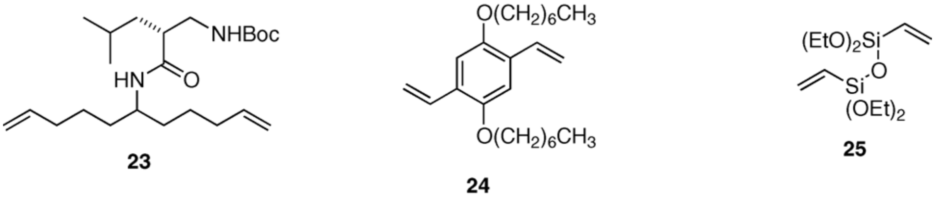
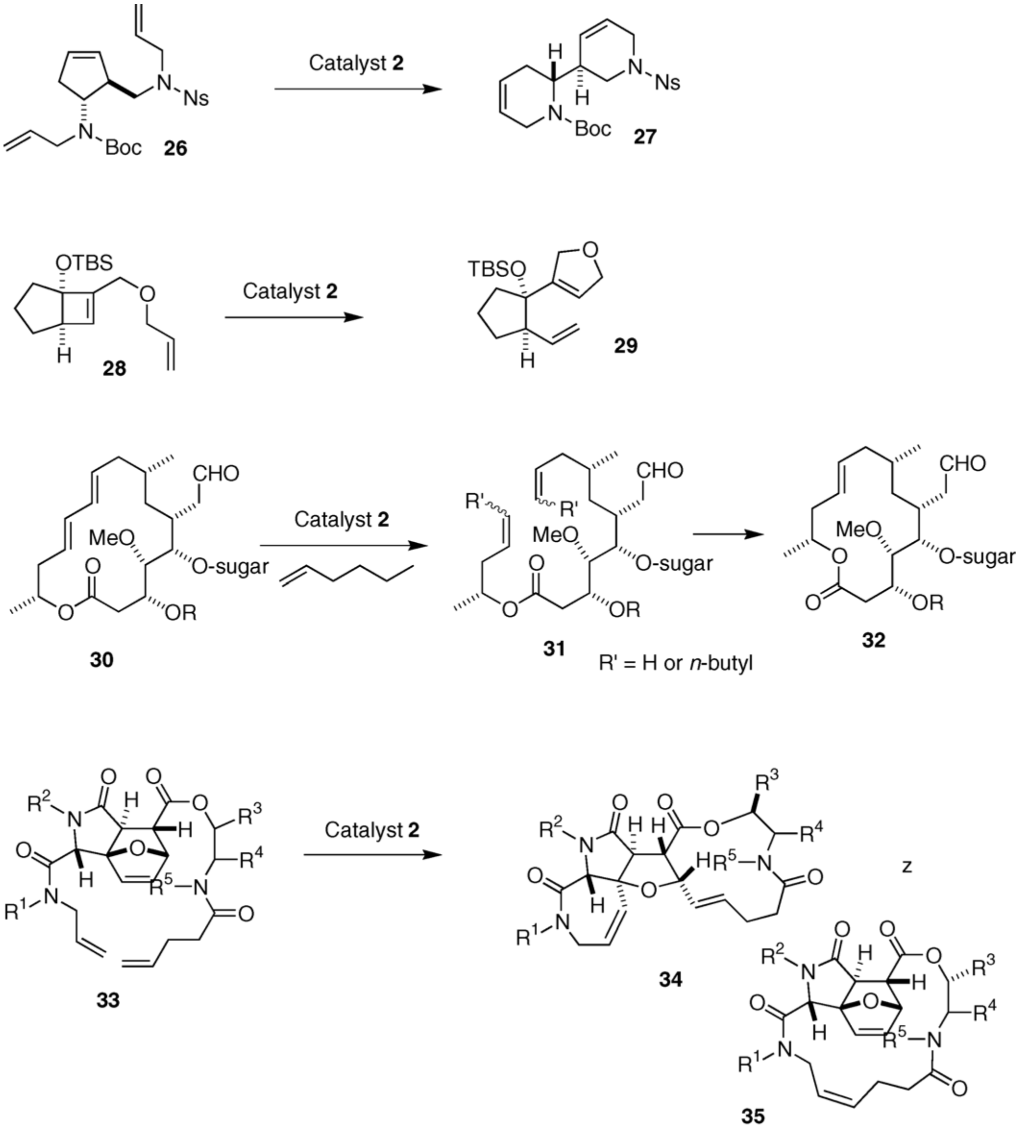


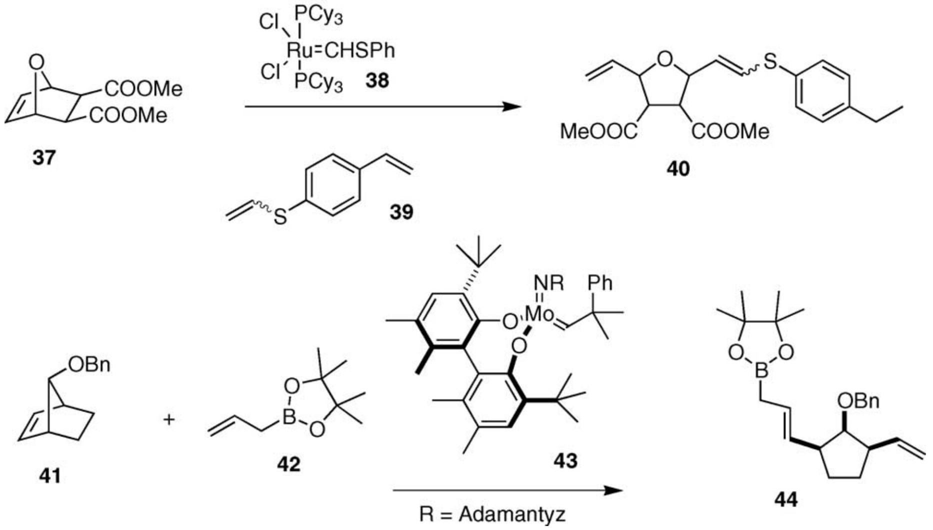
Fig. 4. Representative substrates for ADMET polymerization.

**31** followed by RCM to afford **32** was proposed. Double RORCM in competition with macrocyclic RCM was reported for the reaction of compounds of general structure **33** with Grubbs Catalyst II (**2**) [163]. The stereochemistry of $R^3$ had a profound effect on the direction of the metathesis reaction. Isomers with $R^3$ down favored the macrocyclic RCM product **35**, while isomers with $R^3$ up led to predominantly the double RORCM product **34**.

Several examples of RO-CM (see Scheme 1) were reported in 2003. Representative examples are depicted in Scheme 5. Synthesis of heteroatom analogs of Grubbs Catalyst I (e.g. **38**, Scheme 5) by treatment of Ru(*p*-cymene)(COD) with compounds of general structure $Cl_2CHSR$ (and selenium analogs) in the presence of $PCy_3$was reported [164]. These complexes were effective catalysts for RO-CM reactions of norbornene derivatives (e.g. **37**) with vinyl chalcogenides



Scheme 4.



Scheme 5.

(i.e. $CH_2$=CHSPh, $CH_2$=$CHSCH_2$Ph, $CH_2$=CHSePh). In reactions with complexes featuring a styrene and vinyl sulfide group (e.g. **39**), only the vinyl sulfide participated in the metathesis process. The RO-CM reaction of 7-oxa-2-azanorbornene derivatives and allyltrimethylsilane was reported [165]. Asymmetric RO-CM was reported for *meso* norbornene derivates (e.g. **41**) and allylboranes (e.g. **42**) using chiral and optically pure molybdenum carbene complexes (e.g. **43**) as catalyst [166].

### 2.2.4. Cross metathesis and metathesis-dimerization reactions

Many examples of the cross metathesis reaction (see Scheme 1) of various dissimilar alkenes (usually monosubstituted) were reported in 2003. Representative examples are depicted in Fig. 5. Specific pairs of compounds subjected to cross metathesis include: (1) vinyl sulfones and monosubstituted alkenes [167]; (2) allylic/homoallylic alcohols and α,β-unsaturated esters [168,169]; (3) various alkenes (e.g. **45**) and vinylphosphine oxides (e.g. **46**), and metathesis dimerization of vinylphosphine oxides [170]; (4) C-allyl aminocarbohydrates (e.g. **47**) and monosubstituted alkenes (e.g. **48**) [171]; (5) allylic alcohols and allylic acetates [172]; (6) various alkenes and allyltrimethylsilane [173]; (7) 1-propenylboranes and various monosubstituted alkenes [174]; (8) styrene derivatives and allylic naphthimides [175]; (9) *N*-homoallylamides and α,β-unsaturated ketones [176]; (10) fluorous vinylboronates and styrene [177]; (11) boron-substituted vinylcyclopropanes and monosubstituted alkenes [178]; (12) vinylsilanes and various monosubstituted alkenes [179]; (13) allyl- and homoallylphosphine oxides and various monosubstituted alkenes [180]; (14) protected 3-buten-1,2-diols (e.g. **49**) and *N*-allylpyrimidine derivatives (e.g. **50**) [181]; (15) γ,δ-unsaturated amino acids-nucleobase conjugates with alkene-containing hydrazinocarbene–chromium complexes [182]; (16) various monosubstituted alkenes with

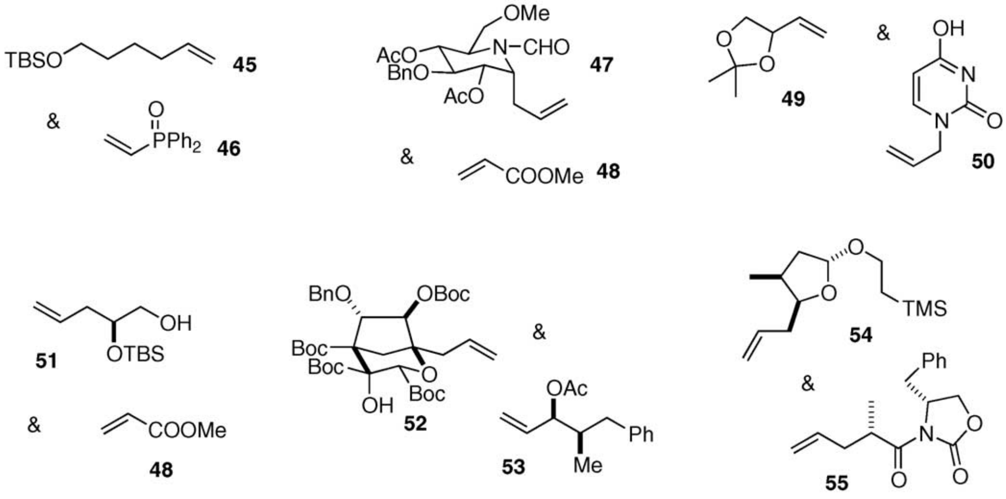


Fig. 5. Represent pairs of alkenes subjected to cross metathesis.

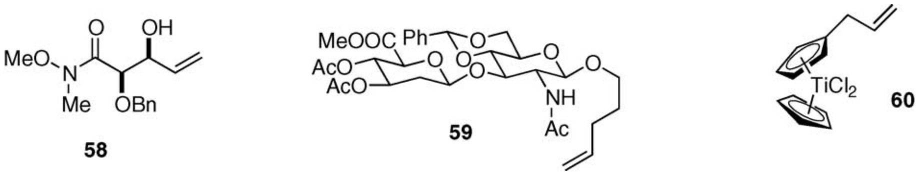


Fig. 6. Representative alkenes subjected to metathesis dimerization.

acrolein using Grubbs Catalyst II in the presence of CuCl [183]; (17) C-allyl glycosides and a vinylamino acid derivative [184]; (18) a pentenol derivative (**51**) and methyl acrylate for leucascandrolide total synthesis [185]; (19) alkenes **52** and **53** for total synthesis of zaragozic acid C [186]; (20) 5-allylbutyrolactone derivatives and 1-dodecen for total synthesis of paraconic acids [187]; (21) acrylic acid and a complex monosubstituted alkene for installation of the side chain of salicylihalamide [188]; (22) cross metathesis of two complex alkenes (**54** and **55**) for amphidinolide T1 total synthesis [189]; (23) a functionalized alkene and methacrolein for total synthesis of furoquinocins [190]; (24) analogs of the drug cyclosporine featuring an alkenyl side chain with various acrylate esters [191]; (25) 5-amino-4-hydroxy-1-alkene (or 5-amino-3-hydroxy-1-alkene) derivatives with β-hydroxy-γ,δ-unsaturated carboxylic acid derivatives [192,193]; (26) alkenes bound to a gold surface with various functionalized monosubstituted alkenes [194,195]; and (27) use of CM to release polymer-bound carbohydrates from a resin [196,197]. An attempt to classify alkenes and development of guidelines for the prediction of success in alkene cross metatheses was also reported [198].

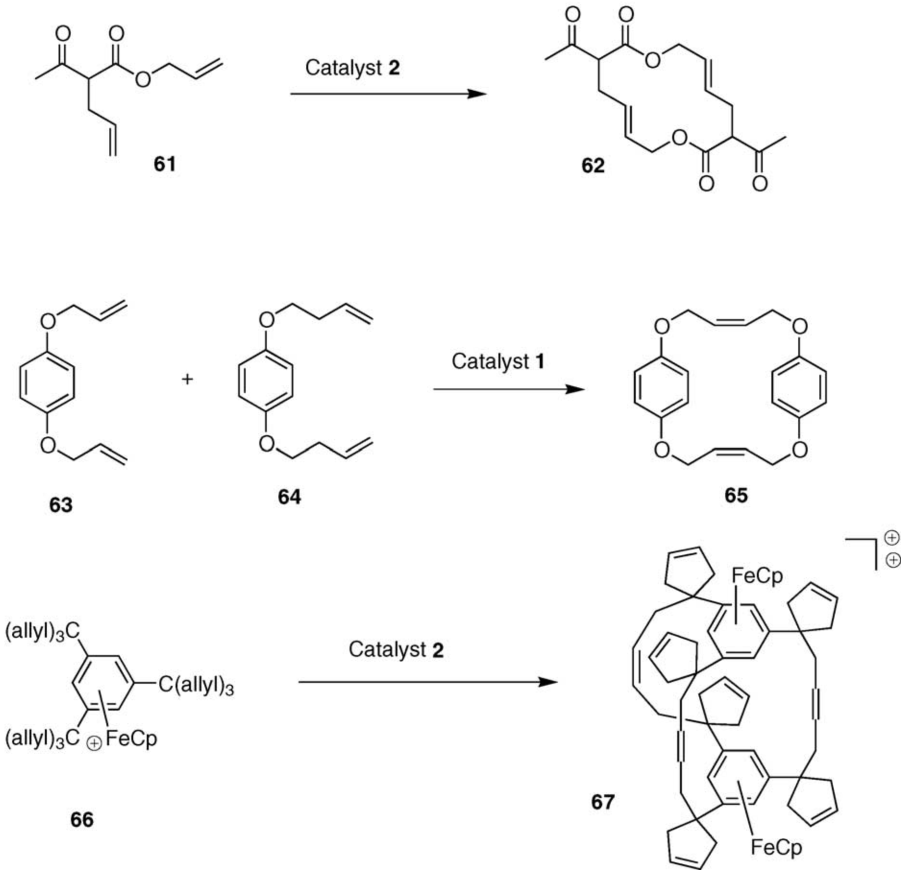
Several examples of dimerization via metathesis (see Scheme 1) were reported in 2003. Compounds subjected to metathesis dimerization are depicted in Fig. 6, and include: (1) 2,3-dihydroxy-4-pentenamide derivatives (e.g. **58**) [199]; (2) 5-hexenyl esters of benzofuran-3-carboxylic acid derivatives [200]; (3) metathesis dimerization and cross metathesis of *O*-pentenyl glycosides (e.g. **59**) [201,202]; (4) 5-thiophenyl-4-hydroxy-1-alkene derivatives [203]; (5)various allyl-Cp titanium complexes (e.g. **60**) [204]; (6) synthesis of porphyrin-containing rotaxanes [205]; (7) 9-decen-1-yl esters featuring hydrogen-bonding associated complexes for rotaxane synthesis [206]; (8) polymer cross linking through metathesis dimerization [207,208]; and (9) allylic alcohols, ethers, and cyanides and competing alkene isomerization processes [209].

Several examples of tandem metathesis dimerization-RCM were reported in 2003. Representative examples are depicted in Scheme 6. Tandem metathesis dimerization-RCM was employed for formation of 14-membered ring diester **62** [210] and in the synthesis of catenane derivatives [211]. Treatment of diene derivative **63** with Grubbs Catalyst I (**1**) led to the dimerization-RCM product **65** [212]. Homodimer-RCM product **65** was the major product when mixtures of **63** and **64** were subjected to Grubbs Catalyst I. No heterodimer-RCM products and only a minor amount the homodimer-RCM product from **64** were observed in this reaction. A trifold dimerization-RCM reaction sequence resulting in cyclophane **67** was observed upon treatment of nonakis(allyl)–iron complex **66** with Grubbs Catalyst II (**2**) [213]. A sequence of metathesis dimerization, followed by a series of organic reactions to make another diene, followed by RCM was employed for the net metathesis dimerization of cyclodextrin derivatives [214].

### 2.2.5. *Ring closing metathesis*

The ring-closing metathesis reaction (RCM) (see Scheme 1) has emerged as a very important method for organic synthesis. Many examples forming diverse ring sizes have been reported in 2003, including macrocycles and medium-size rings, as well as the traditional five- and six-membered ring-forming reactions. Reactions have been classified according to the type of ring system formed as a result of RCM.

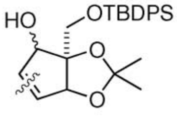
The RCM reaction has been employed for the synthesis of a variety of carbocyclic ring systems (Fig. 7, the indicated bond was formed via the RCM reaction). Examples include: (1) synthesis of cyclopentene derivatives [215,216]; (2) formation of cyclopentenes spiro fused to furanose sugars [217]; (3) formation cyclopentenols [218–221]; (4) formation of aminocyclopentenols [222]; (5) formation of cyclopentenols (e.g. **70**) for total synthesis of pentenomycin [223]; (6) formation of cyclopentenes fused to six-membered rings for total synthesis of pacifigorgianes [224]; (7) formation of a cyclopentene ring (e.g. **71**) for borrelidin total synthesis [225]; (8) formation of indenols (e.g. **72**) [226]; (9) formation of carbocyclic nucleosides [227]; (10) formation 1-cyclopentene-1,5-dicarboxylic acid derivatives [228]; (11) formation of carbocyclic amino acid analogs [229]; (12) formation of tricyclic five-membered rings (e.g. **73**) [230]; (13) formation of cyclopentenylcarbene–chromium complexes [231]; (14) formation of oxygenated cyclohexene derivatives [232]; (15) formation of a cyclohexenone ring for total synthesis of protoilludene [233]; (16) moderately diastereoselective formation of six membered rings (e.g. **74**) from triene derivatives that contain diastereotopic vinyl groups [234]; (17) formation of six-membered rings in the presence of a dicobalt–alkyne complex [235]; (18) determination of electronic effects for the formation of six-membered rings (**76**) through RCM using styryl derivative **75** [236]; (19) formation of 2-cyclohexen-1-ylsilanes [237]; (20) formation of a fused six-membered ring (e.g. **77**) for total synthesis of guanacastepene A and related compounds [238,239]; (21) formation of

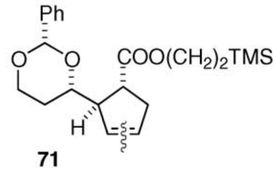


Scheme 6.

a cyclohexene fused to a four-membered ring (**78**) for merrilactone A total synthesis [240]; (22) synthesis of the six-membered ring of the *trans* hydrindane skeleton [241]; (23) formation of cyclohexenes fused to imidazole rings [242]; (24) formation of the *cis* decalin ring system [243]; (25) formation of six-membered rings fused to aromatic rings [244]; (26) formation of spiro-fused six-membered rings (e.g. **79**) [245–248]; (27) formation of cyclic alkenyl chlorides [249]; (28) formation of seven-membered rings fused to γ-lactones [250]; (29) formation of a seven-membered ring (e.g. **80**) from an enol ether for tribolide total synthesis [251]; (30) formation of highly oxygenated seven-membered rings [252]; (31) formation of seven-membered rings featuring a cyclic alkyne complexed to cobalt (e.g. **81**) [253]; (32) preparation of seven- and eight-membered rings fused to bicyclic ring systems in an “inside-out” stereochemical relationship (e.g. **82**) [254]; (33) preparation of seven- and eight-membered rings fused to cyclohexadiene rings [255]; (34) preparation of the eight-membered ring of the bicyclo[5.3.1]undecane ring system present in taxol [256]; (35) preparation of fluorinated carbocycles and heterocycles [257–259]; (36) synthesis of cyclooctenes [260]; (37) formation of a nine-membered ring (**83**) for total synthesis of cornexistins [261]; and (38) synthesis of ten-membered rings (e.g. **84**) as eleutherobin analogs [262–264].

Numerous examples of the formation of nitrogen heterocycles using the RCM reaction (Fig. 8) were reported in 2003, including: (1) formation of dihydropyrrole derivatives [265–267]; (2) formation of dihydropyrroles for total synthesis of antofine (**87**) [268]; broussonetine G (**88**) [269]; and anti-HIV compounds [270]; (3) formation of the dihydropyrrole ring of indolizidenes [271]; (4) formation of tetrahydropyridine derivatives [272,273]; (5) formation of six-membered ring lactams [274]; (6) formation of the six-membered ring of indolizidenes (e.g. **89**) [275,276]; (7) formation of six-membered ring lactams fused to cyclic carbamates [277]; (8) formation of six-membered ring cyclic amides [278]; (9) formation of six- to eight-membered ring cyclic amides that contain a trifluoromethyl group through RCM or intramolecular enyne metathesis [279]; (10) formation of bridged bicyclic amines [280]; (11) formation of six- to nine-membered ring lactams [281]; (12) formation of seven-membered ring amides [282]; (13) formation of seven-membered ring lactams (e.g. **90**) [283,284]; (14) enantioselective formation of benzazepines and aminocyclohexenes using a chiral molybdenum carbene complex catalyst [285]; (15) formation of bridged azabicyclic structures (e.g. **91**) [286]; (16) formation of an azabicyclic ring system for peduncularine total synthesis [287]; (17) formation of seven-membered ring lactams fused to a Cp ring


**70**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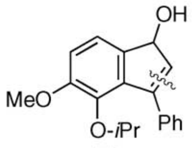
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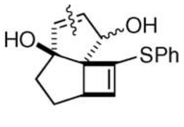
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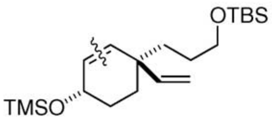
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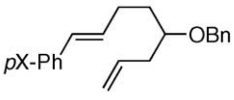
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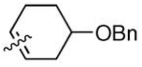
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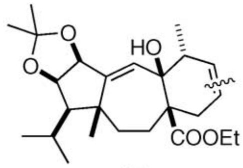
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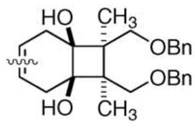
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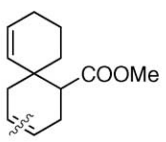
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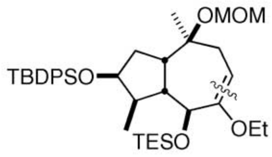
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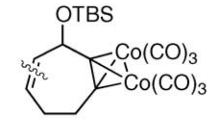
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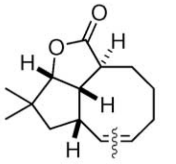
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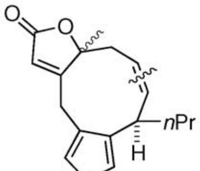
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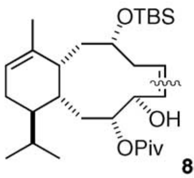
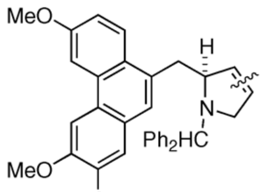

**84**

Fig. 7. Representative carbocycles produced through an RCM reaction (bond constructed through RCM indicated).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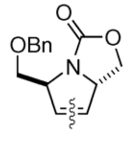
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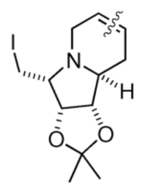
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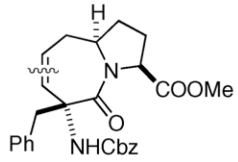
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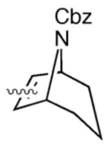
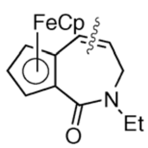

**91**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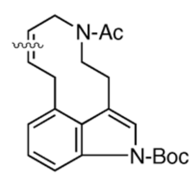
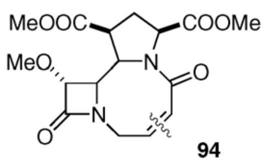
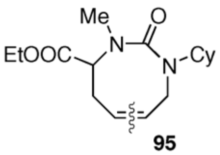

**93**


**94**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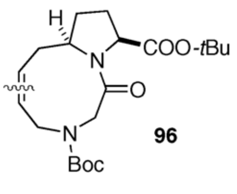
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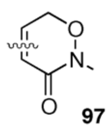

**97**

Fig. 8. Representative *N*-heterocycles produced through an RCM reaction (bond constructed through RCM indicated) (includes *N*,*O*-heterocycles).

of ferrocene (e.g. **92**) [288]; (18) formation of an eight-membered ring cyclic amide and a macrocyclic ring in separate steps of a total synthesis of nakadomarin A [289]; (19) formation of an eight-membered ring lactam in the presence of an alkyne-dicobalt complex [290]; (20) formation of nine-membered ring lactams [291]; (21) formation of ten-membered ring amides fused to an indole ring system (e.g. **93**) [292]; (22) formation of eight- to nine-membered ring cyclic diamides (e.g. **94**) [293]; (23) formation of eight-membered ring cyclic ureas (e.g. **95**) [294]; (24) formation of dinitrogen-containing nine-membered rings (e.g. **96**) [295]; (25) formation of cyclic hydroxamic acid derivatives (e.g. **97**) (*N* and *O* part of same ring) [296]; and (26) preparation of related hydroxylamine derivatives [297,298].

Many examples of oxygen heterocycle synthesis using the RCM reaction were reported in 2003 (Fig. 9), including: (1) synthesis of 2,5-dihydrofurans [299,300]; (2) synthesis of five-membered ring oxygen heterocycles (e.g. **100**) for nucleoside synthesis [301,302,303]; (3) synthesis of 2,5-dihydrofurans followed by alkene isomerization to 4,5-dihydrofurans [304,305]; (4) formation of six-membered ring cyclic ethers [306–308]; (5) formation of six-membered rings cyclic ethers for total synthesis of laulimalide [309], ambruticin S [310], malamycin A (**101**) [311], 4,5-deoxyneodolabelline (**102**) [312], rhopaloic acid [313], and malyngolide [314]; (6) formation of six-membered ring cyclic enol ethers for KDO total synthesis [315]; (7) formation of a six-membered ring cyclic ether fused to an α,β-unsaturated six-membered ring lactone (**103**) [316]; (8) formation of benzo-fused six-membered ring ethers [317]; (9) formation of a benzo-fused six-membered ring ether (**104**) for repinotan total synthesis [318]; (10) formation of α,β-unsaturated δ-lactones [319–322]; (11) formation of α,β-unsaturated δ-lactones for total synthesis of the published structure of passifloricin A [323,324], peloruside A [325–327], aprotoxin A [328], hyptolide (**105**) [329],spicigerolide [330], goniothalamin [331], and goniodiol [332]; (12) formation of an α,β-unsaturated lactone from a triene using a one-pot RCM-CM sequence [333]; (13) formation of α,β-unsaturated lactones attached to nucleosides (e.g. **106**) [334]; (14) formation of the coumarin ring system for total synthesis of ayapin [335]; (15) formation of benzodioxins (e.g. **108**) from *o*-allyloxybenzenes (e.g. **107**) in a one-pot isomerization/RCM sequence [336]; (16) asymmetric formation of cyclic ethers and cyclic siloxanes through use of a chiral catalyst on substrates that contain enantiotopic 1-propen-2-yl groups [337]; (17) formation of cyclic enol phosphates (e.g. **109**) [338]; (18) formation of six- to nine-membered ring oxygen heterocycles for total synthesis of ciguatoxin/brevitoxin and related compounds (e.g. **111**) [339–345]; (19) formation of highly oxygenated seven-membered ring ethers [346]; (20) formation of a seven-membered ring ether for total synthesis of rogioloxepane [347]; (21) formation of α,β-unsaturated seven-membered ring lactones (e.g. **110**) [348]; (22) formation of an eight-membered ring lactone [349]; (23) formation of nine-membered ring cyclic ethers [350]; (24) failed attempts to form a nine-membered ring cyclic ether using RCM [351]; (25) formation of a nine-membered ring cyclic ether (e.g. **112**) for obtusenyne total synthesis [352]; (26) synthesis of ten-membered ring lactones [353]; and (27) formation of a ten-membered ring lactone for total synthesis of microcarpalide [354] and herbarumin II [355,356]. Treatment of octaene **113** with Grubbs Catalyst I (**1**) led to predominantly compound **114**, while treatment with Grubbs Catalyst II (**2**) afforded predominantly compound **115** [357].

Heterocyclic compounds involving elements other than *N* and *O* were also constructed via the RCM reaction (Fig. 10). Examples include: (1) synthesis of cyclic phosphonates [358]; (2) synthesis of cyclic phosphine–borane complexes (e.g. **117**) [359]; (3) synthesis of cyclic sulfonamides [360]; (4) synthesis of cyclic sulfamides [361]; (5) synthesis of cyclic sulfonate esters (e.g. **118**) [362]; (6) synthesis of five-membered ring cyclic silanes [363]; (7) diastereoselective synthesis of cyclic siloxanes (e.g. **119**) from precursors containing diastereotopic propenyl groups [364]; (8) synthesis of cyclic siloxanes for total synthesis of mucocin [365]; (9) formation of cyclic siloxanes as a temporary tether to effect net cross metathesis [366]; (10) synthesis of bridged 1,1′-diphospha [4] ferrocenophanes (e.g. **120**) via RCM [367]; (11) synthesis of platinum complexes featuring *trans* chelating diphosphine ligands (e.g. **121**) [368]; and (12) synthesis of “insulated” butadiyne-bridged dirhenium complexes (e.g. **122**) through RCM of chelating octenylphosphine ligands on the different rhenium atoms [369].

Numerous examples of successful macrocyclic ring closure (formation of rings with ≥11 atoms) using the RCM reaction were reported in 2003 (Fig. 11), including: (1) synthesis of macrocyclic lactones [370]; (2) formation of macrocyclic lactones for total synthesis of salicylihalamide (**125**) [371,372], oximidine II [373], migrastatin [374], amphidinolides [375], myxovirescin analogs [376], cycloproparadicol (**126**) [377] including an example resulting a cyclic cobalt–alkyne complex [378], and epothilone analogs (e.g. **127**) [379–383]; (3) synthesis of a macrocyclic trilactone [384]; (4) synthesis of macrocyclic diamide-bridged crown ethers [385]; (5) synthesis of macrocycle-bridged peptides (e.g. **128**) [386–390]; (6) synthesis of a macrocycle-bridged thiazole derivative for total synthesis of mascothiazole [391]; (7) preparation of a macrocycle-bridged furan ring for total synthesis of anhydrochatancin [392]; (8) preparation of a macrocycle-bridged pyridine ring (e.g. **129**) for total synthesis of muscopyridine [393]; (9) formation of a macrocycle-fused mononucleotide derivative (e.g. **130**) [394]; (10) formation of a macrocycle-bridged dinucleotide derivative [395]; (11) preparation of a macrocyclic lactam–lactone for total synthesis of PF1163B [396]; (12) preparation of a macrocyclic lactam fused to a tricyclic ring system (e.g. **131**) [397]; (13) synthesis of a macrocyclic carbamate–lactam [398]; (14) formation of a

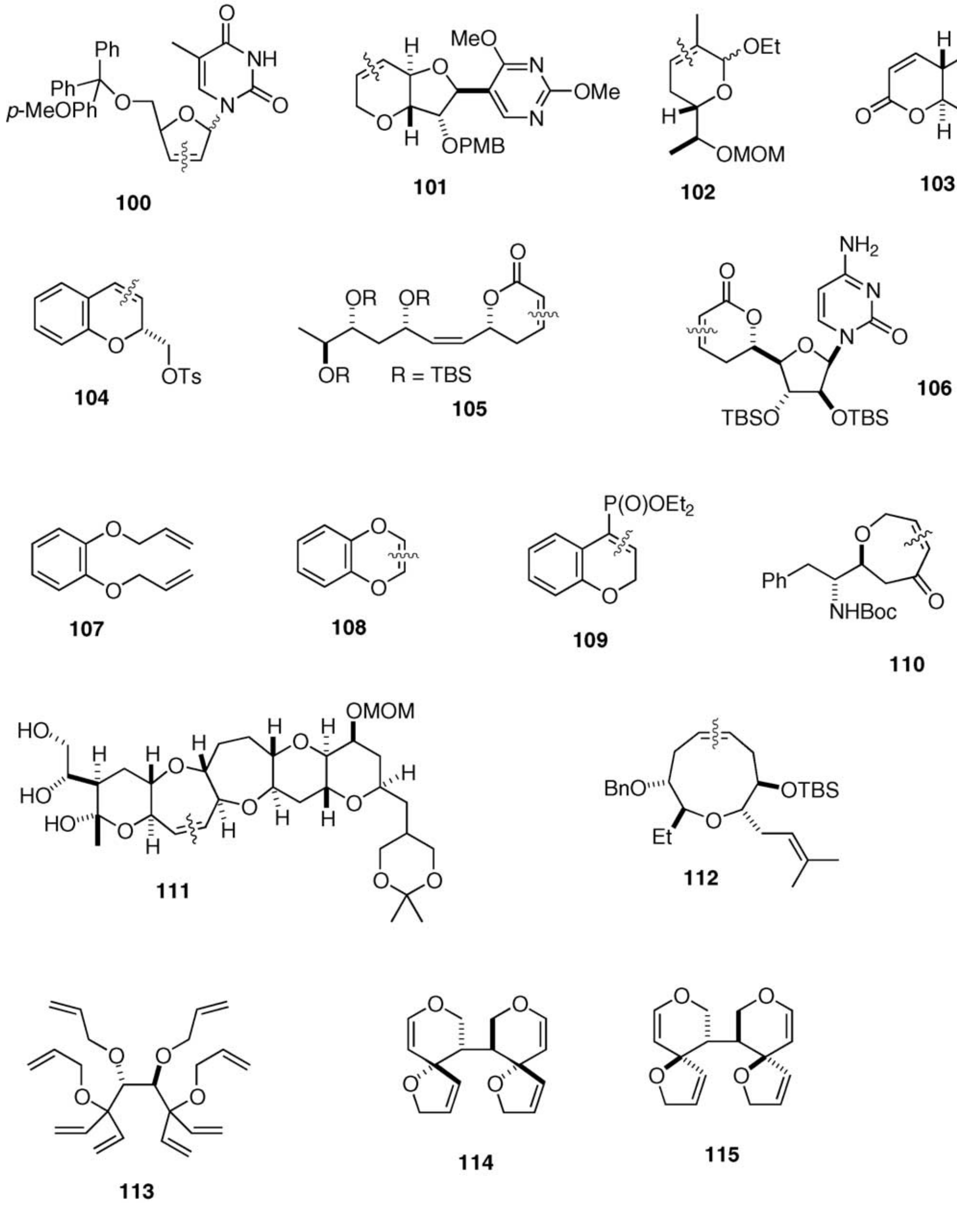


Fig. 9. Representative oxygen-heterocycles produced through an RCM reaction (bond constructed through RCM indicated).

macrocycle-bridged tetrasaccharide for woodrosin total synthesis [399]; (15) formation of macrocycle-bridged cellulose derivatives [400]; (16) synthesis of macrocycle bridged taxol analogs (e.g. **132**) [401]; (17) synthesis of lactone-bridged *p*-cyclophanes [402]; (18) formation of capped cyclodextrins [403]; (19) synthesis of polyether rotaxanes [404]; (20) formation of macrocyclic catenanes [405–408]; (21) closure of dendrimers to organic nanotubes [409]; (22) cyclization of remote vinyl groups attached to calixarene dimmers [410]; (23) macrocycle-bridged ruthenium-bipyridine complexes [411]; (24) macrocycle-bridged triplatinum complexes (e.g. **133**) [412,413]; (25) capping of zinc porphyrins bound to a gold nanocluster [414]; and (26) failure to close an 11-membered ring lactone for preparation of an eleutherobin analog [415].

### *2.2.6. Alkene metathesis involving alkyne components*

Several examples of the synthesis of conjugated dienes through the intramolecular (enyne RCM) and intermolecular (enyne CM) metathesis of enynes (see Scheme 1) were reported in 2003. Examples of intermolecular enyne metathesis reactions (Fig. 12) include: (1) formation of functionalized dienes (e.g. **135**) through metathesis of terminal alkynes and enol ethers or enol acetates [416,417] and (2) E-selective metathesis of terminal alkynes and monosubstituted alkenes [418]. Examples of intramolecular enyne metathesis include: (1) formation of highly oxygenated six-membered ring carbocycles [419]; (2) synthesis of butadienyl-substituted cycloalkenes (e.g. **136**) through intramolecular metathesis of a conjugated enyne and a monosubstituted alkene [420]; (3) synthesis of six-membered ring

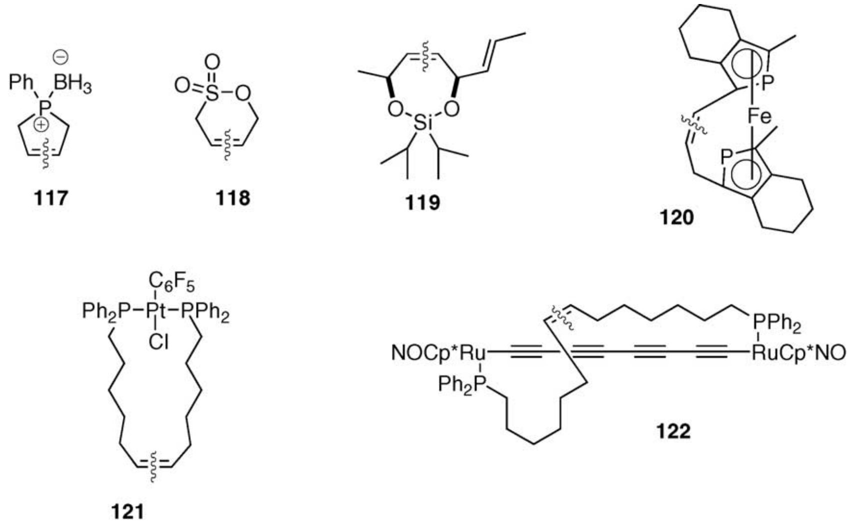


Fig. 10. Representative examples of other heterocycles prepared via the RCM reaction (bond constructed through RCM indicated).

cyclic amide-dienes (e.g. **137**) [421]; (4) use of Grubbs Catalyst II (**2**) and noncarbene complex catalysts for intramolecular enyne metathesis of *N*-allyl-*N*-propargyl-*N*-tosylamines [422]; (5) synthesis of cyclic siloxane-dienes (e.g. **138**) using a noncarbene–ruthenium catalyst [423]; (6) synthesis of cyclic hydroxylamine derivatives (*O* and *N* part of newly-formed ring) [424]; (7) formation of seven-membered ring cyclic ethers featuring epoxide and conjugated diene functionalities (e.g. **139**) [425]; (8) use of intramolecular enyne metathesis to form macrocyclic dilactones (e.g. **140**) [426]; and (9) tandem intramolecular enyne metathesis—cross metathesis reactions [427,428].

Some more complex examples of enyne metathesis are depicted in Scheme 7. The synthesis of cyclic ethers (e.g. **142–144**) from diene–alkynes (e.g. **141**) could be controlled through alkene substitution pattern [429]. A novel ring expansion process (e.g. formation of **148**) was observed when cyclic alkenes (e.g. **145**) were treated with Grubbs Catalyst II (**2**) in the presence of terminal alkynes (e.g. **146**) [430]. A mechanism involving initial ring opening metathesis, followed by alkyne insertion of the intermediate carbene complex, followed by intramolecular metathesis was proposed. In order to account for the relatively high yield (the yield is higher than the anticipated E:Z selectivity) of the process, a second source of the observed product involving metathesis of an additional mole of cyclopentene from intermediate **147** was suggested. When enyne **149** was treated with Grubbs Catalyst II (**2**) in the presence of ethylene, tandem ethylene-CM and enyne metathesis (resulting in triene **150**) followed by intramolecular Diels–Alder reaction resulting in **151** was observed [431]. A tandem intramolecular enyne–metathesis–RCM process was observed when dienyne **152** was treated with Grubbs Catalyst I (**1**), resulting the tricyclic amine **153** [432]. Amine **153** was an intermediate in the total synthesis of erythravine. Tandem enyne metathesis, ROM–RCM was demonstrated for a dialkyne–norbornene derivative [433].

Polymerization via sequential intramolecular enyne metathesis occurred upon treatment of dialkyne **154** (Scheme 8) with $MoCl_4/Bu_4Sn$/quinuclidine mixtures [434]. Only the five-membered ring containing polymer **157** was observed and not the six-membered ring analog **158**.

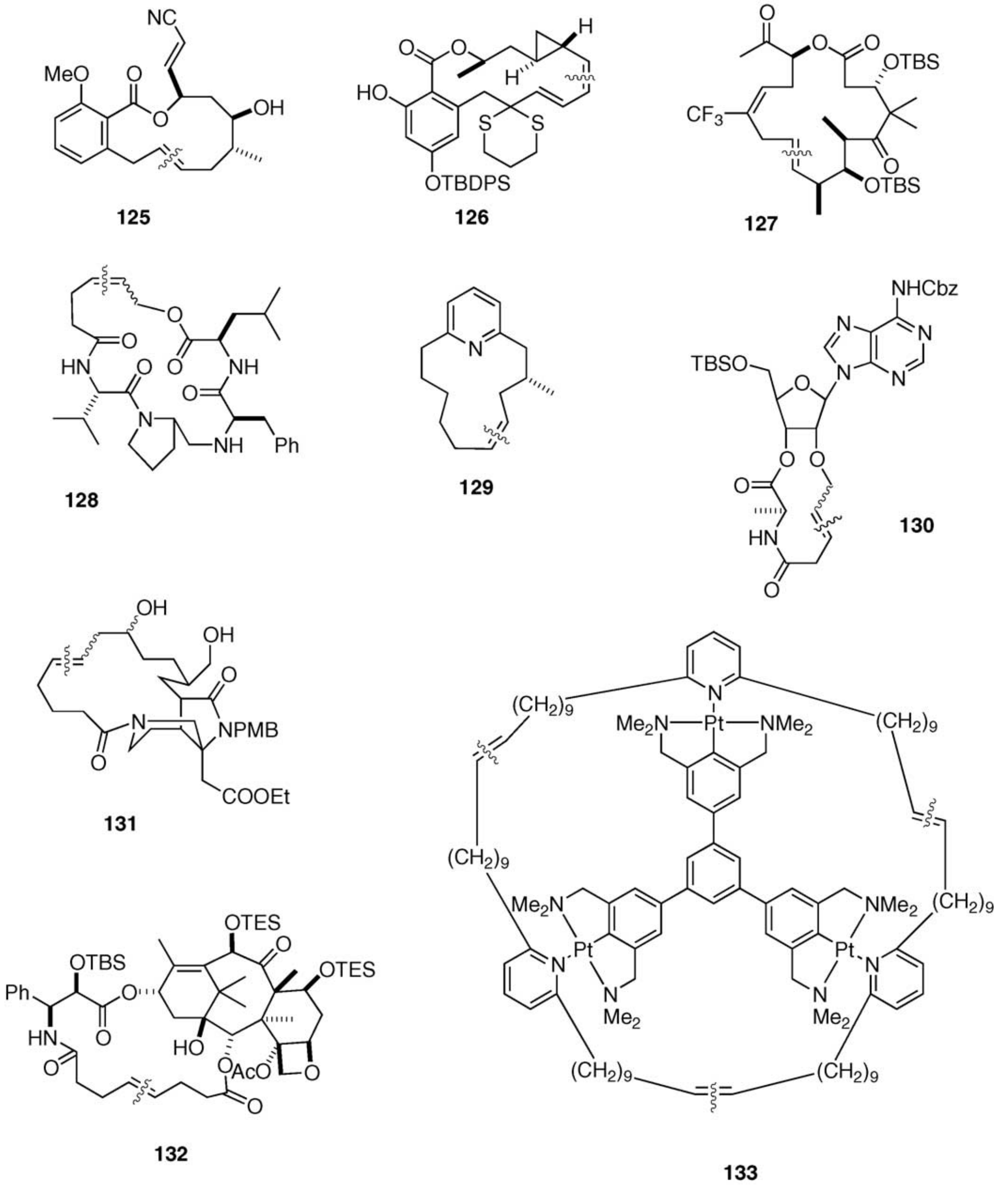
### *2.2.7. Non-metathesis reaction processes involving the Grubbs and related catalysts*

Several publications in 2003 report on processes unrelated to metathesis that are initiated by ruthenium–carbene complex catalysts **1**–**2** and structurally-related carbene complexes.

Several examples employing ruthenium–carbene complexes to initiate free-radical reactions were reported in 2003 (Scheme 9). Examples include: (1) use of derivatives of the Grubbs Catalyst (e.g. **162**) to promote the Kharasch reaction [435] and (2) a stereoselective intramolecular variant of the Kharasch reaction [436].

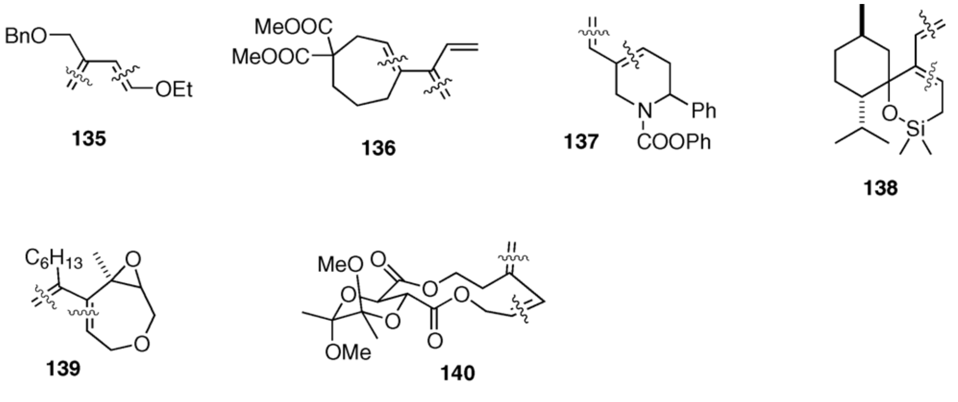
The alcohol-induced decomposition of Grubbs Catalyst I (**1**, Scheme 10) was studied [437]. Reaction with methanol resulted in the formation of ruthenium hydride complex **163**. The depicted mechanism was proposed and supported by labeling studies using $CH_3CH_2OD$, the Ru=CDPh analog of Grubbs Catalyst I, and carbon-13 labeled ethanol. Numerous organic byproducts in addition to toluene were observed. Reaction with water led to the phenylruthenium complex **167**. The use of the ruthenium hydride complex as an olefin isomerization catalyst was studied. Formation of the hydride **163** was suggested as a possible source of alkene isomerization products during metathesis reactions. Related studies were reported for Grubbs Catalyst II (**2**) [438].

Several studies utilizing ruthenium–carbene complexes as alkene isomerization catalysts were reported in 2003 (Scheme 11). Grubbs Catalyst I (**1**) was useful for the deallylation of amines [439]. Treatment of allylamines (e.g. **170**) with Grubbs Catalyst I at 110 °C induces isomerization to the enamine (e.g. **171**), which is then cleaved to afford the free



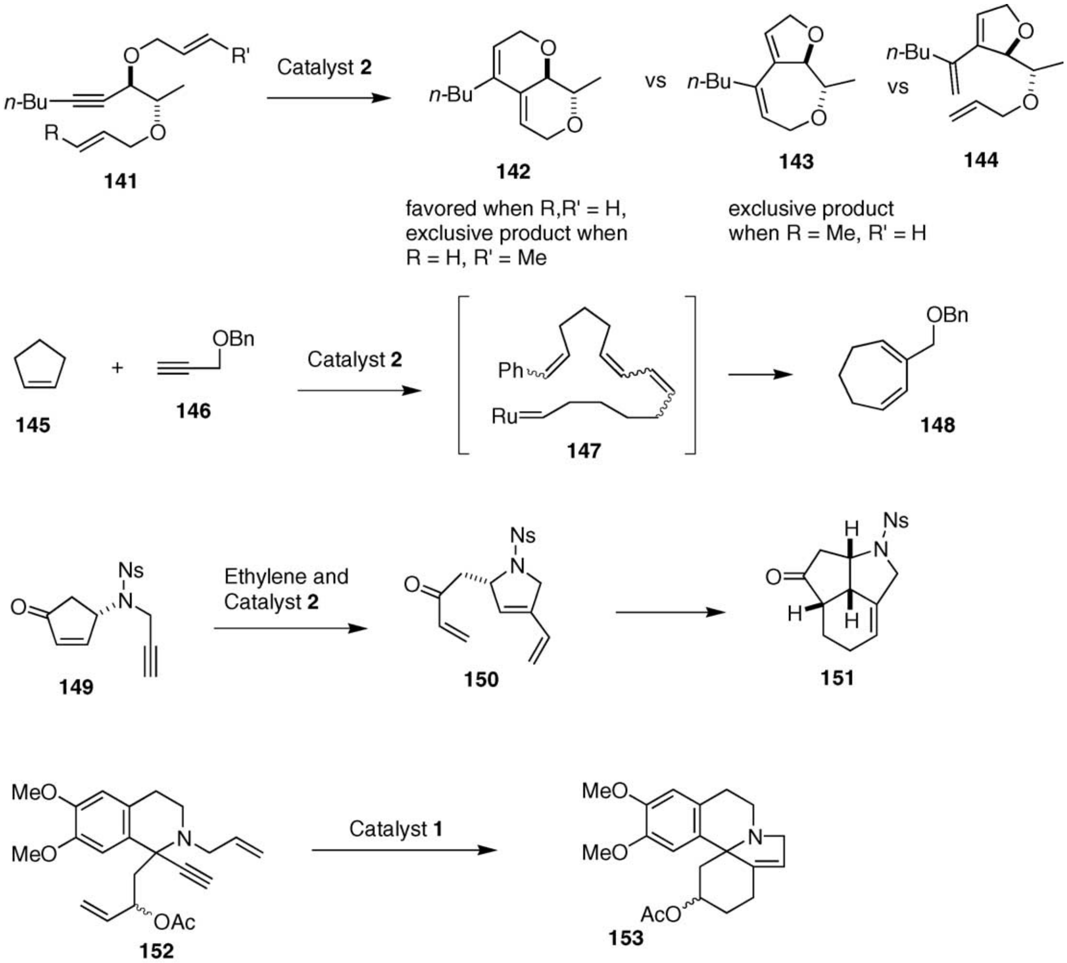
**125** **126** **127** **128** **129** **130** **131** **132** **133**

Fig. 11. Representative macrocycles (ring size > 10) prepared using the RCM reaction (bond constructed through RCM indicated).

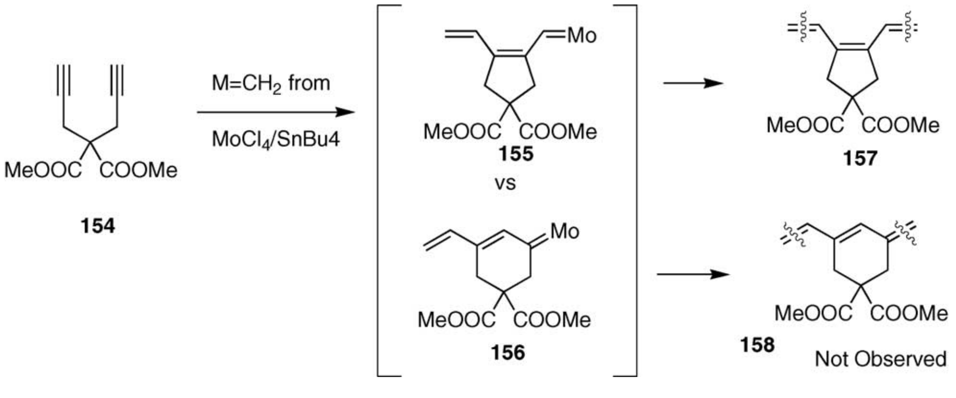


**135** **136** **137** **138** **139** **140**

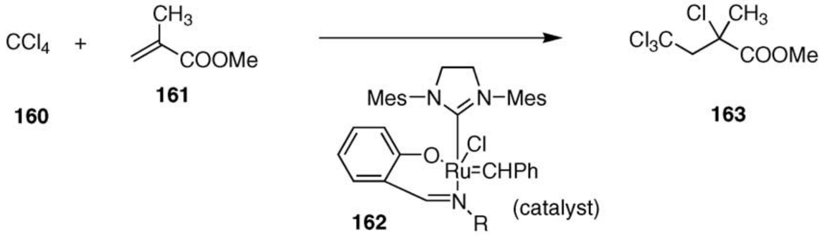
Fig. 12. Representative conjugated dienes prepared using an enyne metathesis reaction (bonds constructed through RCM indicated).



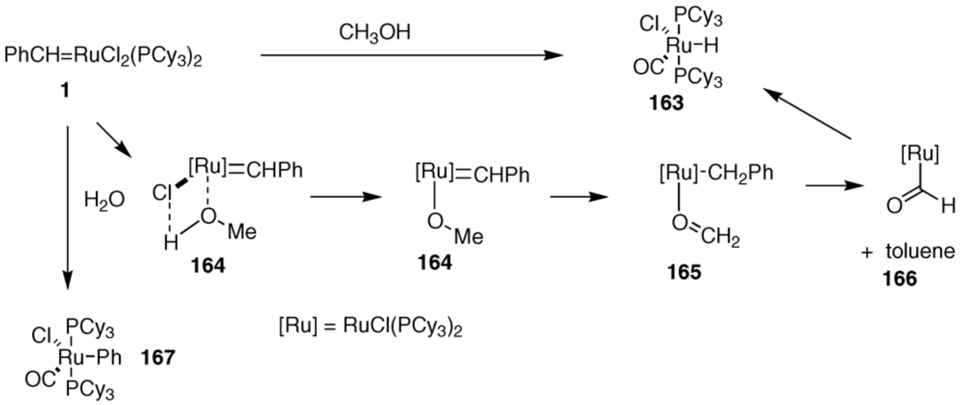
Scheme 7.



Scheme 8.

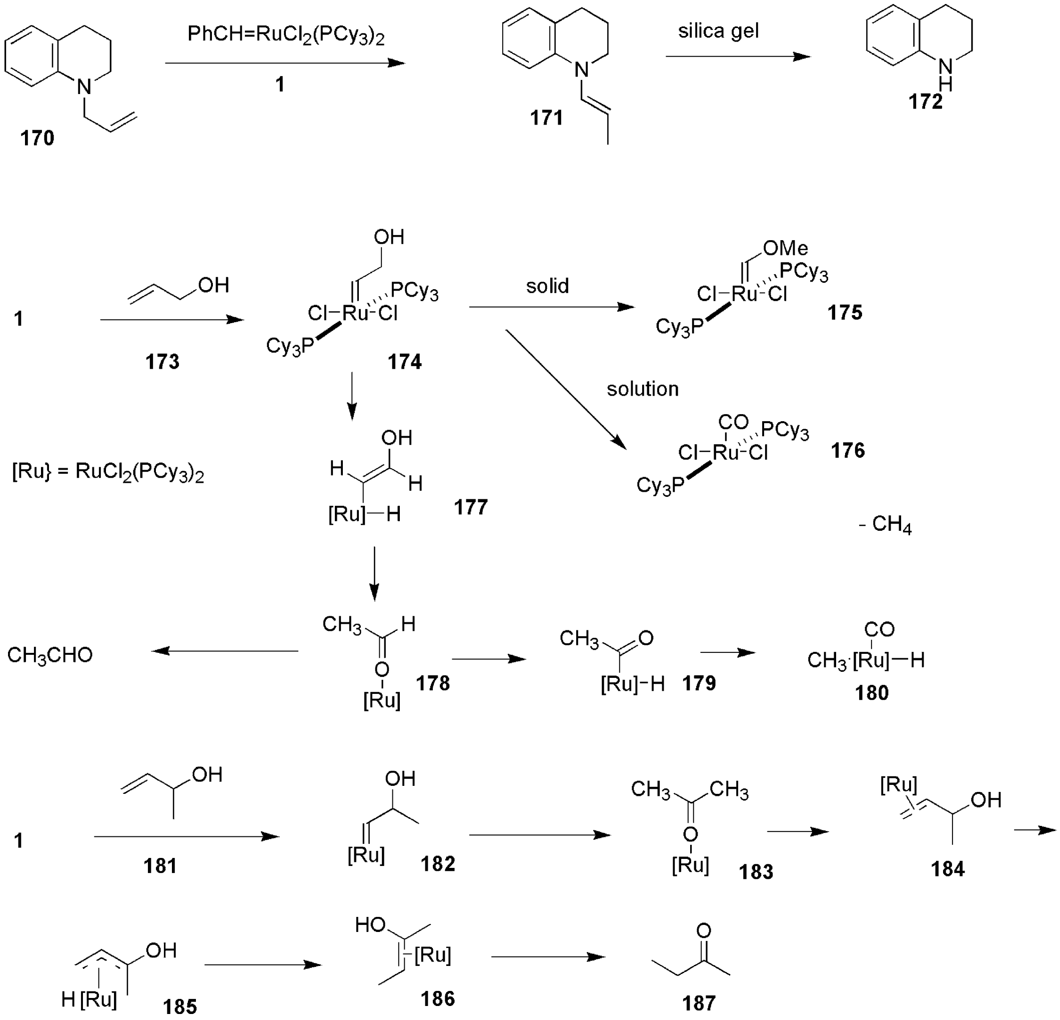


Scheme 9.

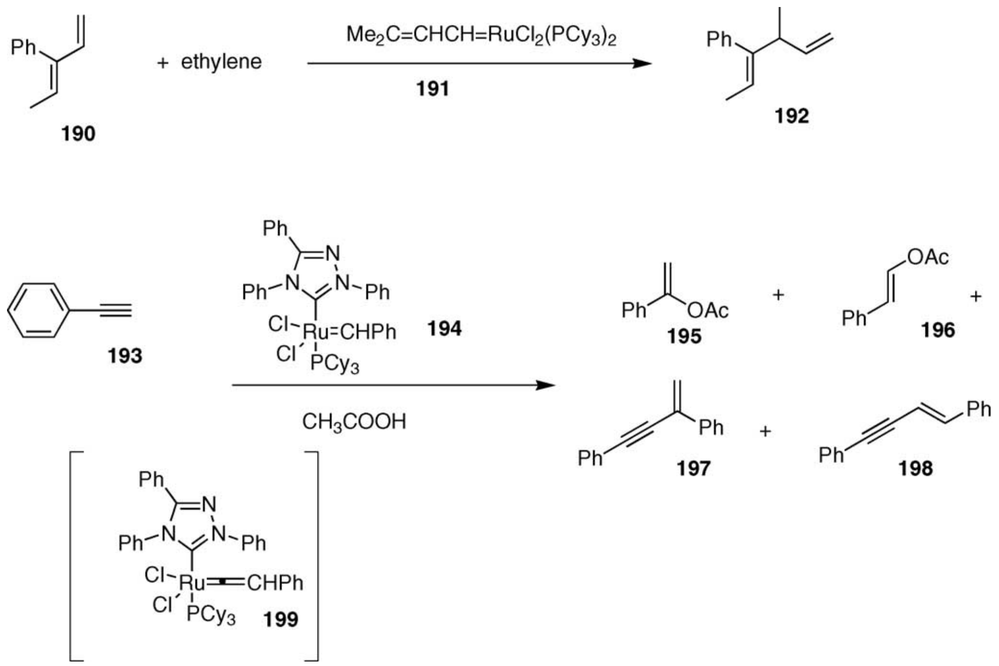


Scheme 10.

amine. A study of the reaction of Grubbs Catalyst I with allylic alcohols was reported [440]. Reaction with allyl alcohol (**173**) or 3-butene-2-ol (**181**) led to the isomerization products propionaldehyde or 2-butanone and a noncarbene–ruthenium complex (**176**), in addition to acetaldehyde. Initially, the metathesis product **174** was produced, which decomposed to ruthenium complex **175** in the solid state and to carbonyl-ruthenium complex **176** in solution. The mechanism depicted in Scheme 11 was proposed for formation of the carbonyl complex. An alternative mechanism was proposed for the isomerization of 3-buten-2-ol, involving a net hydride shift and decomplexation of the enol ligand from intermediate **186**.



Scheme 11.



Scheme 12.

Additional non-metathesis reactions exhibited by the Grubbs Catalysts and related complexes reported in 2003 are depicted in Scheme 12 and include: (1) use of ruthenium–carbene complex **191** as catalyst for hydrovinylation of dienes (e.g. **190**) [441]; (2) use of a Grubbs Catalyst II analog (**194**) to promote the addition of carboxylic acids to triple bonds and alkyne dimerization (ruthenium vinylidene **199** is a potential intermediate in these reactions) [442]; and (3) the use of Grubbs Catalyst I (**1**) and alkoxycarbene complex analogs as catalyst for the hydrogenation of ROMP polymers [443].

## *2.3. Individual carbene or alkylidene complexes classified according to metal*

One manuscript describes the bonding modes in $CH_2$ complexes for a variety of transition metals [444] and cannot be assigned to a specific metal.

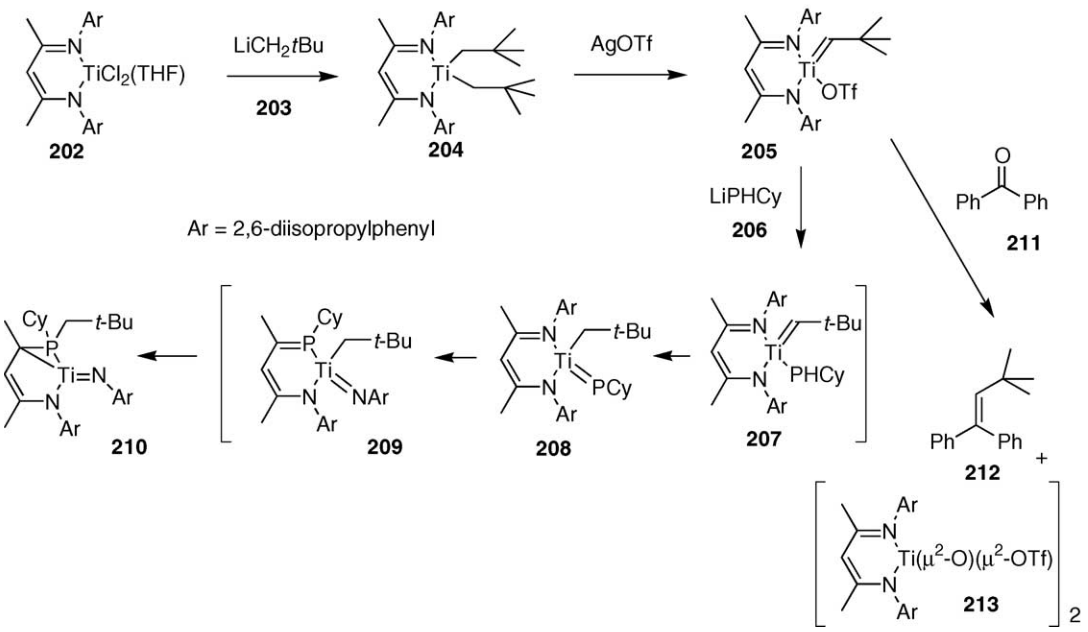
### *2.3.1. Group IV metal–carbene complexes*

Both isolable titanium–carbene complexes and reactions that involve titanium alkylidene complexes are covered in this section.

A titanium–carbene complex (**205**, Scheme 13) was prepared through alkylation of titanium dichloride **202** with neopentyllithium followed by treatment with silver triflate [445]. Treatment of the carbene complex with benzophenone led to the carbonyl olefination product **212** and dimeric titanium complex **213**. Reaction with phosphide **206** led to the imine complex **210** [446]. A mechanism involving triflate displacement, followed by P–H activation and H-transfer to afford neopentyl complex **208**, followed by N–P exchange was proposed for the formation of **210**. The mesityl analog of phosphide **206** led to a stable analog of phosphinidene complex **208** [447]. Silica-bound neopentylidene complexes of zirconium and titanium were similarly prepared through thermolysis of silica-bound bis(neopentyl) complexes [448]. The zirconium complex afforded 3,3-dimethyl-1-butene upon reaction with styrene, and a stable titanium–alkene complex was formed using the titanium analog.

Titanium carbene complexes featuring bridges to the Cp ligand (e.g. **217** and **218**, Scheme 14) were prepared through reaction of titanocene dichloride with bis(neopentyl)magnesium [449]. The reaction initially affords the Cp-bridged complex **217**, which converts to the alkylidene/Cp-bridged complex **218** upon thermolysis in the presence of trimethylphosphine. A C–D activation product, **220**, was formed when complex **218** was reacted with benzene-$d_6$.

Several examples employing in situ-generated titanium–carbene complexes in synthetic organic chemistry were demonstrated in 2003; representative examples are depicted in Scheme 15. Titanium-induced carbonyl olefination using the Tebbe reagent (**225**) was demonstrated for various allylic esters (e.g. **226**) [450]. Several examples of the generation of titanium alkylidene intermediates (e.g. **230**) from dithioacetals (e.g. **228**) and low-valent titanium complexes (e.g. **229**) were reported in 2003. The use of dithioacetal-derived titanium carbene complexes for solid-phase ketone/benzofuran synthesis was reported [451,452]. Treatment of polymer-bound esters (e.g. **231**) with titanium carbene complex intermediate **230** afforded polymer-bound enol ethers (e.g. **232**) which hydrolyzed to afford either simple ketones (e.g. **234**) benzofurans (e.g.



Scheme 13.

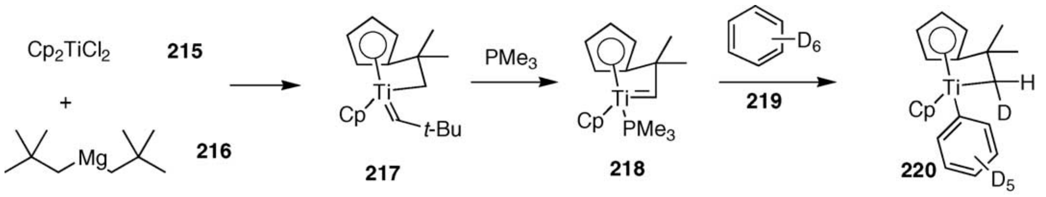
**235**). An arylborane functional group was compatible with all of these reaction processes. Thioacetal-generated carbene complexes were similarly employed for the carbonyl olefination of *N*-phenylamide derivatives [453]. An intramolecular variant of this olefination process was demonstrated in a complex molecule for formation of a six-membered ring present in marine toxin ciguatoxin [454]. Generation of titanium carbene complex intermediates (e.g. **237**) through reaction of titanium complex **229** with chloromethyl ethers (e.g. **236**) was also demonstrated [455]. If this reaction was conducted in the presence of ketones, enol ethers (e.g. **240**) were produced. Two equivalents of the titanium reagent were required in this process, and the corresponding methyl ether **238** was obtained as a byproduct. Oxatitanacyclobutane intermediates in the titanium-based carbonyl olefination using $Cp_2TiMe_2$ were detected by chemical ionization mass spectrometry [456].

Theoretical studies of the reaction of titanium–vinylidene complexes with multiply-bonded organic species were reported [457]. Nonpolarized multiply-bonded species (e.g. alkenes, alkynes) were proposed to undergo direct cycloaddition to the carbon–titanium double bond of $Cp_2Ti{=}C{=}CH_2$. Polarized species (e.g. $CO_2$, nitriles) were proposed to coordinate to titanium prior to cycloaddition.

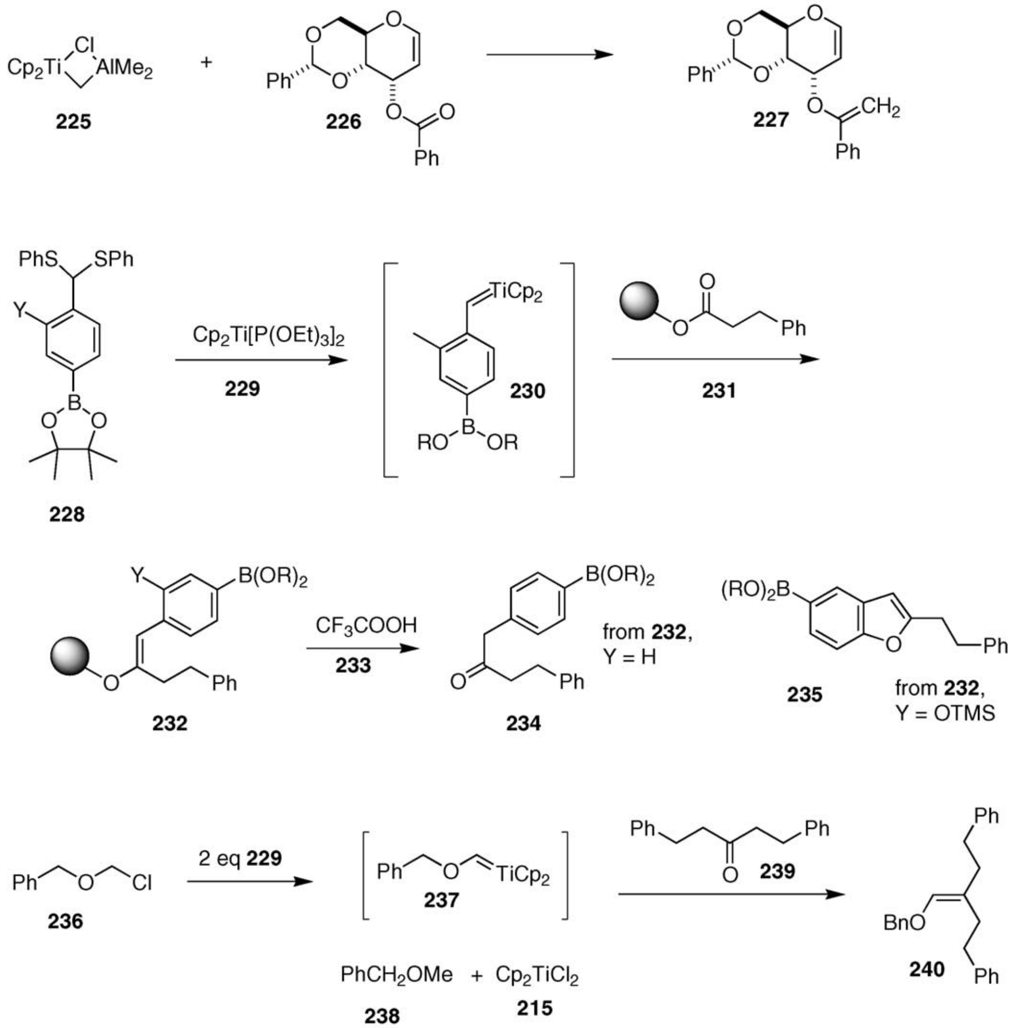
### 2.3.2. *Group V metal–carbene complexes*

The synthesis and reactivity of tantalum–carbene complex **244** (Scheme 16) was reported [458]. The complex was prepared directly from the reaction of diene complex **243** with dibenzylmagnesium. Similar reactions had previously been reported to provide dibenzyltantalum species. Reaction of a variety of organic compounds with carbene complex **244** was examined. Addition products (**245** and **246**) were obtained from *p*-methoxyaniline or methanol. Reaction with alkenes resulted in [2 + 2]-cycloaddition products (e.g. **247**), however carbene complex **244** displayed low activity for the ROMP polymerization of norbornene. The insertion product **248** was obtained from the reaction with 2,2-dimethylpropionitrile.

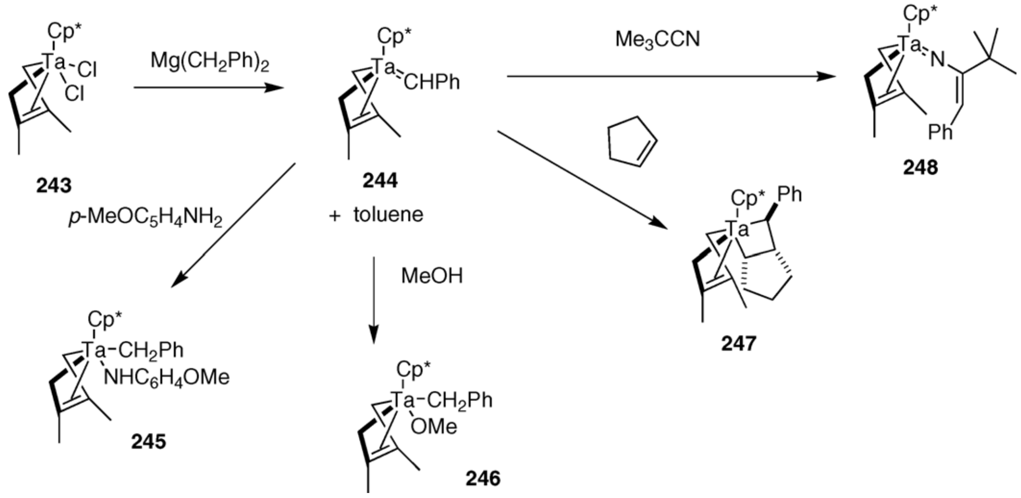
The tantalum carbene complex **252** (Scheme 17) featuring an agostic C–H interaction was prepared by reaction of ditantalum species **251** with 3,3-diphenylcyclopropene (**250**) [459]. Reduction of this species led to the chelated carbene complex **253**. A similar reduction of the tantalum–carbene complex **254** resulted in the formation of bis(carbene)ditantalum complex **255** [460]. Treatment of tantalum carbene complex **256** with tris(pentafluorophenyl)borane (**257**) led to the agostic alkyl complex **258** [461]. Isocyanide insertion occurred selectively at the borylated group to afford the $\eta^2$-iminoacyl complex **260**.



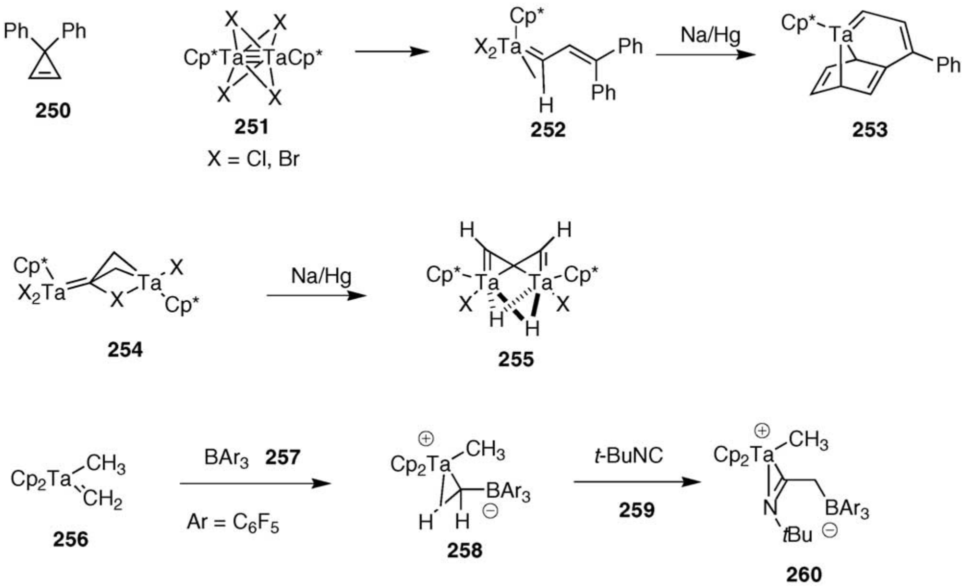
Scheme 14.



Scheme 15.



Scheme 16.



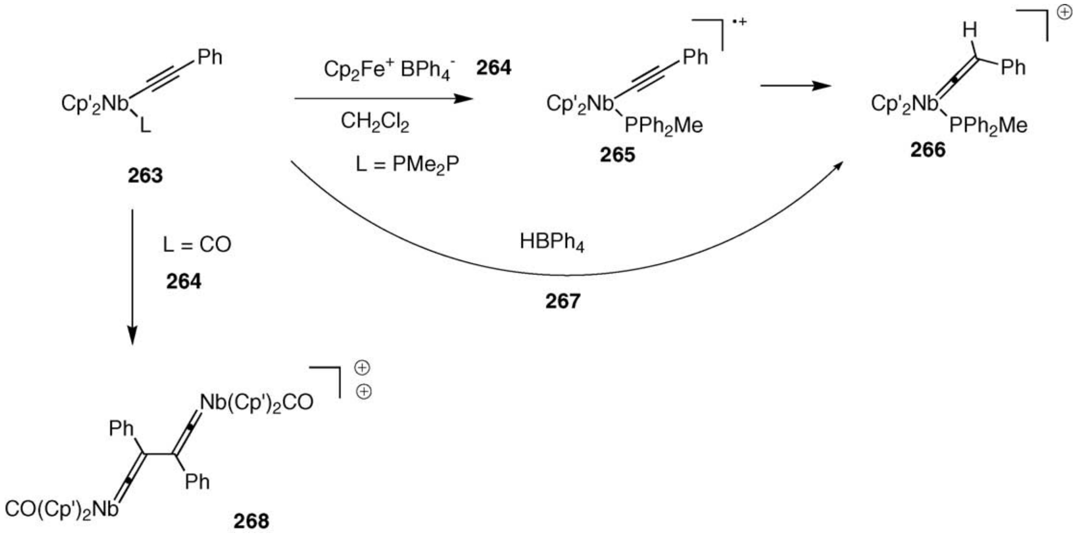
Scheme 17.

The synthesis of niobium–vinylidene complexes (e.g. **266**, **268**, Scheme 18) was reported [462]. Oxidation of alkynylniobium complex **263** (L = $PMe_2Ph$) led to radical anion intermediate **265**, which afforded the vinylidene complex **266** after hydrogen atom abstraction from the solvent. The carbonyl analog (**263**, L = CO) afforded the dicationic dimeric complex **268** upon oxidation by ferrocenium ion.

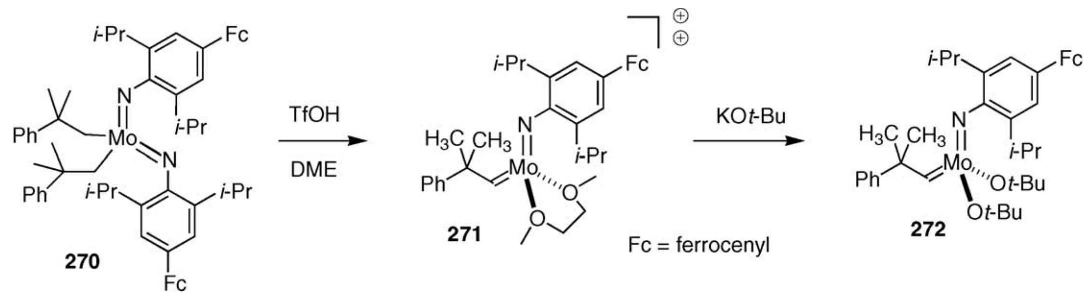
### 2.3.3. *Group VI metal–carbene complexes (further classified according to structure and reaction type)*

*2.3.3.1. Schrock-type carbene complexes.* A significant portion of this subject material has already been presented in the alkene metathesis section; the Schrock Catalyst (**3**) belongs to this class. Ferrocenyl derivatives of the Schrock Catalyst (e.g. **272**, Scheme 19) were prepared, however they were too unstable for evaluation as metathesis catalysts [463]. A study of the equilibration of alkoxy ligands in analogs of the Schrock carbene complex was reported [464]. Determination of the rate of equilibration and position of equilibrium were the focus of these studies.

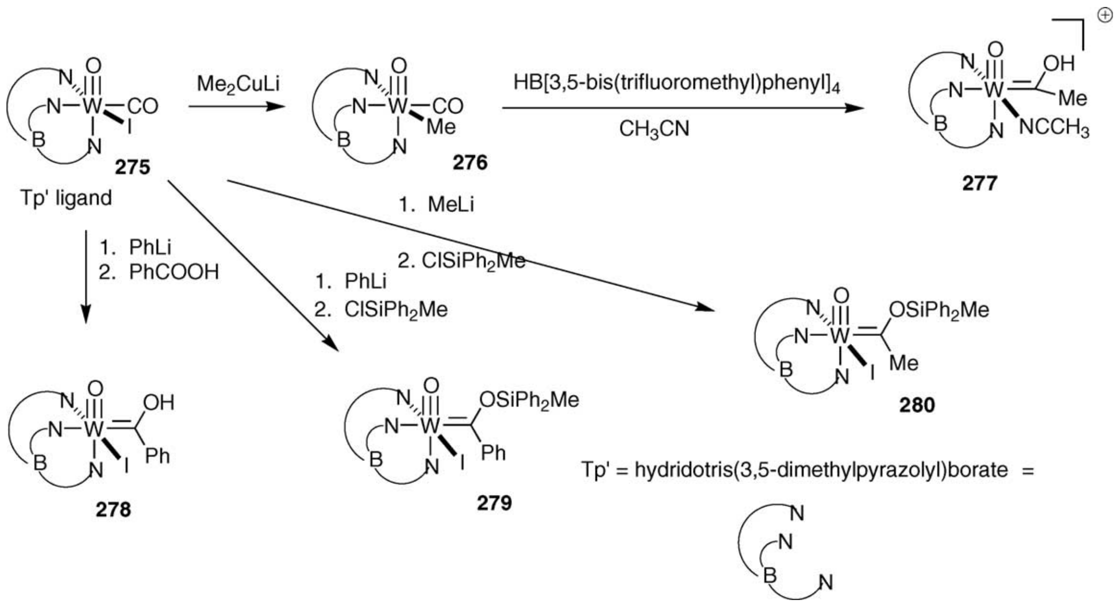
Tungsten(IV) carbene complexes (e.g. **277**–**280**, Scheme 20) were prepared through the reaction of iodo–tungsten complex **275** with organolithium reagents followed by treatment with an electrophile [465]. Formation of the methyl complex **276** was observed upon treatment with lithium dimethylcuprate. Protonation of **276** in neat acetonitrile led to hydroxycarbene complex **277**. Methylation of **275** followed by silylation led to the silyloxycarbene complex **280**. Related carbene complexes were prepared from phenyllithium.



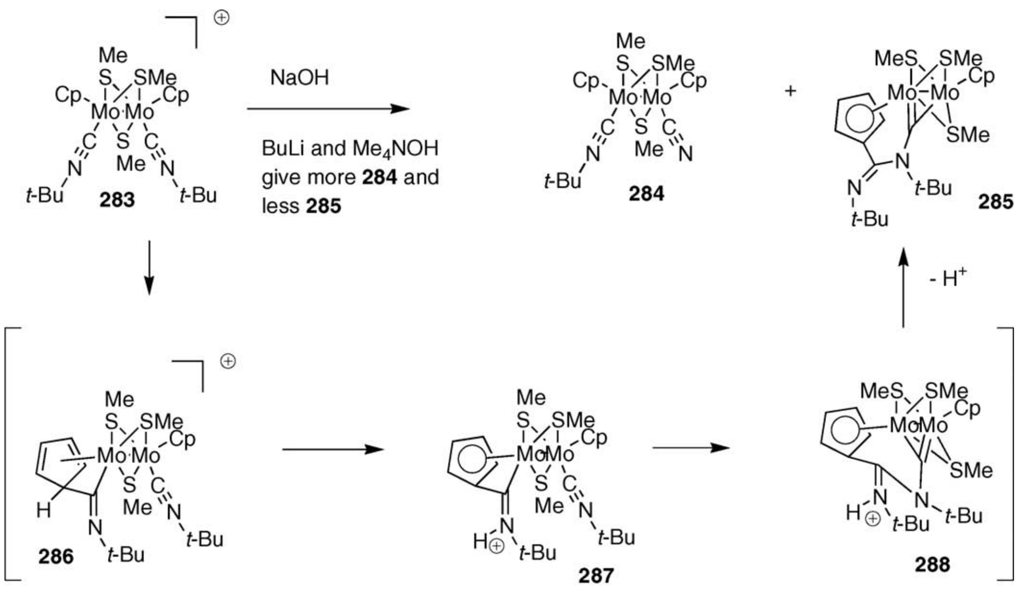
Scheme 18.



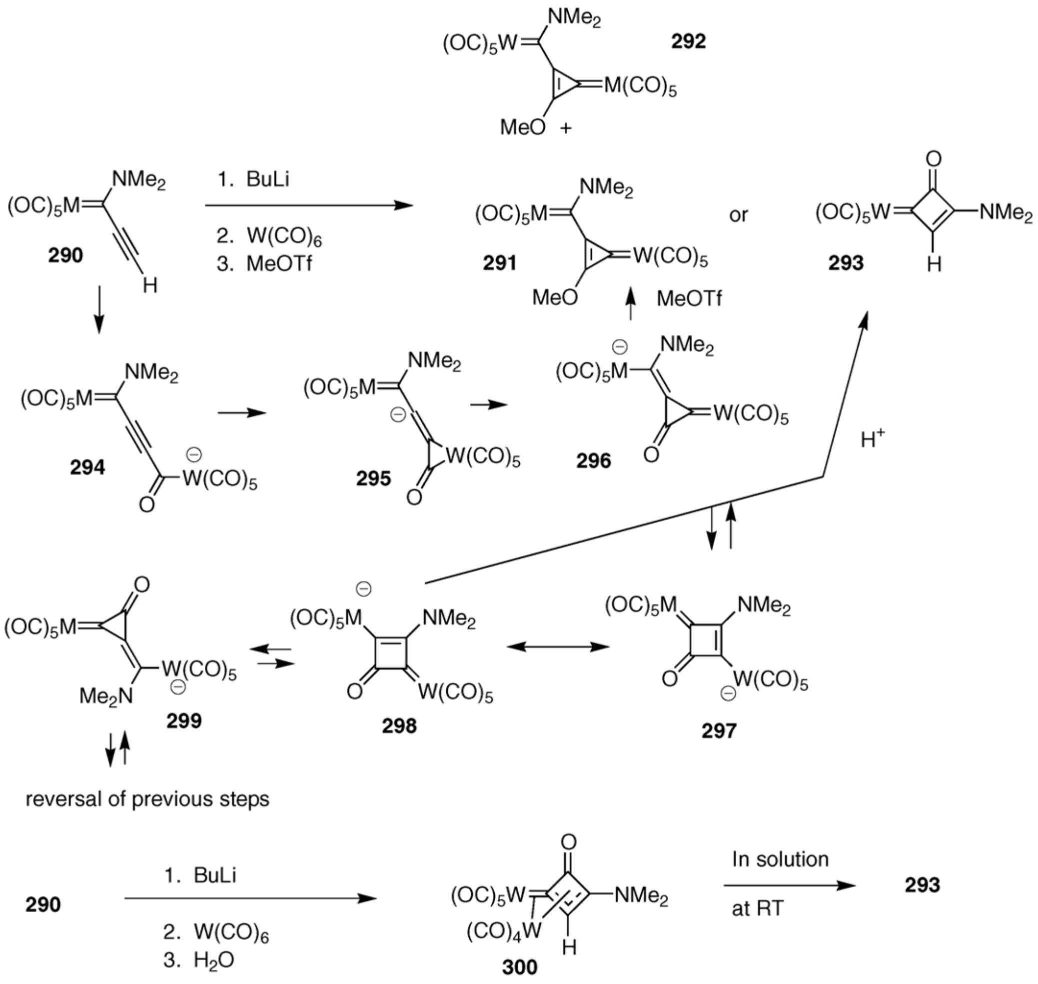
Scheme 19.



Scheme 20.



Scheme 21.



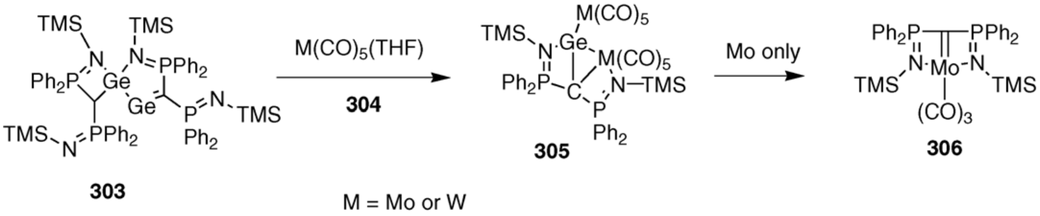
Scheme 22.

Molybdenum carbene complex **285** (Scheme 21) was produced upon treatment of diisocyanide–dimolybdenum complex **283** with base [466]. Optimal formation of **285** was observed using NaOH as the base; cyanide complex **284** typically accompanied carbene complex **285**. The proposed mechanism involves migration of the isonitrile ligand to the Cp ligand followed by 1,3-H shift to afford Cp complex **287**, followed by a 1,3-shift of the isonitrile ligand to afford bridging carbyne complex **288**, followed by deprotonation to afford carbene complex **285**. Related sulfur-rich dimolybdenum–carbene complexes were produced through reaction sodium azide with bridging vinylidene–dimolybdenum complexes [467].

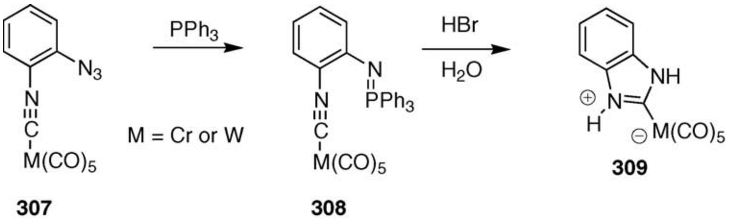
Chromium(III)–carbene complexes have been suggested as intermediates in the conversion of alkenes to iodocyclopropanes via the reaction of alkenes with iodoform, chromium(II) chloride and tetraethyl ethylenediamine [468].

*2.3.3.2. Publications focusing on synthesis, formation, or physical properties 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. Emphasis in this section is on the newer synthetic routes to these complexes. Two of the papers cited in the metathesis section concern reactions that occur at remote alkene substituents in group VI metal carbene complexes [182,231]. This can be regarded as an additional synthetic route to this class of compounds. A crystal structure was reported for a chromium carbene complex [469] and a molybdenum carbene complex [470].

Tungsten–cyclobutenylidene complexes (e.g. **293**, Scheme 22) were prepared through deprotonation of the ethynylcarbene complex **290** followed by reaction with a group VI metal carbonyl, followed by methyl triflate [471]. The reaction had to be performed in THF; the product in ether were the bimetallic cyclopropenylidene complexes **291** and **292**. The mechanism depicted in Scheme 22 was proposed to explain the formation of **291**–**293**. A critical step in the formation of cyclobutenylidene complexes is the ring expansion of cyclpropenone complex **296** to cyclobutenylidene complex **297**/**298**. Methyl triflate apparently serves as a source of protons in the conversion of



Scheme 23.



Scheme 24.

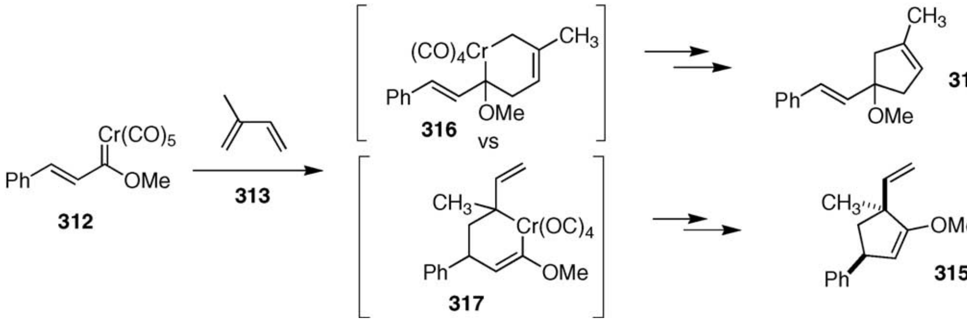
intermediate **297**/**298** to cyclobutenylidene product **293**. Cyclobutenylidene complex **297**/**298** is also an important intermediate for the formation of the metal transposition product **292**. The bimetallic complex **300** was formed if water was used as the quench, and this complex slowly decomposed to the simple cyclobutenylidene complex **293** in solution.

The preparation of molybdenum carbene complexes featuring pincer ligands was reported [472]. Treatment of the germanium species **303** (Scheme 23) with molybdenum hexacarbonyl led to dimolybdenum species **305**, which upon further reaction affords the carbene complex **306** as a mixture of *fac* and *mer* isomers. Reaction with $(CO)_5W(THF)$ led to the complex analogous to **305** and did not afford a carbene complex.

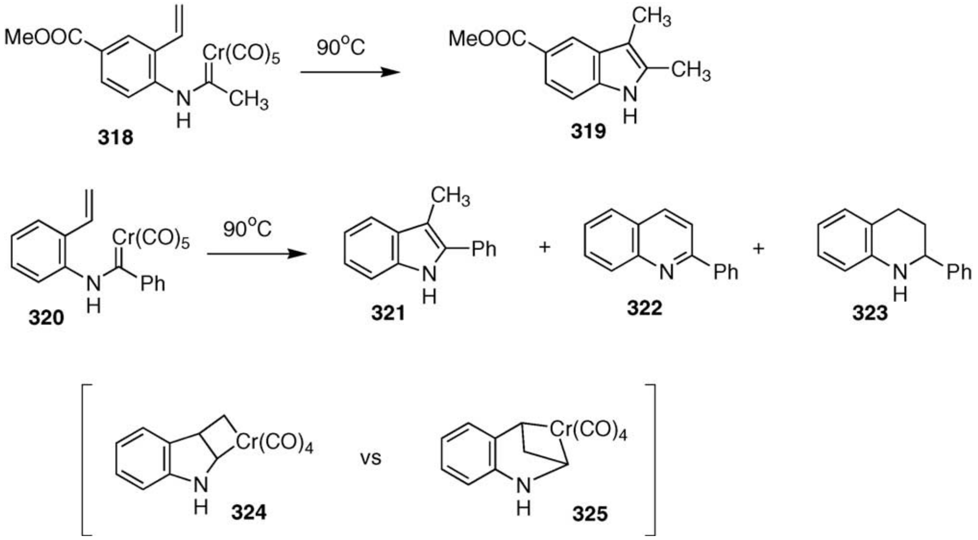
The preparation of *N*-heterocyclic carbene–$Cr(CO)_5$ complexes (and tungsten analogs) (e.g. **309**, Scheme 24) was reported [473]. The synthesis involves initial preparation of the *o*-azidophenyl isocyanide complex (**307**), followed by closure to the benzimidazolylidene complex by treatment with triphenylphosphine and aqueous HBr. A similar process was reported for azidomethylphenyl isocyanide complexes [474]. Preparation of related carbene complexes by cyclization of phenolic isocyanide–tungsten complexes was also reported [475]. Attempts to prepare Fischer carbene–group VI metal complexes from acyclic diaminocarbenes and $M(CO)_5$ sources were reported [476]. Reaction of bis(diisopropylamino)carbene and $(Et_2O)Cr(CO)_5$ afforded $\eta^2$-[bis(diisopropylamino)carbene]$Cr(CO)_4$, which converted to the $\eta^1$-(carbene)$Cr(CO)_5$ complex upon treatment with CO. The analogous tungsten and molybdenum $M(CO)_5$ complexes were generated in a single reaction.

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

Coupling of α,β-unsaturated carbene–chromium complexes (e.g. **312**, Scheme 25) with electroneutral 1,3-dienes (e.g. isoprene, **313**) was reported [477]. Cyclopentane derivatives **314** (a [4 + 1] adduct) and **315** (a [3 + 2] adduct) were obtained from the heating of carbene complex **312** in the presence of excess isoprene. The distribution was solvent and temperature dependent; however exclusive formation of **314**



Scheme 25.

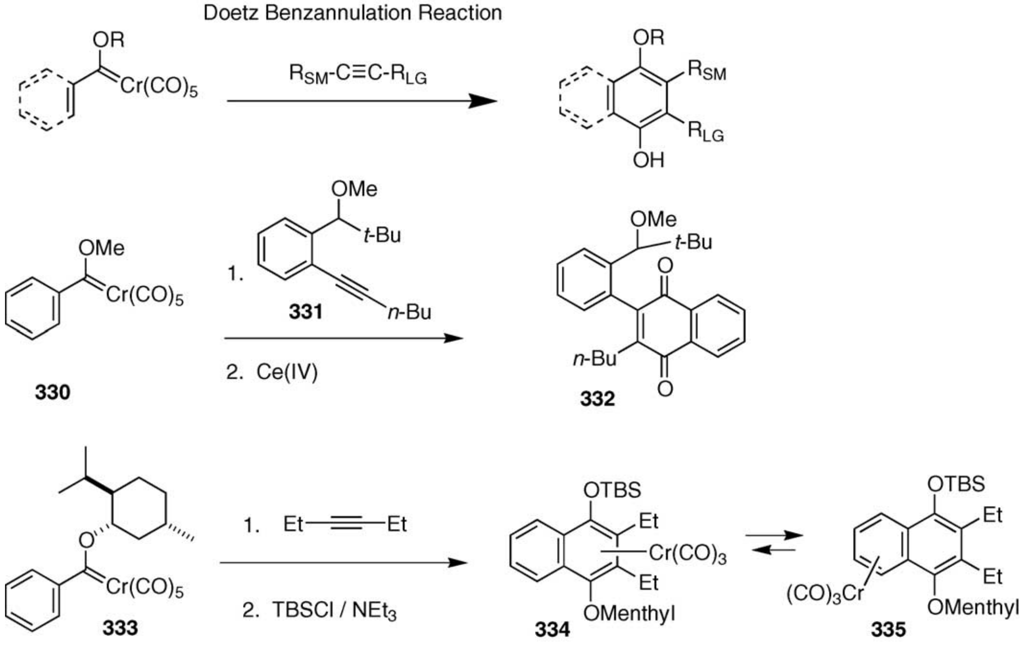


Scheme 26.

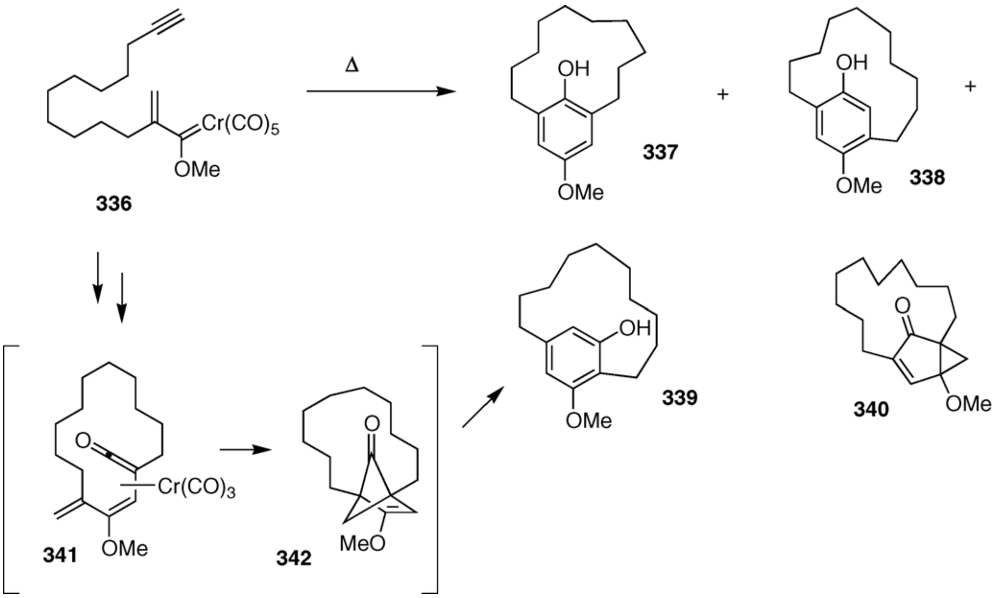
was observed in THF at 120 °C while **315** was the exclusive product from the reaction conducted at 90 °C in toluene. The [3 + 2]-adduct was obtained exclusively from the analogous tungsten carbene complexes. The proposed mechanism involves a metalla-Diels–Alder reaction followed by reductive elimination. The cycloaddition mode is determined by whether the metalla-Diels–Alder reaction utilizes the carbene complex as the 2π-component (affording intermediate **316**) or the 4π-component (affording intermediate **317**).

Thermolysis of a variety of *o*-alkenylphenylaminocarbene complexes (e.g. **318** and **320**, Scheme 26) was reported [478]. These reactions proceed to form either indole or quinoline derivatives. The reaction pathway was highly substrate dependent. Formation of indole versus isoquinoline substrates was correlated with the regiochemistry in an early event in the proposed mechanistic pathway, [2 + 2]-cycloaddition of the carbene complex and alkene resulting in regioisomeric metallacyclobutenes of general structures **324** or **325**.

*2.3.3.4. Reaction of group VI metal–carbene complexes with alkynes—benzannulation.* Many examples of benzannulation using α,β-unsaturated chromium–carbene complexes (Scheme 27) and alkynes (commonly known as the Dötz reaction) were reported in 2003. Examples are depicted in Scheme 27 and include: (1) atroposelective ben-



Scheme 27.



Scheme 28.

zannulation reactions involving arylacetylene derivatives that contain a chiral substituent *ortho* to the alkyne group (e.g. **331**) [479]; (2) diastereoselective benzannulation reactions using menthyloxycarbene complexes (e.g. **333**) and studies of the haptotropic isomerization of the resulting naphthalene-chromium complexes (e.g. interconversion of **334** and **335**) [480]; and (3) highly diastereoselective coupling of carbohydrate-bound alkenylcarbene complexes and carbohydrate-bound alkynes [481].

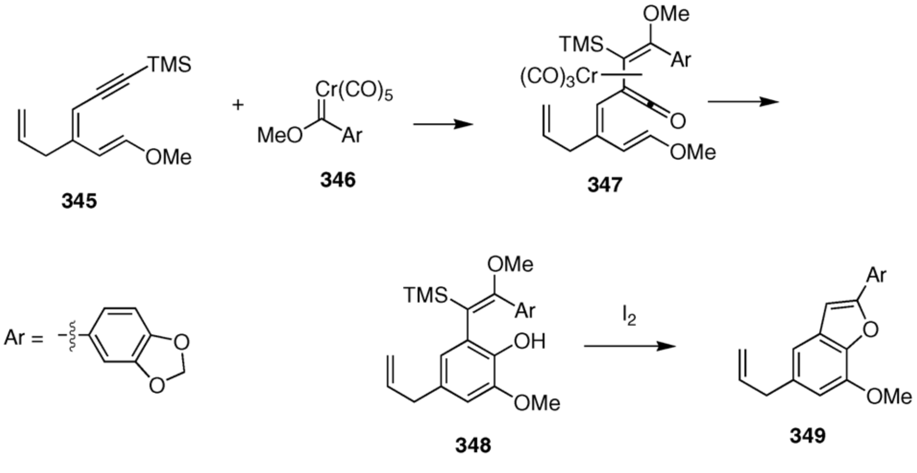
Macrocycle-forming benzannulation reactions were reported (Scheme 28) [482]. In addition to the expected *m*- and *p*-cyclophanes **337** and **338**, additional products were observed, including cyclopropane **340** and *m*-benzannulation product **339**. The unusual *m*-benzannulation product **339** was proposed to arise via intramolecular ketene addition in dienylketene intermediate **341** followed by acid-catalyzed rearrangement of cyclobutenone **342**.

The preparation of benzofuran derivatives (e.g. **349**, Scheme 29) via coupling of Fischer carbene complexes (e.g. **346**) with conjugated dienynes (e.g. **345**) was reported [483]. This alternative benzannulation reaction proceeds via alkyne insertion followed by CO insertion to form a dienylketene intermediate (e.g. **347**). Cyclization to afford a phenol-enol ether (e.g. **348**) followed by workup with iodine lead to the benzofuran. This reaction was used as a cornerstone for formal total synthesis of the natural product egonol.

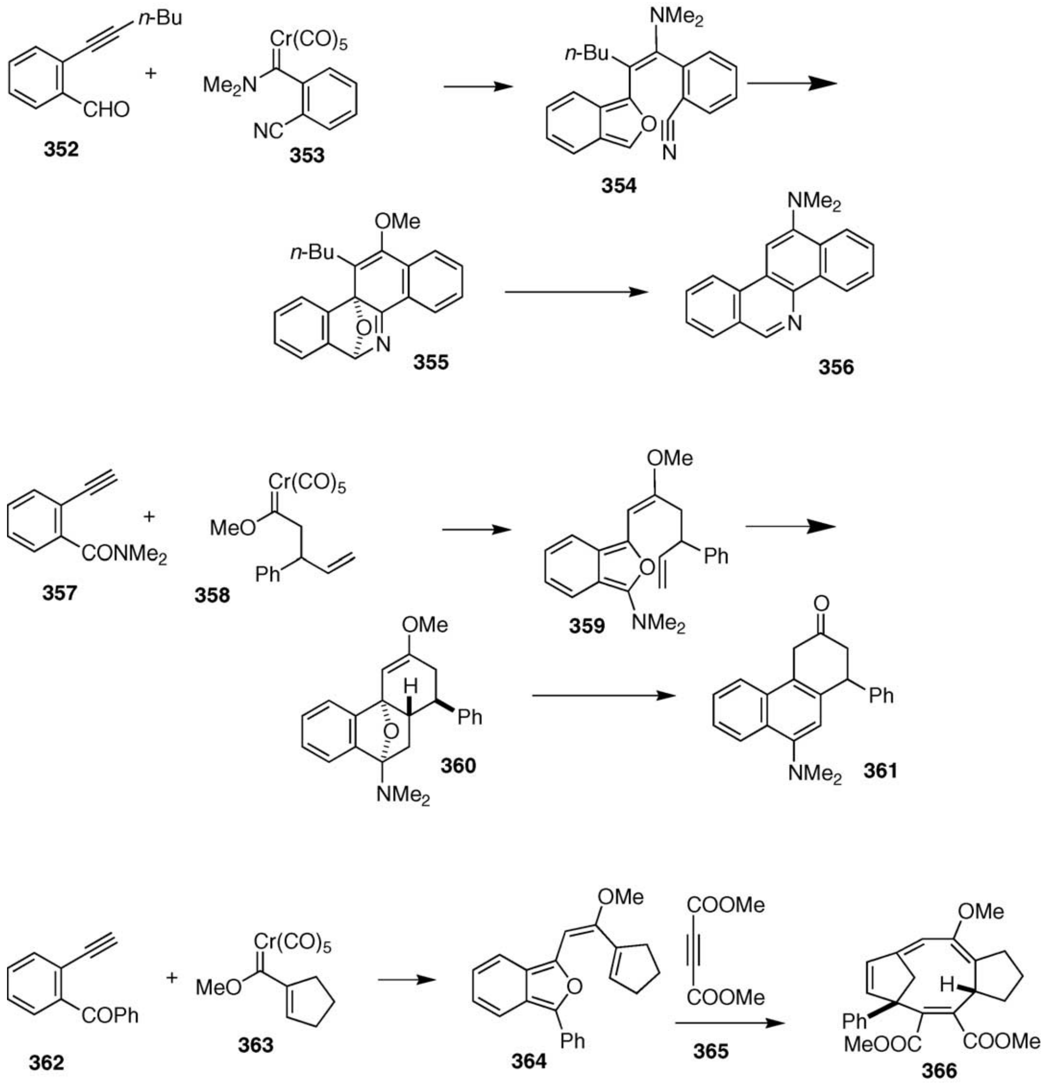
### 2.3.3.5. *Nonbenzannulation reactions of group VI metal–carbene complexes with alkynes.*

Other processes involving the capture of vinylcarbene complexes generated from the coupling of carbene complexes and functionalized alkynes were reported in 2003.

Several papers report on the generation of isobenzofuran intermediates from the coupling of carbene com-



Scheme 29.

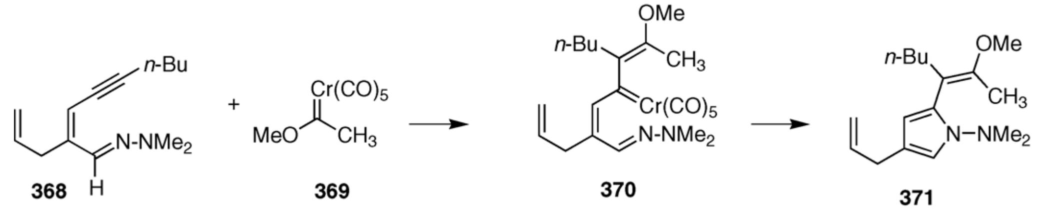


Scheme 30.

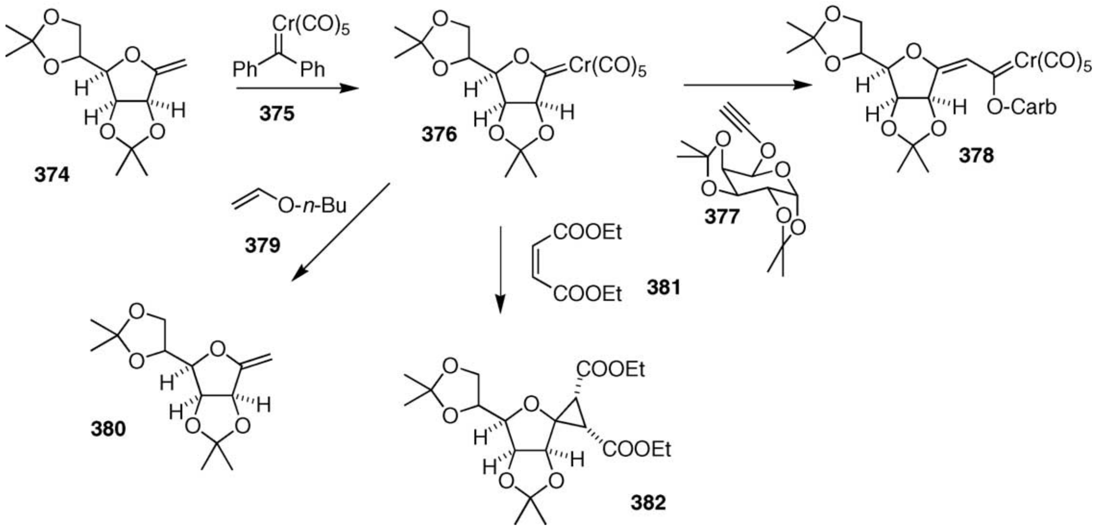
plexes and *o*-alkynylbenzoyl systems (Scheme 30). Coupling of *o*-alkynylbenzaldehyde derivatives (e.g. **352**) with β-cyanocarbene complexes (e.g. **353**) led to isoquinoline derivatives (e.g. **356**) [484]. A mechanism involving generation of an isobenzofuran (e.g. **354**), followed by an intramolecular Diels–Alder reaction between the isobenzofuran and nitrile, followed by reductive deoxygenation was proposed. A similar isobenzofuran intermediate (e.g. **359**) was generated from the coupling of carbene complexes with *o*-alkynylbenzamides (e.g. **357**) [485]. Formation of the isobenzofuran was less efficient in this case, however it could be trapped through intramolecular reaction with alkenes that were originally tethered to either the carbene complex or the amide nitrogen. Aminonaphthalenes (e.g. **361**) were obtained after acidic workup conditions. Isobenzofuran intermediates (e.g. **364**) that are derived from α,β-unsaturated carbene complexes could be captured by DMAD (**365**) to provide [8 + 2]-cycloaddition products (e.g. **366**) as single diastereomers [486].

Coupling of carbene complexes (e.g. **369**, Scheme 31) with enyne–hydrazones (e.g. **368**) was reported [487]. This reaction affords pyrrole derivatives (e.g. **371**) through a mechanism involving alkyne insertion followed by nucleophilic addition of the imine nitrogen to the carbene carbon of the intermediate alkenylcarbene complex **370**.

Several carbohydrate-substituted carbene complexes (e.g. **376**, Scheme 32) were prepared by metathesis reactions of enol ethers and carbene complex **375**, and subsequently treated with electron-rich acetylenes (e.g. **377**) [488]. These reactions typically afforded α,β-unsaturated carbene complexes (e.g. **378**). Disaccharides linked through a carbene complex (e.g. **378**) could be obtained using carbohydrate-substituted alkoxyacetylenes. Cyclopropanation reactions of these carbene complexes were also reported. Reaction with *n*-butyl vinyl ether led to a metathesis product (e.g. **380**), while cyclopropanation products (e.g. **382**) were obtained with electron-deficient alkenes (e.g. **381**).

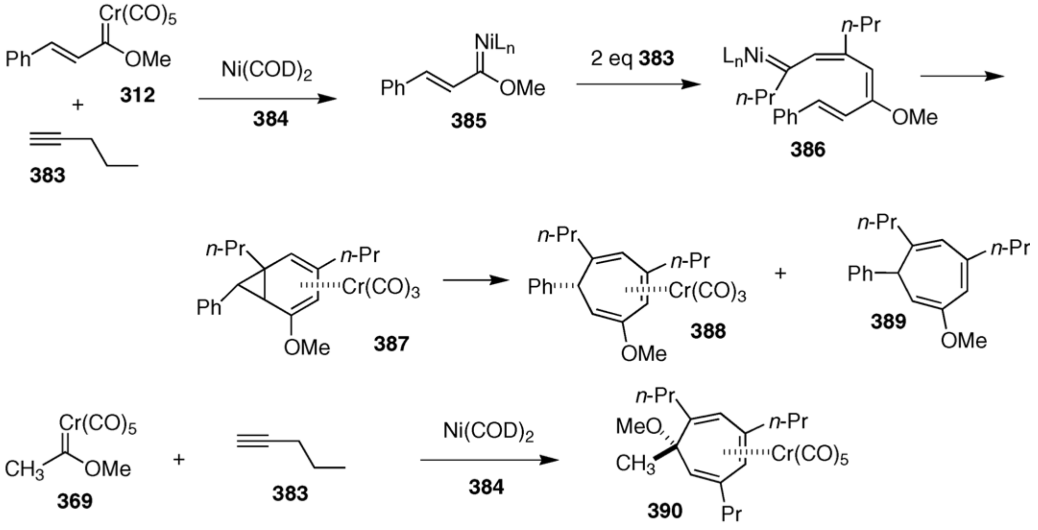


Scheme 31.

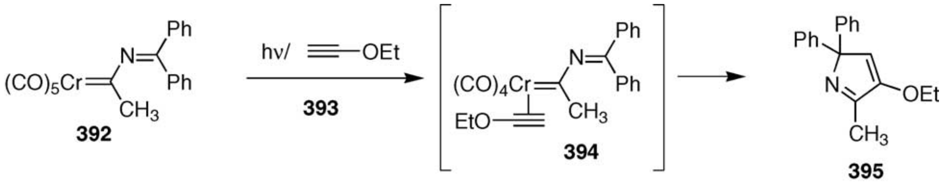


Scheme 32.

Nickel-catalyzed chromium carbene–alkyne coupling processes were reported (Scheme 33) [489]. Cycloheptatrienes (e.g. **389** and **390**) were synthesized through either the coupling of an alkenylcarbene complex (e.g. **312**) with two equivalents of an alkyne or through coupling of an alkylcarbene complex (e.g. **369**) or arylcarbene complex with three equivalents of an alkyne. A mechanism involving formation of a nickel carbene complex (e.g. **385**) through carbene transfer to nickel, followed by insertion of 2–3 mol of alkyne, followed by intramolecular cyclopropanation to afford an intermediate norcaradiene species (e.g. **387**), followed by an electrocyclic ring opening was proposed.



Scheme 33.



Scheme 34.

Photolytic coupling of iminocarbene group VI metal complexes (e.g. **392**, Scheme 34) and various alkynes led to 1-pyrrolines (e.g. **395**) [490]. The mechanism of this reaction was studied by DFT calculations.

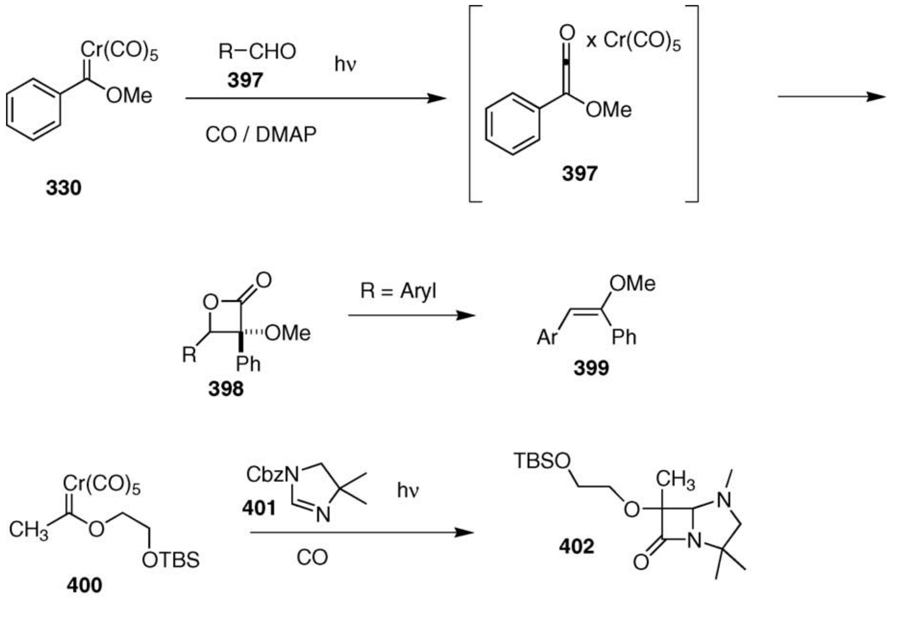
*2.3.3.6. Photolytic generation of ketenes from group VI metal–carbene complexes.* The formation of chromium ketene complexes (e.g. **397**, Scheme 35) through photolysis of Fischer carbene–chromium complexes was reported. Chromium carbene-derived ketenes couple with aldehydes in the presence of DMAP to afford β-lactones (e.g. **398**) or the alkenes (e.g. **399**) derived from $CO_2$ loss [491]. Chromium carbene-derived β-lactams (e.g. **402**) were used as starting materials for the synthesis of several cyclam derivatives [492,493].

*2.3.3.7. Reactions occurring at the conjugated C–C π-bond of α,β-unsaturated group VI metal–carbene complexes.* Numerous reaction processes were reported in 2003 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").

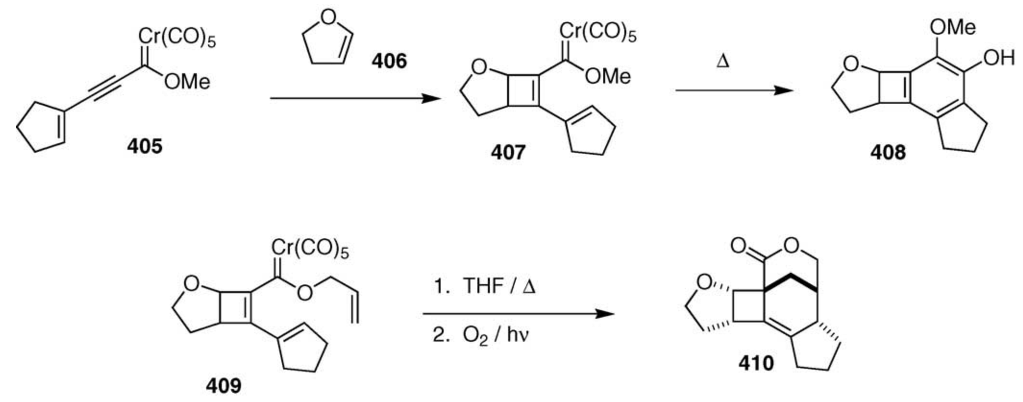
Coupling of enynylcarbene complexes (e.g. **405**, Scheme 36) with enol ethers (e.g. **406**) afforded [2 + 2]-cycloaddition products (e.g. **407**) [494]. Phenol derivatives (e.g. **408**) were obtained upon thermolysis. The corresponding allyloxycarbene complex (**409**) afforded compound **410** in a sequence involving intramolecular Diels–Alder reaction followed by oxidation of the carbene complex to the lactone.

The coupling of α,β-unsaturated carbene complexes with enamines was reported (Scheme 37) [495]. A mixture of compounds **415** and **416** was obtained from the coupling of carbene complex **412** with enamine **413**. A mechanism involving formation of bicyclic intermediate **414** via Michael addition followed by proton transfer and addition of the reformed enamine to the carbene carbon was proposed. Formation of alkene **416** occurs upon treatment of this intermediate with acid. The proposed mechanism involves loss of the methoxy group followed by conversion of the resultant unstabilized carbene complex **417** to the alkene, followed by enamine hydrolysis. Carbene complex **417** (M = W) could be observed by low-temperature NMR. Thermolysis of intermediate **414** afforded the cyclopropane **415** through addition of the metal–carbon bond to the enamine functionality. The individual steps in the conversion of **414** to **417** to **416** were demonstrated in less complex systems.

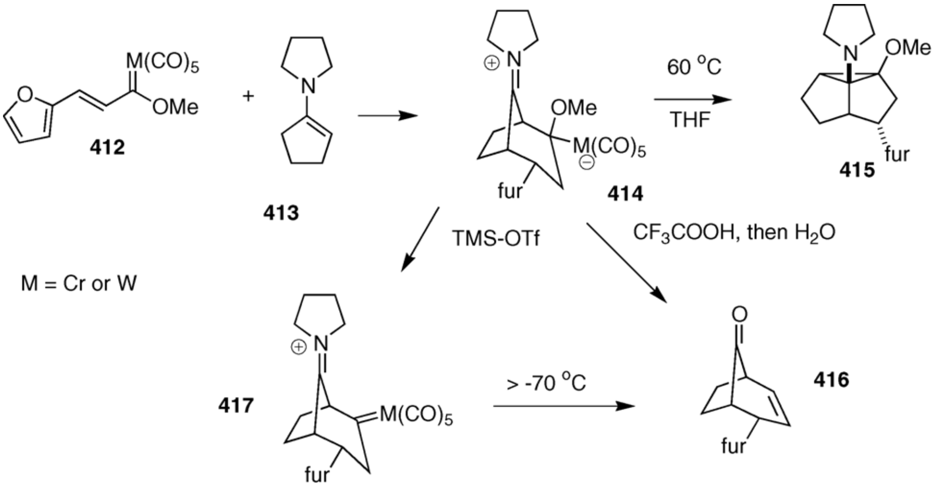
The reaction of 3-furylcarbene complexes (e.g. **420**, Scheme 38) with nucleophiles was reported [496]. The reaction of organolithium reagents and menthyloxycarbene complexes afforded Michael addition products (e.g. **421**)



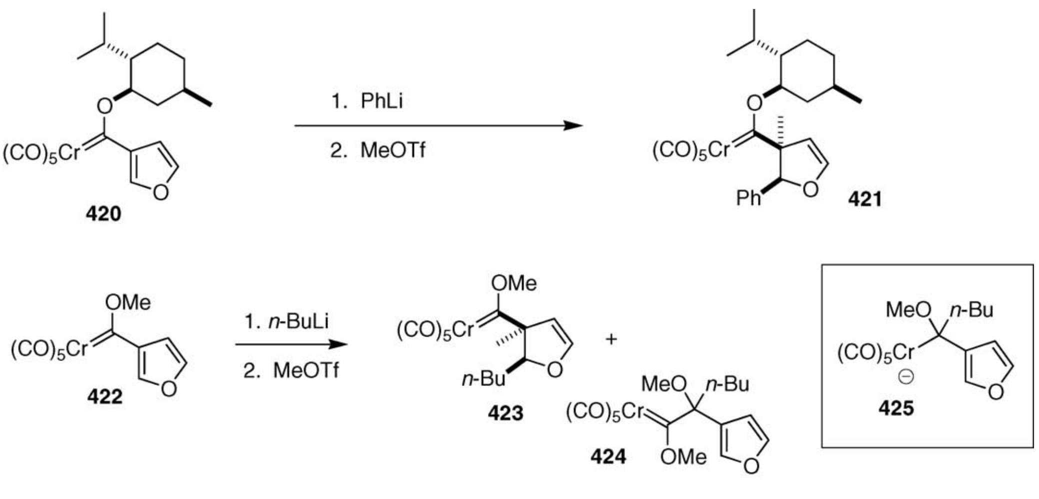
Scheme 35.



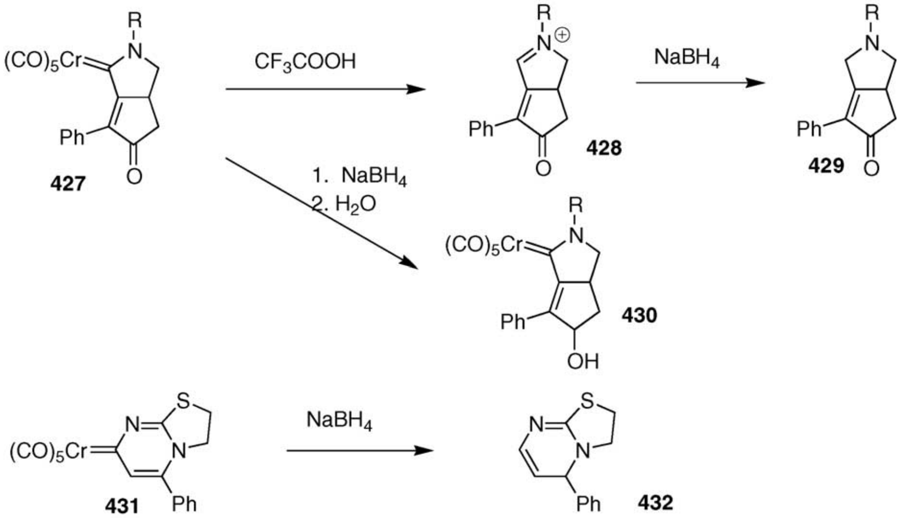
Scheme 36.



Scheme 37.



Scheme 38.



Scheme 39.

with a moderate degree of diastereoselectivity. Analogous reactions employing methoxycarbene complex **422** led to Michael adducts (e.g. **423**) in addition to α-methoxycarbene complexes (e.g. **424**). The mechanism for formation of α-methoxycarbene complexes involves 1,2-addition (affording intermediate **425**) followed by CO insertion and alkylation.

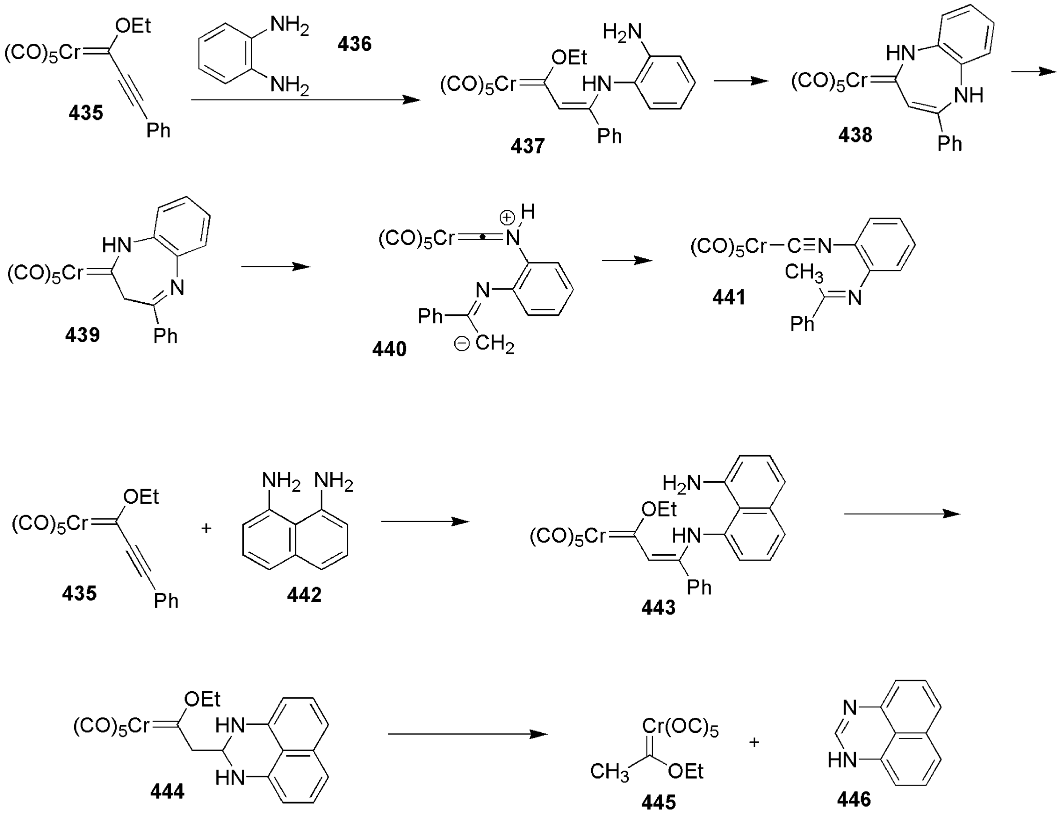
Hydride reductions of bicyclic α,β-unsaturated aminocarbene complexes (e.g. **427** and **431**, Scheme 39) were reported [497]. Treatment of complex **427** with sodium borohydride resulted in reduction of the ketone functionality. However, reduction in the presence of trifluoroacetic acid led to the carbene complex reduction product **429** via the iminium salt **428**. Reduction of carbene complex **431** led to the conjugate reduction product **432**. The conjugate reduction mechanism was supported through deuterium labeling studies.

An unusual reaction resulting in the formation of isocyanide derivatives (e.g. **441**, Scheme 40) was observed in the coupling of aromatic diamines (e.g. **436**) with alkynylcarbene complexes (e.g. **435**) [498,499]. Initially the reaction leads to the Michael adduct **437**, which transforms to the isonitrile complex upon treatment with silica gel or by mild thermolysis. A mechanism involving intramolecular aminolysis of the carbene complex functionality in **437**, followed by tautomerization, followed by ring opening to afford the protonated isocyanide/enamide complex **440**, followed by proton transfer was proposed. In one case an ethanol adduct of cyclic aminocarbene complex **439** could be isolated. Reaction of complex **435** with 1,8-diaminonaphthalene (**442**) led to perimidine derivative **446** and the methylcarbene complex **445**. A mechanism involving double Michael addition of the free amines followed by expulsion of the carbene complex anion from cyclic intermediate **444** was proposed.

Reaction processes employing bis(α,β-unsaturated-carbene-complexes) were demonstrated (Scheme 41). The reaction of dicarbene complexes (e.g. **448**) with various aromatic diamines was reported [500]. Macrocyclic tetracarbene complexes (e.g. **450**) were obtained via a Michael addition process. The electrochemistry of these complexes was examined. Chemoselective Diels–Alder reactions were demonstrated for bis(carbene-complex) derivative **451** [501]. Reaction with 1 mol of cyclopentadiene afforded adduct **452** from selective reaction at the α,β-unsaturated alkoxycarbene complex functionality.

*2.3.3.8. Physical organic chemistry of group VI Fischer carbene complexes.* The kinetic parameters for reaction of group VI metal–thiocarbene complexes (e.g. **455**, Scheme 42) with amines were evaluated in aqueous acetonitrile [502,503]. The nucleophilic addition step ($k_1$) was rate-limiting for most simple primary amines, and for piperidine and pyrazine derivatives. Leaving group departure ($k_3$) was rate limiting for morpholine at low concentrations and for cyanomethylamine. The $k_1$ values were lower for the secondary amines; this observation was attributed to a steric effect. A substituent effect using *p*-phenyl substituted analogs of carbene complex **455** was also reported [504]. Regardless of the *p*-substituent, the initial attachment of the amine to the carbene complex was rate limiting, however the substituent effect was weaker than that observed for methoxycarbene complex analogs.

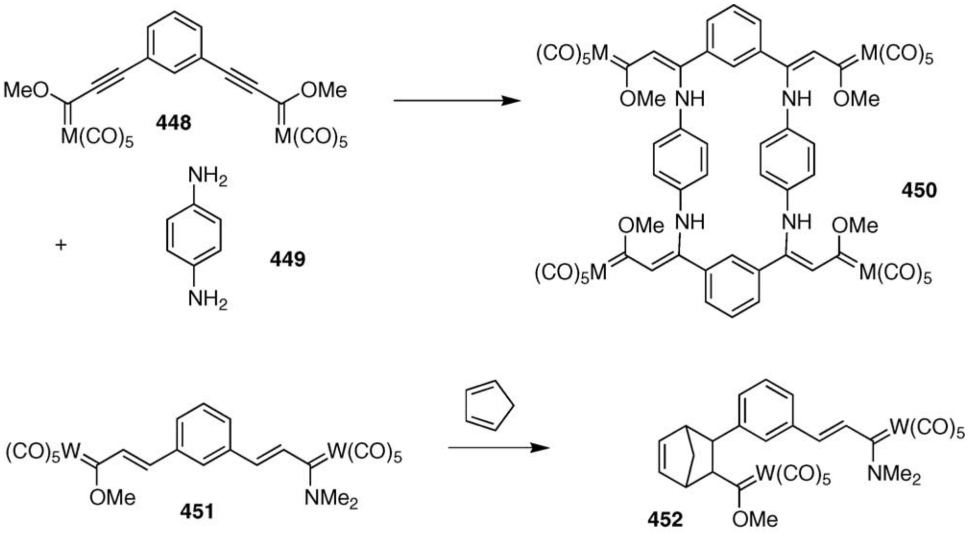
*2.3.3.9. Synthesis and reactivity of group VI metal–vinylidene complexes, and reactions that involve vinylidene–metal complexes as intermediates.* Tungsten- and molybdenum–vinylidene complexes (e.g. **461**, Scheme 43) were prepared through protonation of the corresponding alkynyl complexes (e.g. **460**) [505]. When the complexes were heated, equilibrium of the $\eta^2$-alkyne complex (e.g. **462**) and vinylidene complex was established. The metal and the vinylidene substituent had a profound effect on the position of equilibrium. An alternative route to transform alkynyl complex **460** into carbene complexes was also developed employing neutral alkynyl complex **463** [506]. Tungstenafurans (e.g. **467**) were obtained by reaction of complex



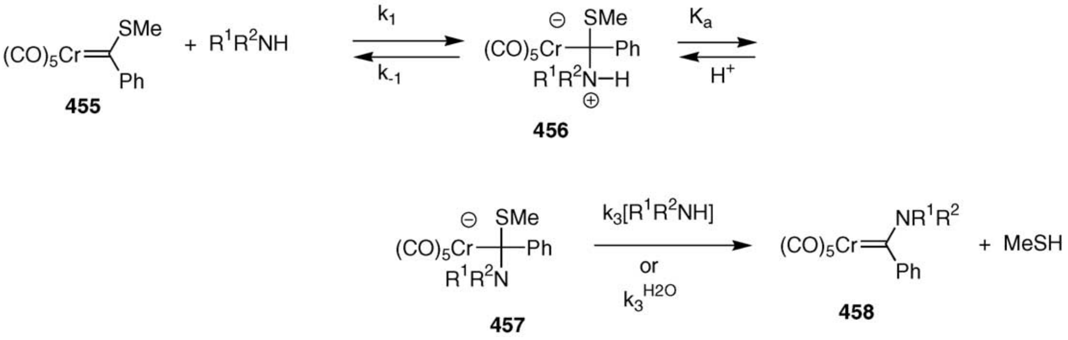
Scheme 40.

**463** with various organolithium reagents followed by electrophilic quench. Regioisomeric tungstenafurans were obtained in some cases. A mechanism involving nucleophilic attack at the carbonyl ligand followed by reductive elimination to afford the tungsten–alkyne complex (**465**), followed by isomerization to the η$^3$-allenyl–enolate complex (**466**) followed by protonation of the enolate was proposed to account for formation of the major regioisomer **467**.

The synthesis of pentacarbonyl–group VI metal allenylidene complexes (general structure **473**, Scheme 44) was reported [507]. Treatment of alkynyl anions of general structure **470** with $(CO)_5M(THF)$ (M = W or Cr) followed by reaction with an electrophile led to the allenylidene complex **473**. Reaction of complex **474** with dimethylamine led to the Fischer carbene complex **475** through α-attack, whereas reaction with the alkoxy analog **476** led to the diaminoallenylidene com-



Scheme 41.



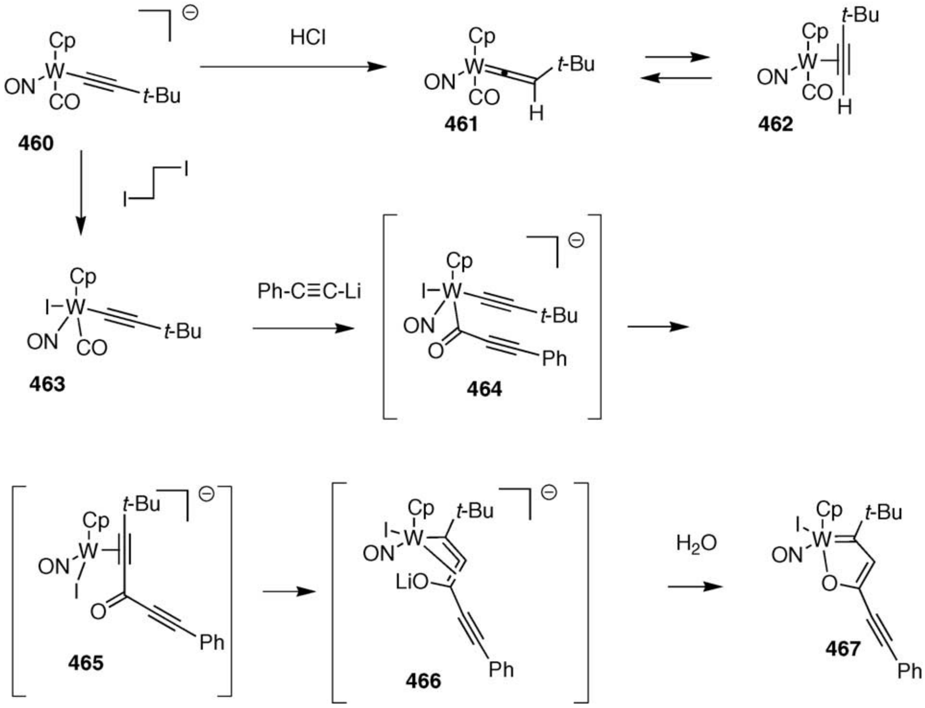
Scheme 42.

plex **477** through γ-attack followed by alkoxy displacement. Ligand exchange with triphenylphosphine could be effected under photolysis conditions.

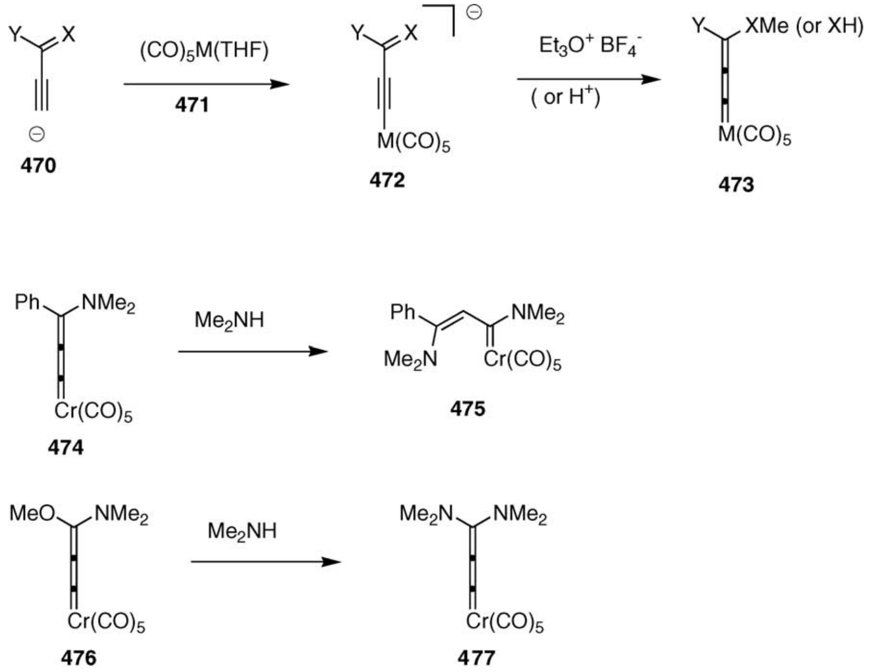
Reaction of $K_2Cr(CO)_5$ with α,β-unsaturated acid chlorides (e.g. **478**, Scheme 45) followed by trifluoroacetic anhydride affords unstable vinylidene complexes (e.g. **479**) [508]. The vinylidene complexes convert to the binuclear complexes (e.g. **480**) upon warming to room temperature in dichloromethane solution. The *t*-butylvinylidene complex was prepared through reaction of *t*-butylacetylide anion with $(CO)_5Cr(THF)$ followed by methylation; this complex also converted to the binuclear species upon warming. Reaction of related complexes (e.g. **482)** with diazo compounds led to the heterocyclic compounds (e.g. **484**) [509]. Cycloaddition through the alkyne–metal complex form (**483**) was proposed. A binuclear tungsten vinylidene complex was formed upon treatment of (*N*,*N*′,*N*″-trimethylhexahydrotriazine)$W(CO)_3$ complex with three equivalents of bis(diphenylphosphino)acetylene [510].

Reaction of alcohol **487** (Scheme 46) with catalytic tungsten hexacarbonyl under combined thermal/photolytic conditions led to a mixture of five-membered ring compound **492** and six-membered ring compound **491** [511]. Formation of the six-membered ring compound was attributed to intramolecular reaction of the alcohol group with the vinylidene functionality in intermediate complex **488**. Formation of the five-membered ring was attributed to reaction of the alcohol group with the π-alkyne functionality of intermediate **489**. The direction of the reaction was controlled by the stereochemistry of the propargyl alcohol substituent.

Coupling of tungsten acetylides that contain epoxide functionality (e.g. **495**, Scheme 47) with Lewis acids was reported [512]. The reaction affords a dihydrofuryltungsten derivative (e.g. **497**) through a mechanism involving complexation of



Scheme 43.

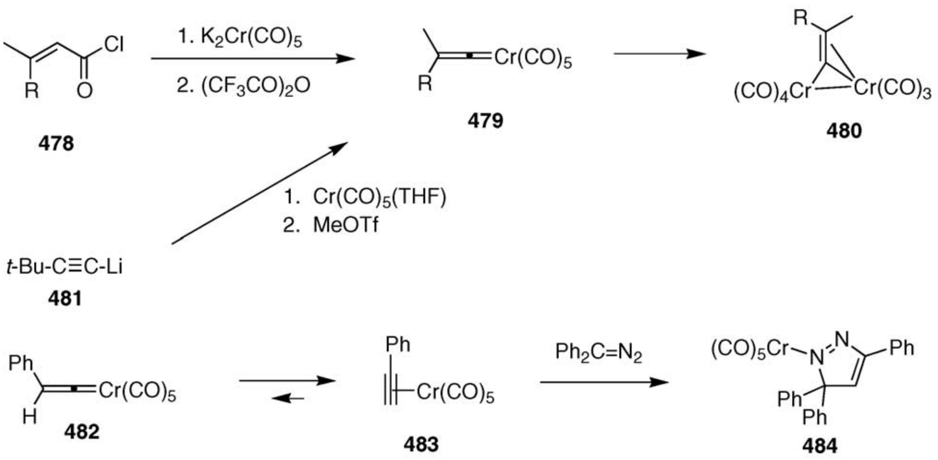


Scheme 44.

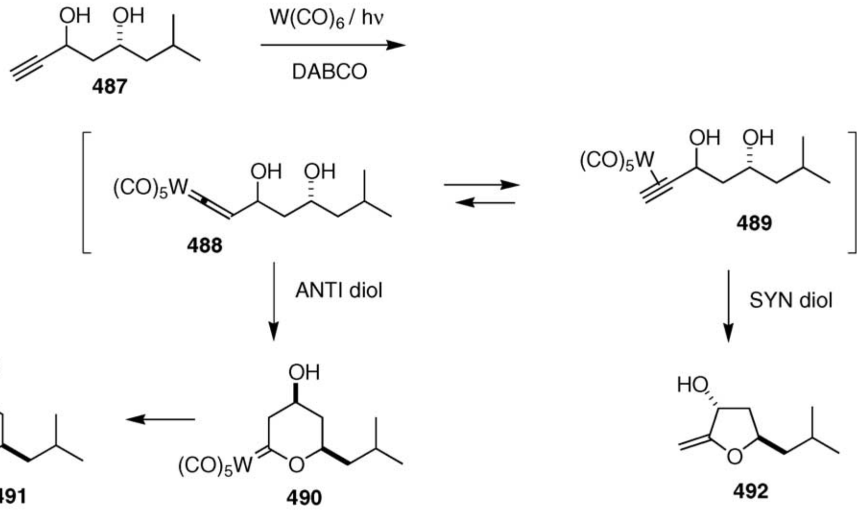
the Lewis acid with the epoxide and reaction with the alkyne to afford a vinylidene intermediate (e.g. **496**), followed by attack of the alkoxide at the vinylidene to generate the dihydrofuran. Tungsten acetylide **499** was converted to the dihydrofuran derivative **503** by treatment with acetaldehyde and Lewis acids [513]. A mechanism involving coupling of the vinyltungtsen with the Lewis acid-activated aldehyde to form the vinylidene complex (**500**), followed by coupling of the vinylidene and alcohol functionalities to form the dihydrofuran (**501**), followed by elimination of water was proposed.

*2.3.3.10. Reactions involving carbanions derived from deprotonation of 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 2003.

Several examples of the coupling of carbene complexes (e.g. **506** and **513**, Scheme 48) with in situ-generated alkynyliminium salts (e.g. **509**) were reported [514]. Reaction of alkoxyiminium salts with carbene complexes that contain α-substitution (e.g. **506**) led to highly unsaturated carbene complexes (e.g. **512**). The mechanism for this transformation involves Michael addition of the carbene complex-derived anion (**508**) to the iminium salt (**509**), followed by intramolecular coupling of the enamine and carbene complex functionalities, followed by electrocyclic ring opening of the resulting cyclobutene (**511**). Reaction of the analogous methylcarbene complex with **513** led to the condensation products **514** and



Scheme 45.

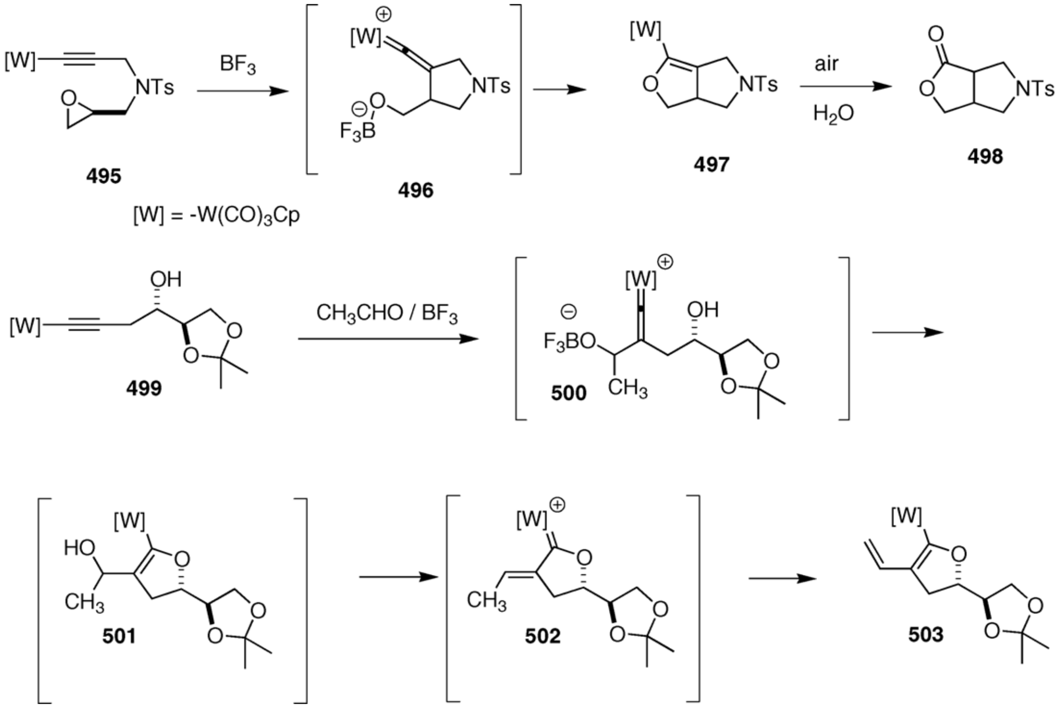


Scheme 46.

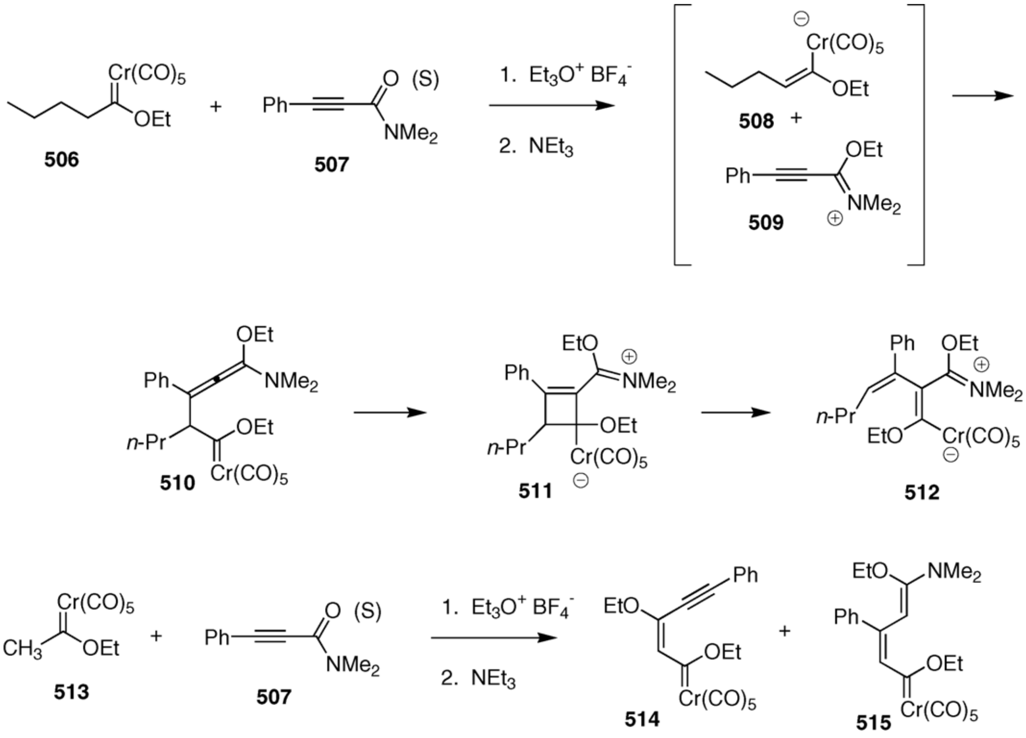
**515**. Compound **515** undergoes a cyclization reaction upon thermolysis at 60 °C.

The coupling of hydrazinocarbene complex stabilized anions (e.g. **518**, Scheme 49) with α,β-unsaturated carbonyl compounds and simple carbonyl compounds was reported [515]. The reaction proceeded with a high degree of diastereoselectivity in most cases when conducted at −78 °C. The anionic intermediate **518** was studied by proton and carbon-13 NMR spectroscopy. The product carbene complexes were readily transformed to the corresponding organic hydrazides by treatment with buffered calcium hypochlorite solution. Aldol-type reactions were also reported for simple methylcarbene complex **369** with various carbohydrate aldehydes (e.g. **523**) [516] and other chiral aldehydes [517].

*2.3.3.11. Reactions involving the addition of nucleophiles to the carbene carbon.* The coupling of tungsten–carbene complexes (e.g. **528** and **533**, Scheme 50) with dihydroquinoline (**529**) to form ylide complexes (e.g. **530**, **535**) was reported [518]. The reaction using the phenylcarbene complex **533** failed. However, if the reaction was conducted in the presence of pyridine then successful formation of the analogous pyridinium ylide complex (**535**) was noted. Reaction of the phenylcarbene complex with dihydroquinoline in the pres-



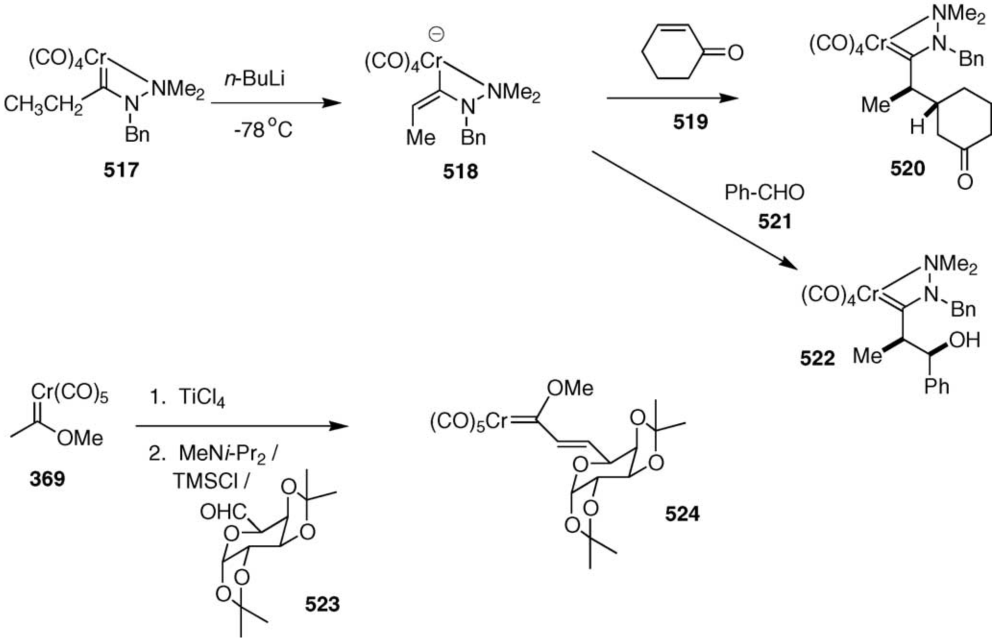
Scheme 47.



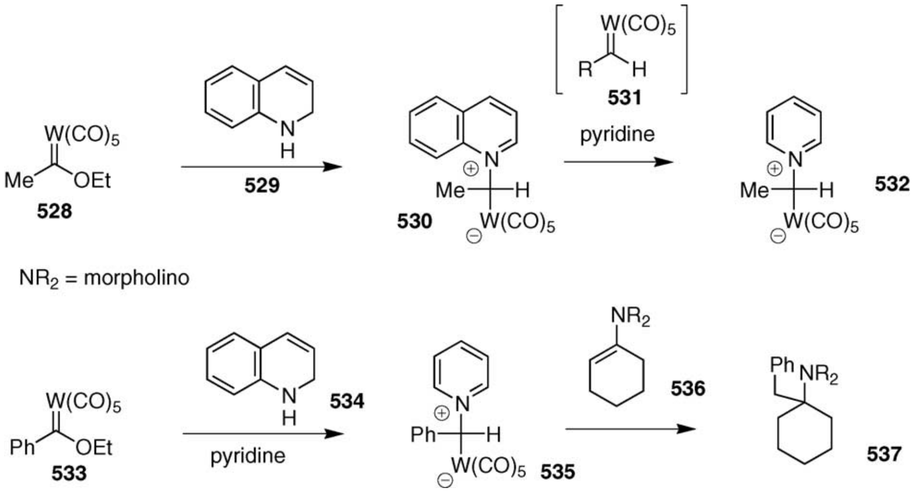
Scheme 48.

ence of enamine **536** led to the amine **537** via a mechanism involving addition of anionic tungsten to the iminium salt from **536** followed by reductive elimination.

Reactions that involve additions to both the carbene carbon and the β-carbon of α,β-unsaturated carbene complexes were reported. The synthesis of uracil–carbene complex derivatives (e.g. **540**, Scheme 51) through reaction of alkynylcarbene complexes with ureas was reported [519]. A mechanism involving nucleophilic attack at the alkyne carbon followed by cyclization through nucleophilic attack at the carbene complex was proposed. Mixtures were obtained when unsymmetrical ureas were employed. However, a moderately regioselective process was observed using *N*-allylurea. Both microwave and traditional thermal processes were examined.



Scheme 49.



Scheme 50.

The synthesis of cyclopentenols (e.g. **544** and **545**) through coupling of α,β-unsaturated carbene complexes (e.g. **541**) with enolates (e.g. **542**) was reported [520]. A mechanism involving 1,2-addition followed by nucleophilic addition to the carbonyl group with allylic rearrangement was proposed. The stereochemistry of the reaction was controlled by choice of solvent (ether versus THF).

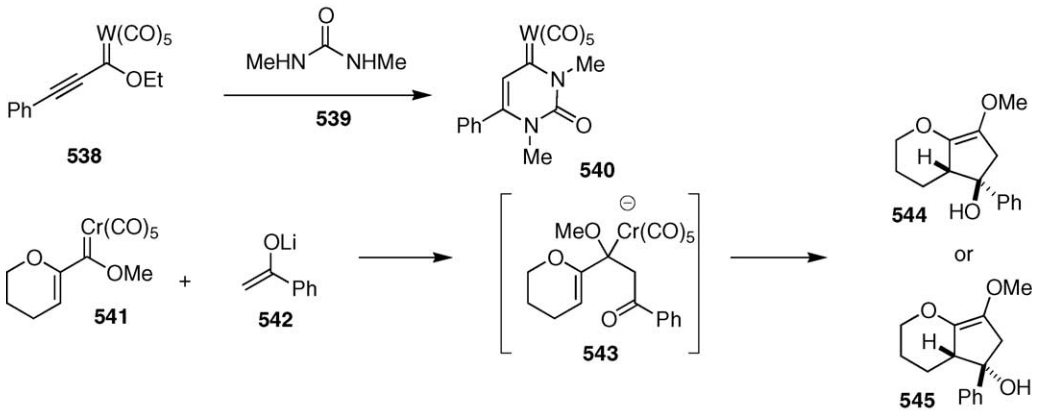
The transformation of pyranylidene-chromium complexes (e.g. **547**, Scheme 52) to the corresponding piperidinylidene complexes (e.g. **549**) was reported [521]. The pyranylidene complexes were prepared by the novel synthetic route from alkenylstannane **546**. Treatment of pyranylidene complex **547** with ammonia led to the open chain alcohol–aminocarbene complex derivative **548**. Reclosure of the ring was effected using the Mitsunobu reaction. A similar set of reactions was used to prepare organochromium nucleoside analogs [522].

The three-component coupling of carbene complexes (e.g. **330**, Scheme 53), enolates (e.g. **552** and **557**), and allylmagnesium bromide was reported [523]. Substituted enolates (e.g. **552**) led to five-membered ring derivatives (e.g. **556**) in a reaction sequence involving addition of the enolate to the carbene carbon, followed by addition of allylmagnesium bromide to the ketone, followed by intramolecular alkene insertion and cyclopropanation. Unsubstituted enolates (e.g. **557**) afforded six-membered rings (e.g. **560**) by a similar mechanism except that CO insertion occurs in intermediate **558**, which then undergoes a net oxidative addition into the alkene C–H bond to afford the six-membered ring product. In both cases the reaction was highly stereoselective.

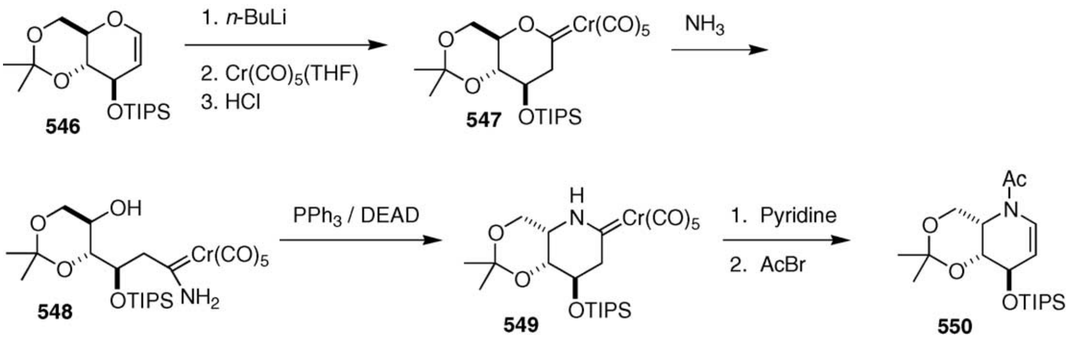
#### *2.3.3.12. Insertion of group VI metal–carbene complexes into σ-bonds.*

Intramolecular C–H insertion processes were reported for boryloxycarbene–molybdenum complexes (e.g. **561**, Scheme 54) [524]. Thermolysis of carbene complex **561** followed by treatment with peroxide anion afforded diol **562** as a single diastereomer.

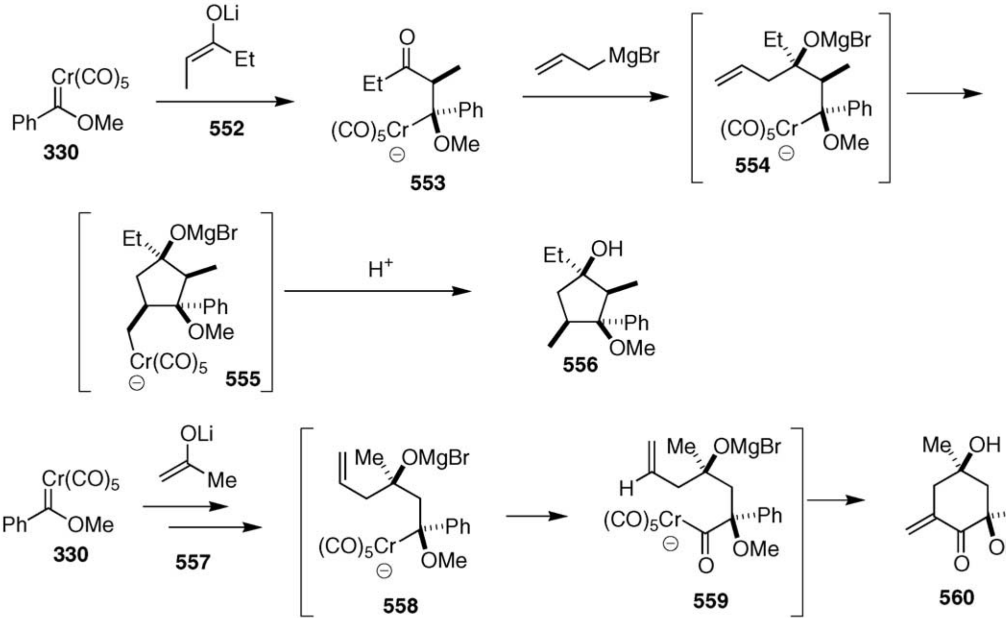
Molybdenum–carbene complexes (e.g. **566**, Scheme 55) were proposed as intermediates in C–H activation reactions of dialkylmolybdenum complex **565** [525]. Room temperature thermolysis of complex **565** in tetramethylsilane resulted in the dialkyl complex **567**. Room temperature reaction of complex **565** with *p*-xylene resulted in an aryl C–H activation product (**569**) and a benzylic C–H activation product



Scheme 51.



Scheme 52.

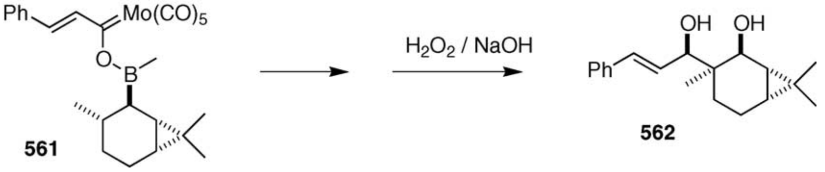


Scheme 53.

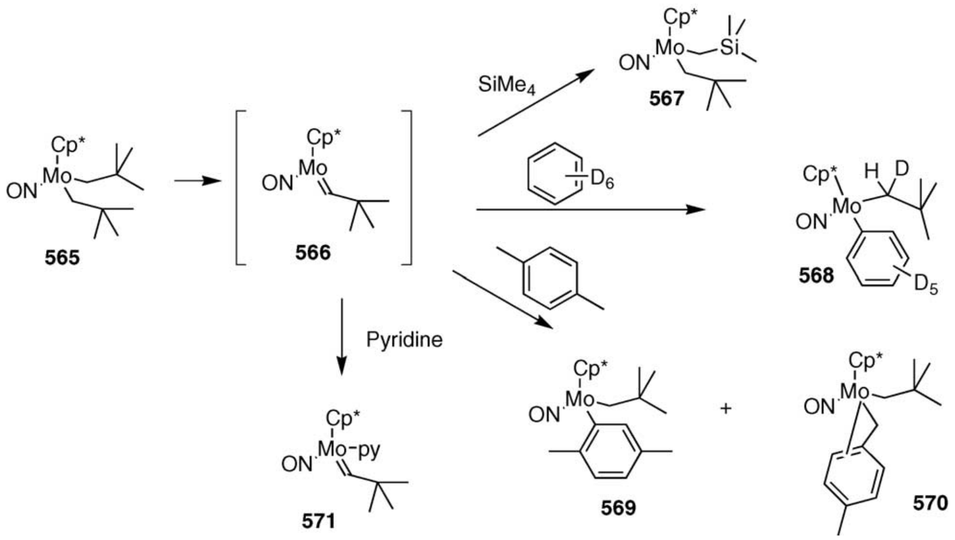
(**570**). Reaction of complex **565** with benzene-d$_6$ resulted in phenyl complex **568**. A mechanism involving α-elimination followed by reductive elimination to generate carbene complex **566** followed by C–H activation was proposed. Reaction of complex **565** with pyridine resulted in an isolable carbene complex (**571**).

Insertion of alkynylcarbene complexes (e.g. **575** and **577**, Scheme 56) into the B–H bond of $BH_3CN^-$ was reported [526]. The coupling of alkynylcarbene complex **575** with $NaBH_3CN$ led to the B–H insertion product **576**. Aminocarbene analogs were unreactive to $NaBH_3CN$. Less reactive ferrocenylalkynylcarbene complex **577** led to the alcohol **578** at 0 °C accompanied by the ether **579**. The insertion process appears to be restricted to alkynylcarbene complexes; alkenylcarbene complexes afforded hydride addition products. Other boron hydrides were tested in their reaction with alkynylcarbene complexes, however B–H insertion products were not obtained.

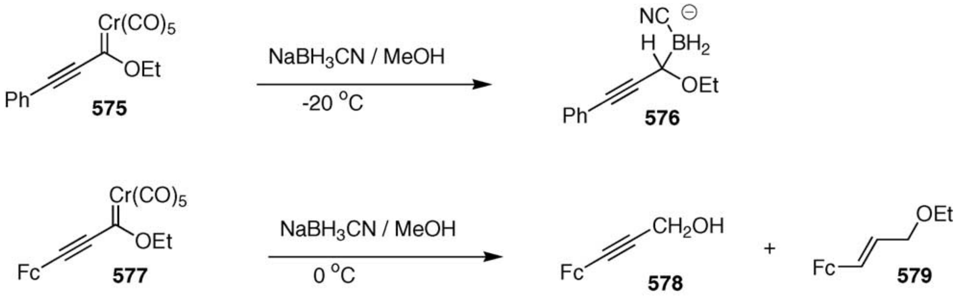
*2.3.3.13. Other reactions of group VI metal–carbene complexes.* The preparation of carbene complexes ligated to chiral diphosphines (e.g. **583** and **584**, Scheme 57) was reported [527]. Reaction of molybdenum carbene complex **581** with phosphine **582** at 60 °C led to the air-stable complex **583**. Iso-



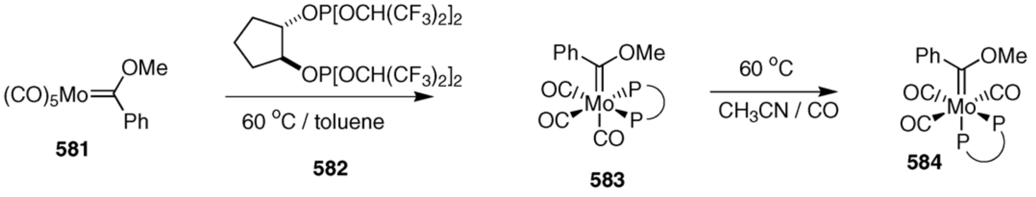
Scheme 54.



Scheme 55.



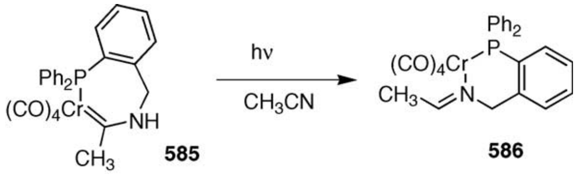
Scheme 56.



Scheme 57.

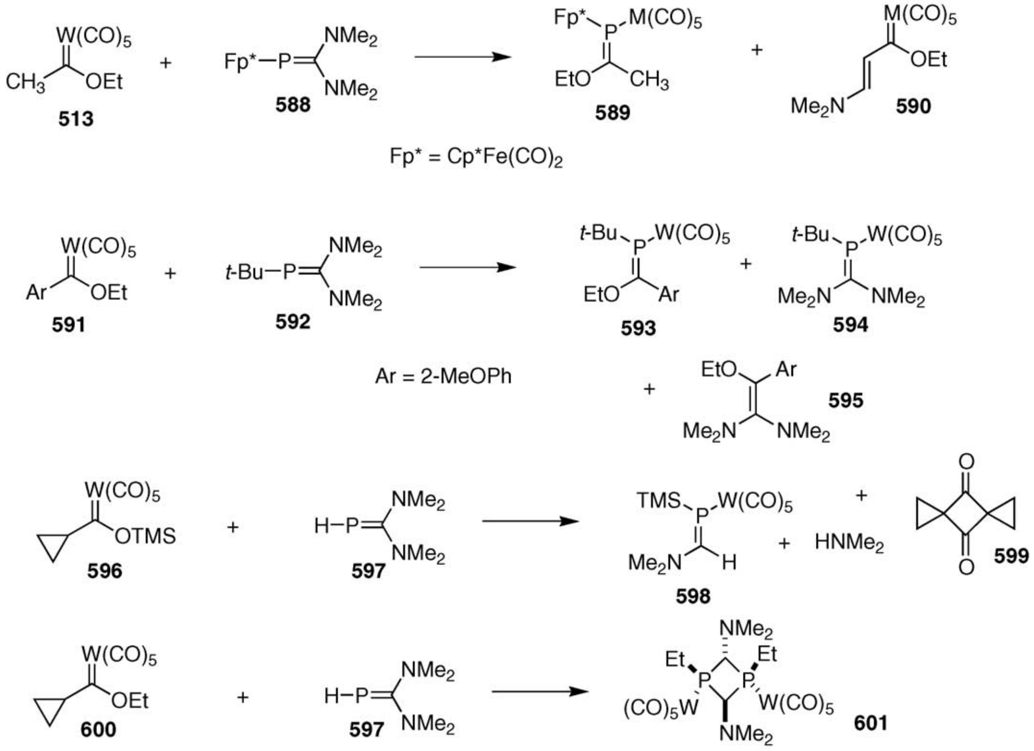
merization to the *mer* isomer **584** was effected by heating at 60 °C in a carbon monoxide atmosphere. Chromium analogs were produced at higher temperature (80 °C) and yielded exclusively the *mer* isomers.

Photoinduced rearrangement of phosphine-chelated aminocarbene complexes (e.g. **585**, Scheme 58) to imine–phosphine chelates (e.g. **586**) was reported [528]. Various mechanistic pathways were evaluated computationally. A free-radical mechanism was determined to be the most energetically reasonable reaction pathway.



Scheme 58.

The reaction of Fischer carbene complexes (e.g. **513**, **591**, **596** and **600**, Scheme 59) with phosphaalkenes (e.g. **588**, **592**, and **597**) was reported [529]. The reaction pathway was highly dependent on the structure of the carbene complex. A condensation product **590** and phosphine complex **589** were observed from coupling of methylcarbene complex **513** and phosphaalkene **588**. Metathesis products **593**–**595** were formed from coupling of phosphaalkyne **592** and arylcarbene complex **592**. Silylation products were obtained from silyloxycarbene complex **596** and phosphaalkyne **597**. This product was proposed to form through nucleophilic addition

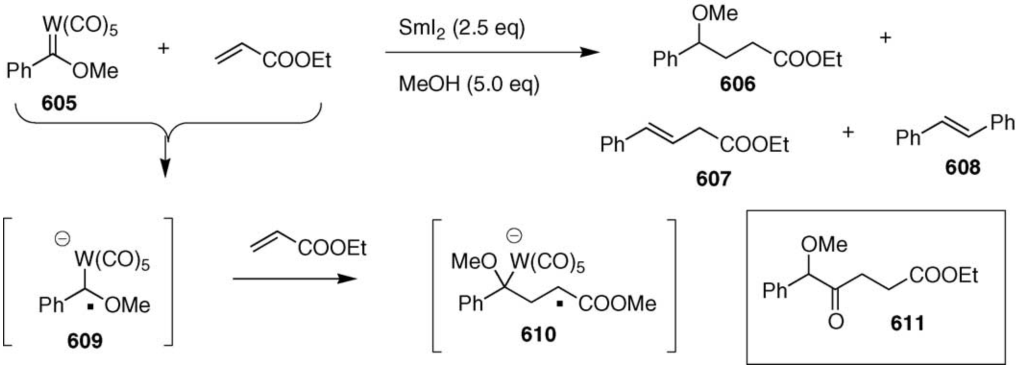


Scheme 59.

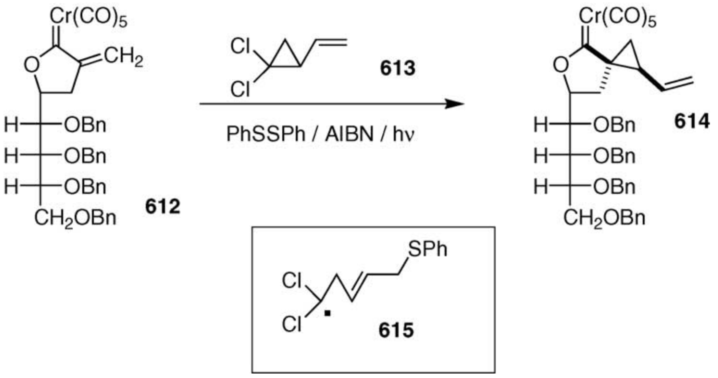
of phosphorous to the carbene carbon, followed by elimination of tungsten and simultaneous hydrogen migration to the diamino carbon and coordination of tungsten to phosphorus, followed by deprotonation of the resulting phosphaalkene and ejection of silicon forming a ketene and silylated phosphaalkene complex **598**. The ketene dimer **599** could be detected by mass spectrometry. An alkyl group transfer product (**601**) was obtained from the coupling of cyclopropylcarbene complex **600** with phosphaalkyne **597**.

Samarium(II) iodide-induced reductions of tungsten carbene complexes were reported (Scheme 60) [530]. Reduction of phenylcarbene complex **605** in the presence of ethyl acrylate led to the net Michael addition product **606** and corresponding elimination product **607**, accompanied by stilbene (**608**). The amount of stilbene was minimized through use of large excesses of ethyl acrylate. A mechanism involving formation of the carbene complex radical anion (**609**) followed by Michael addition and hydrogen abstraction was proposed. The corresponding chromium complex afforded mixtures of **606** and **607**, accompanied by a CO insertion product, **611**. Compound **611** was proposed to arise through protonation of the radical anion followed by CO insertion, alkene insertion, and protonation. Dimerization products were formed upon treatment of α,β-unsaturated carbene–tungsten complexes with samarium(II) iodide.

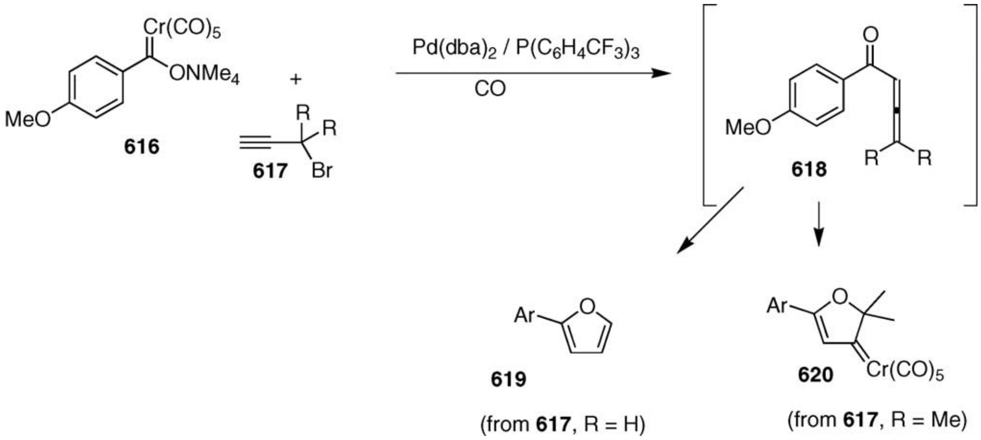
Radical-based cycloaddition reactions for exo-methylene–oxopentylidene complexes of chromium (e.g. **612**, Scheme 61) were reported [531]. Treatment of complex **612** with vinylcyclopropane **613** in the presence of AIBN and diphenyl disulfide led to the spirocyclic carbene complex **614**.



Scheme 60.



Scheme 61.

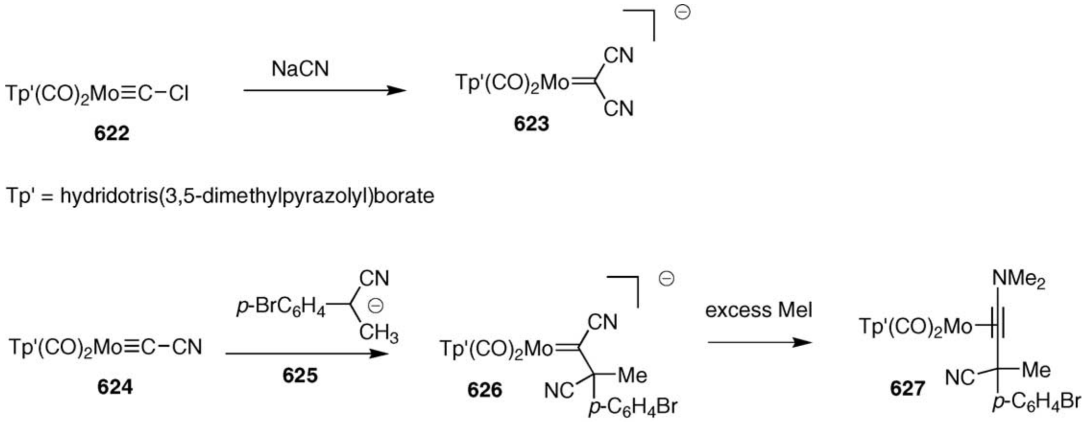


Scheme 62.

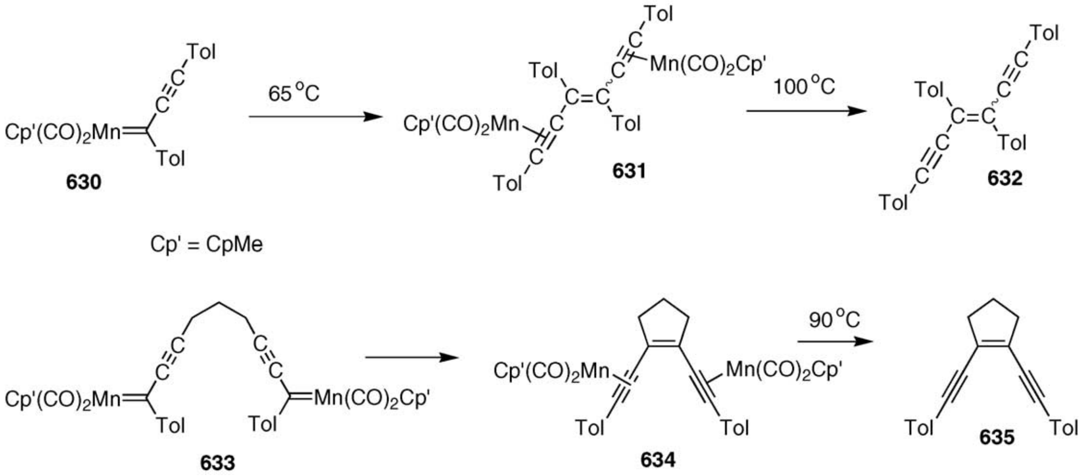
The key mechanistic event in this reaction is the addition of radical **615** (generated through addition of thiophenyl radical to **613**) to the alkene of the carbene complex. A high degree of stereoselectivity for formation of the depicted stereoisomer was observed.

Chromium carbene complex **620** (Scheme 62) was obtained from the coupling of chromium acylate **616** and propargyl halide **617** (R = Me) in the presence of a palladium catalyst [532]. Palladium-catalyzed coupling initially affords the allenyl ketone **618**, which couples with chromium byproducts to afford the carbene complex intermediate **620**. When R = H, the carbene complex decomposes to the corresponding furan **619**.

The anionic carbene complex **623** (Scheme 63) was prepared by treatment of the carbyne complex **622** with cyanide anion [533]. Addition of carbanion **625** to cyanocarbyne complex **624** afforded cyanocarbene complex **626**, which could be double alkylated to form the ynamine complexes **627**.



Scheme 63.



Scheme 64.

Additional experimental studies concerning group VI metal carbene complexes include: (1) attempts to characterize Fischer carbene–chromium and tungsten complexes by electrospray ionization mass spectrometry, which requires the addition of hydroquinone or tetrathiafulvalene for successful ionization [534]; (2) preparation of carbene complexes that can function as gelators for benzene and chloroform [535]; (3) formation of a bridged aminocarbyne–platinum–tungsten complex through protonation of the corresponding bridging isocyanide complex [536]; and (4) a mechanistic hypothesis suggesting that molybdenum carbene complexes are intermediates in the formation of π-allyl complexes from molybdenum hydrides and 2-methyl-1-buten-3-yne [537].

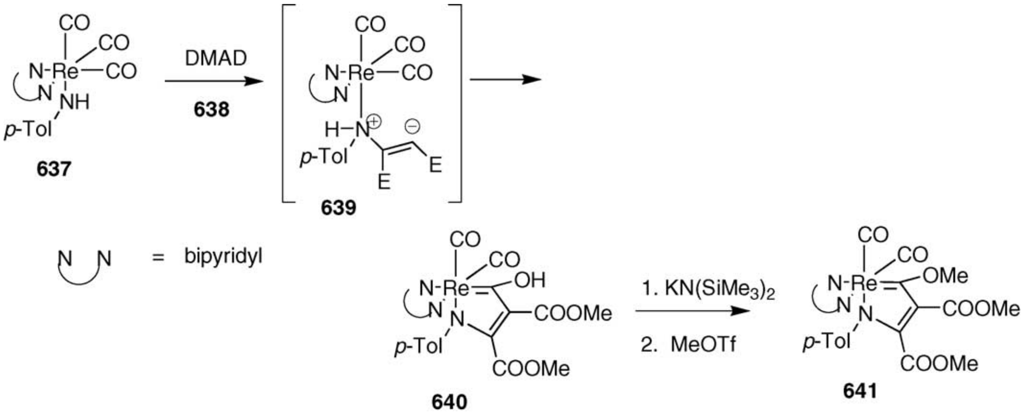
An electron pairing analysis for various Fischer carbene complexes was reported [538]. For carbene complexes of general structure $(CO)_5CrC(X)R$, electron delocalization between Cr═C and C–X groups are related to the π-donor strength of the X group and the degree of back-bonding between the $Cr(CO)_5$ and C(X)R fragments. Electron delocalization between the Cr and X group is consistent with a three-center, four-electron interaction in the Cr═C–X segment of the molecule.

### 2.3.4. Group VII metal–carbene complexes

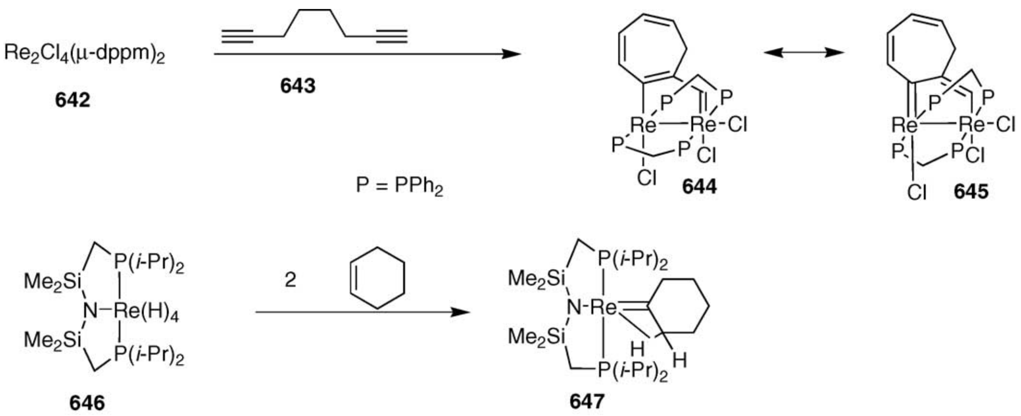
Thermolysis of alkynylcarbene–manganese complex **630** (Scheme 64) led to dimeric enediyne complex **631** as a mixture of E and Z isomers [539]. Thermolysis at higher temperature led to the manganese-free enediynes **632**. Attempted synthesis of tethered complex **633** afforded only the cyclic enediyne complex **644**, which afforded the free enediyne upon thermolysis at 90 °C. The conversion of complexes related to **630–631** can be accelerated by adding a catalytic amount of Na/K alloy [540]. Improved procedures for the preparation of alkynylcarbene–manganese complexes were reported [541,542].

Neutral hydroxycarbene complex **640** (Scheme 65) was generated through the coupling of amide complex **637** with dimethyl acetylenedicarboxylate (**638**) [543]. A mechanism involving Michael addition, followed by ring closure, followed by proton transfer was proposed. Hydroxycarbene complex **640** was transformed to the corresponding methoxycarbene complex **641** through deprotonation followed by methylation.

Other syntheses of Group VII metal–carbene complexes reported in 2003 are depicted in Scheme 66 and include: (1)



Scheme 65.



Scheme 66.

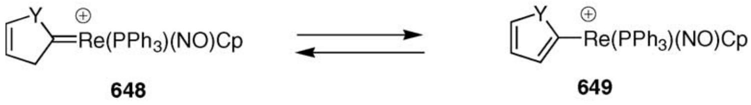
formation of dirhenium complex **644**/**645** from the reaction of dirhenium complex **642** with 1,7-octadiyne (**643**) [544]; (2) formation of rhenium–carbene complex **647** through reaction of rhenium tetrahydride **646** with cyclohexene [545]; and (3) methylation of a benzoylruthenium complex, affording a mixture of the expected carbene complex and an acetophenone complex [546].

The acidity of rhenium–carbene complexes of general structure **648** (Scheme 67) was determined [547]. A correlation between kinetic acidity and the aromaticity of the conjugate base was noted. The kinetic acidity follows the order Y = S > Se > O, which parallels the aromaticity of thiophene versus selenophene versus furan. This result implies that the development of aromatic character precedes the actual deprotonation step.

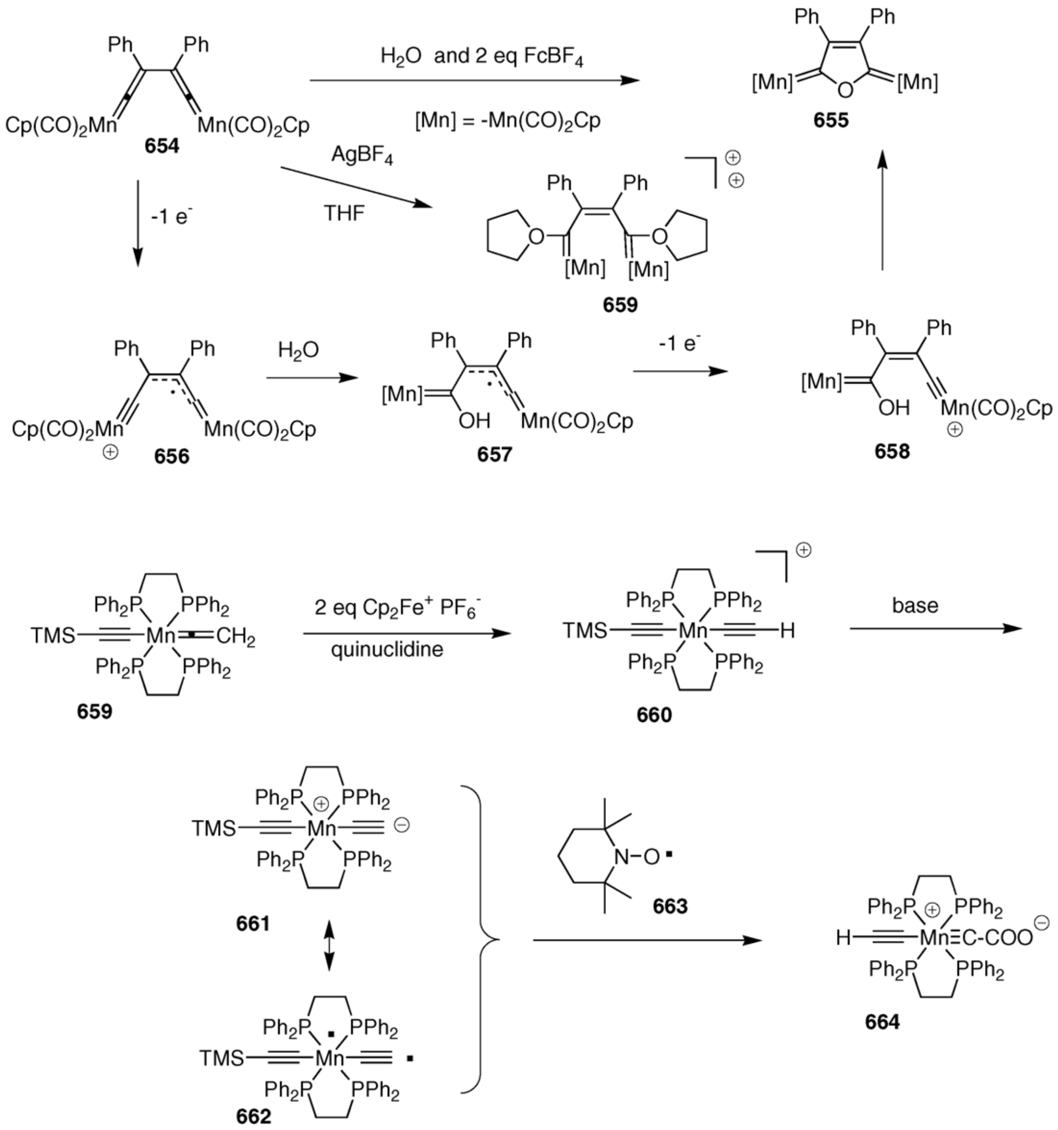
Several examples of group VII metal–cumulene complexes were reported in 2003. Oxidatively-induced nucleophilic addition to bis(vinylidene)–dimanganese complexes (e.g. **654**, Scheme 68) resulted in the cyclic dicarbene complex **655** [548]. A mechanism involving one-electron oxidation to the radical cation–dimanganese complex **656**, followed by nucleophilic addition of water, followed by a second oxidation and intramolecular nucleophilic addition of oxygen was proposed. The THF adduct (**659**) of bis(carbyne)–dimanganese complex **654** could be observed upon treatment of starting compound **654** with $AgBF_4$. Oxidation of manganese–vinylidene complexes (e.g. **659**) was reported [549,550]. Two electron oxidation of manganese vinylidene complex **659** by ferrocenium ion in the presence of quinuclidine led to the cationic dialkynylmanganese complex **660**. Treatment with base in the presence of excess TEMPO radical (**663**) led to the carbyne–carboxylate complex **664**.

Cationic rhenium allenylidene complexes (e.g. **666**, Scheme 69) were prepared and their reaction with phosphine nucleophiles examined [551]. The product from attack at the γ-position (**667**) was the kinetic product of the reaction, which in most cases rearranged to the product resulting from attack at the α-position (**668**). The product from diphenylphosphine was the α,β-unsaturated carbene complex **669**, which likely results from proton transfer within the α-addition product. The cycloaddition of rhenium–allenylidene complex **666** and pyrazole was also reported [552]. The mechanism involves attack at the α-position followed by proton transfers and eventual attack of the other nitrogen at the γ-position. The simple γ-addition product **671** can be formed by treatment of the cycloadducts **670** with base, which can subsequently be transformed back into the starting allenylidene complex **666** through protonation. The synthesis of manganese butatrienylidene complexes was also reported [553].

Several papers in 2003 report on reaction processes that propose group VII metal–carbene complexes as intermediates. Rhenium–carbene complexes were proposed as intermediates in a carbonyl olefination reaction using aldehydes (e.g. **676**, Scheme 70), diazo compounds, triphenylphosphine, and a rhenium-oxo catalyst (e.g. **677**) [554]. The carbene complex **679** was identified and characterized spectroscopically. High oxidation state rhenium–carbene complexes were also identified as intermediates in the rhenium-catalyzed carbonyl olefination of carbonyl compounds using diazoacetates and triphenylphosphine as stoichiometric reagents [555]. Rhenium–carbene complexes (**681** and **682**) have been identified in the electrospray ionization mass spectrum of rhenium dioxo complex **680** [556]. Rhenium $\eta^2$-alkenyl complexes



Scheme 67.



Scheme 68.

were suggested as intermediates in the *cis–trans* isomerization of rhenium–(3,5-diacylcyclopentene) complexes [557].

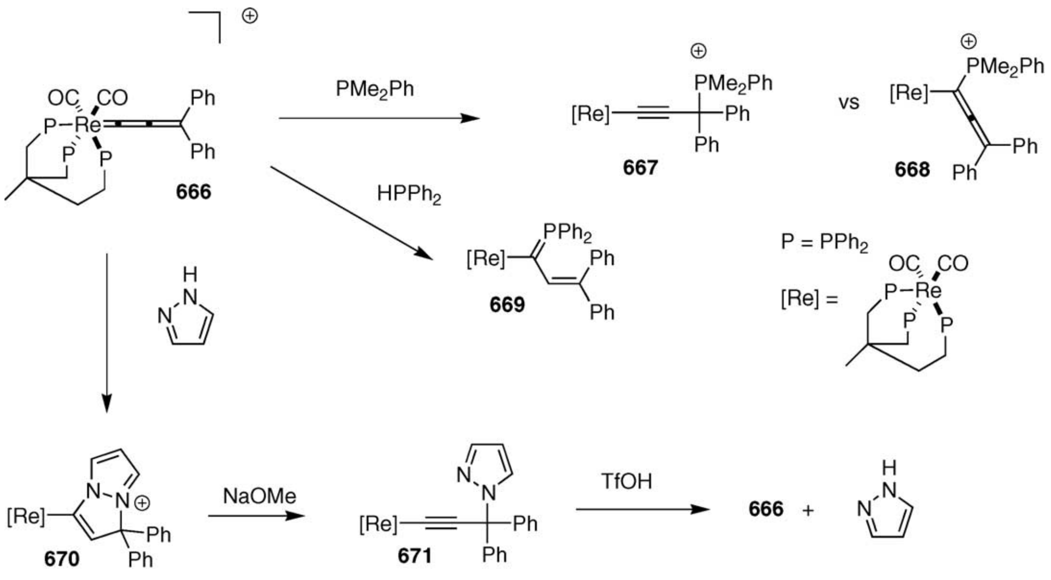
The feasibility of rhenium–carbene-catalyzed alkene polymerization was studied by DFT calculations (Scheme 71) [558]. A thermodynamically feasible reaction pathway for chain growth was identified involving formation of metallacyclobutane **686** followed by conversion to rhenium–propylene complex **688**. Formation of the carbene complex **687** from the metallacyclobutene was considerably less exothermic. Rhenium–propylidene complexes and π-alkene complexes are of comparable energies if the nitrosyl ligands in **687** and **688** are replaced by trimethylphosphine ligands.

Other studies of group VII metal carbene complexes include: (1) evaluation of the relative importance of the carbene complex resonance form for several rhenium isocyanide complexes [559] and (2) a theoretical study of $\eta^5$-$M_eC_p(CO)M_n\{C(OEt)CH_2PPh_2\}$ using Fenske–Hall calculations [560].

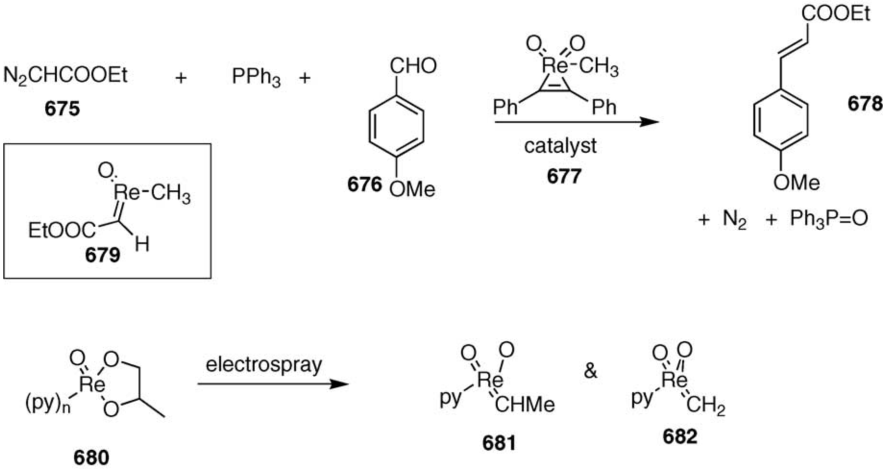
### *2.3.5. Group VIII metal–carbene complexes*

*2.3.5.1. Cationic metal–carbene complexes that are not cumulenes.* The coupling of cationic iron carbene complex **696** (Scheme 72) with in situ-generated anionic arene–manganese complex **695** (through treatment of the analogous cationic complex with potassium naphthalide(KNp)) was reported [561]. The product from nucleophilic addition to the carbene complex (**697**) was obtained. The anticipated product, cyclopropane **698**, was not observed. Further, KNp-induced reductions of the bimetallic compound **696** were reported.

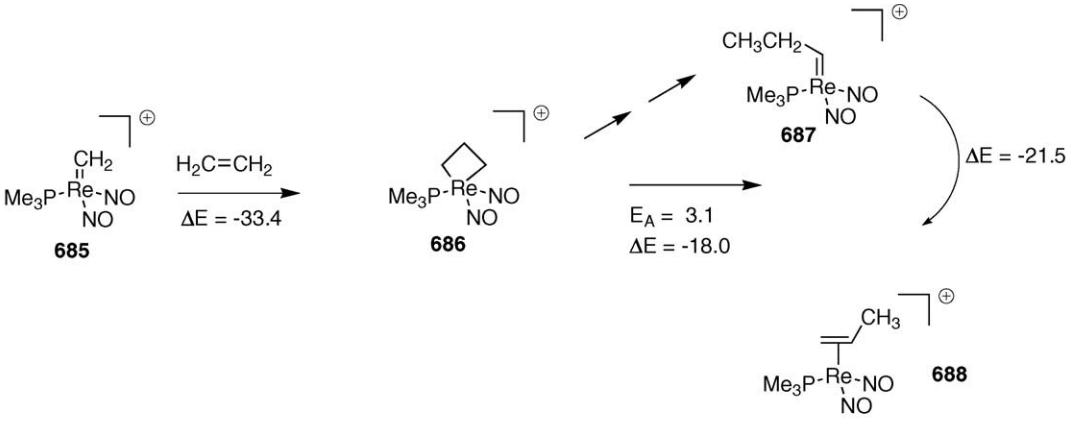
Cationic bridging carbyne–diiron complexes (e.g. **701**, Scheme 73) were prepared by treatment of the bridging Fischer carbene complex **700** with acid [562]. Coupling of this complex with a variety of nucleophiles was reported. Addi-



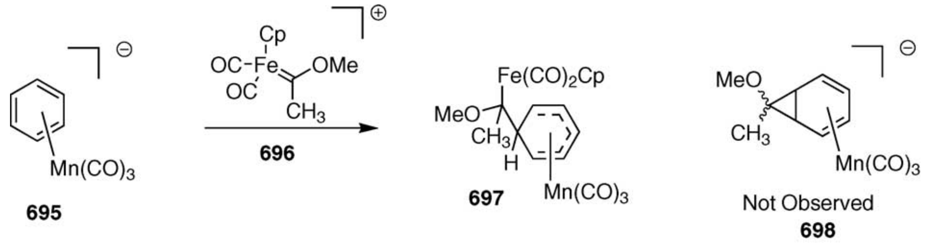
Scheme 69.



Scheme 70.



Scheme 71.



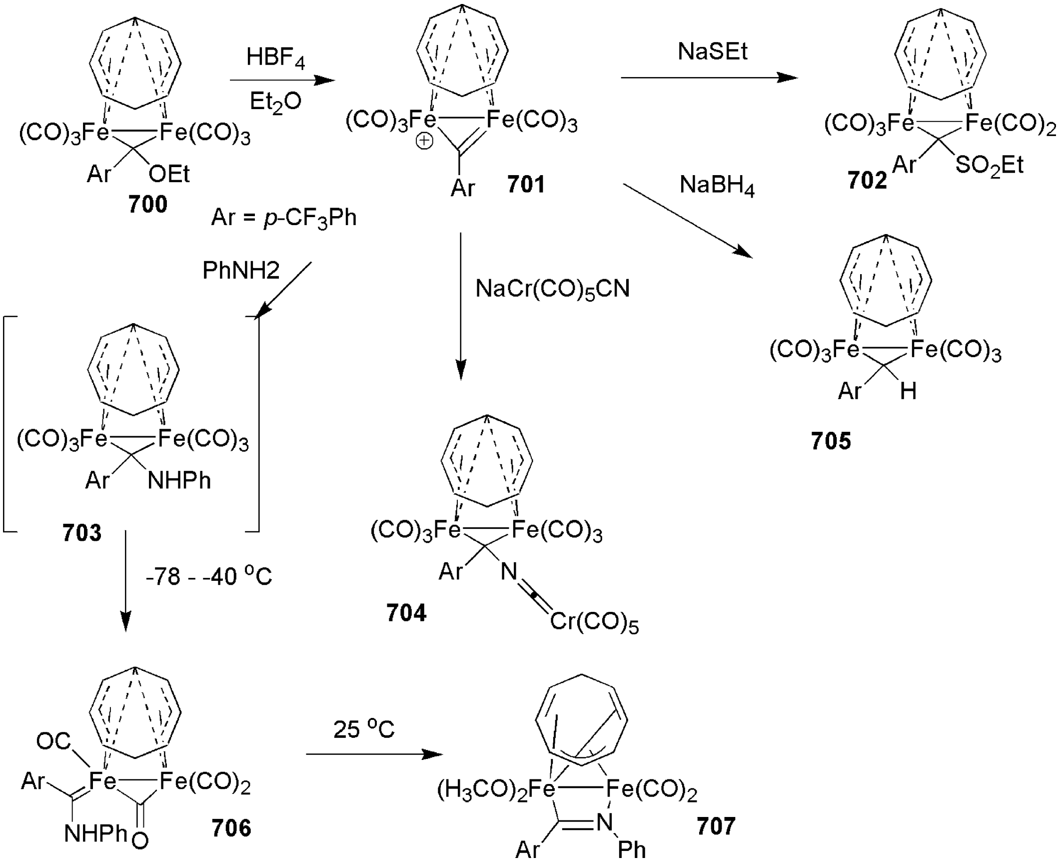
Scheme 72.

tion of a thiolate anion led to the unusual sulfone compound **702**; only the complexes where Ar = *p*-trifluoromethylphenyl underwent this reaction. The cationic complexes were also reactive to hydride reducing agents and metal carbonyl anions. Reaction with an arylamine led to the non-bridging carbene complex **706**, which slowly converts to the nitrogen-bridged structure **707** at room temperature. Reaction with amide anions led to eight-membered ring substitution products or ring opening products [563].

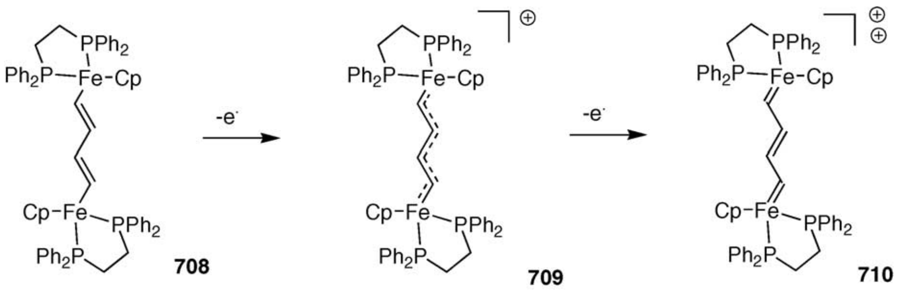
Additional studies of this class of compounds include: (1) formation of dicationic four carbon-bridged dicarbene–iron carbene complexes (e.g. **710**, Scheme 74) via the electrochemical oxidation of butadiene-bridged diiron complex **708** [564] and (2) DFT studies of osmium-induced methane dehydrogenation, which showed that cationic osmium carbene complexes are energetically reasonable intermediates for this process [565]. Formation of bis(carbene)–ruthenium cations from coupling two alkynes with a cationic ruthenium complex accounts for a most of the papers in 2003 that discuss cationic group VIII metal carbene complexes. This major area of investigation has been organized into a separate section (see next section).

#### 2.3.5.2. *Bis(carbene)–ruthenium complexes from coupling of two alkynes and a ruthenium complex.*

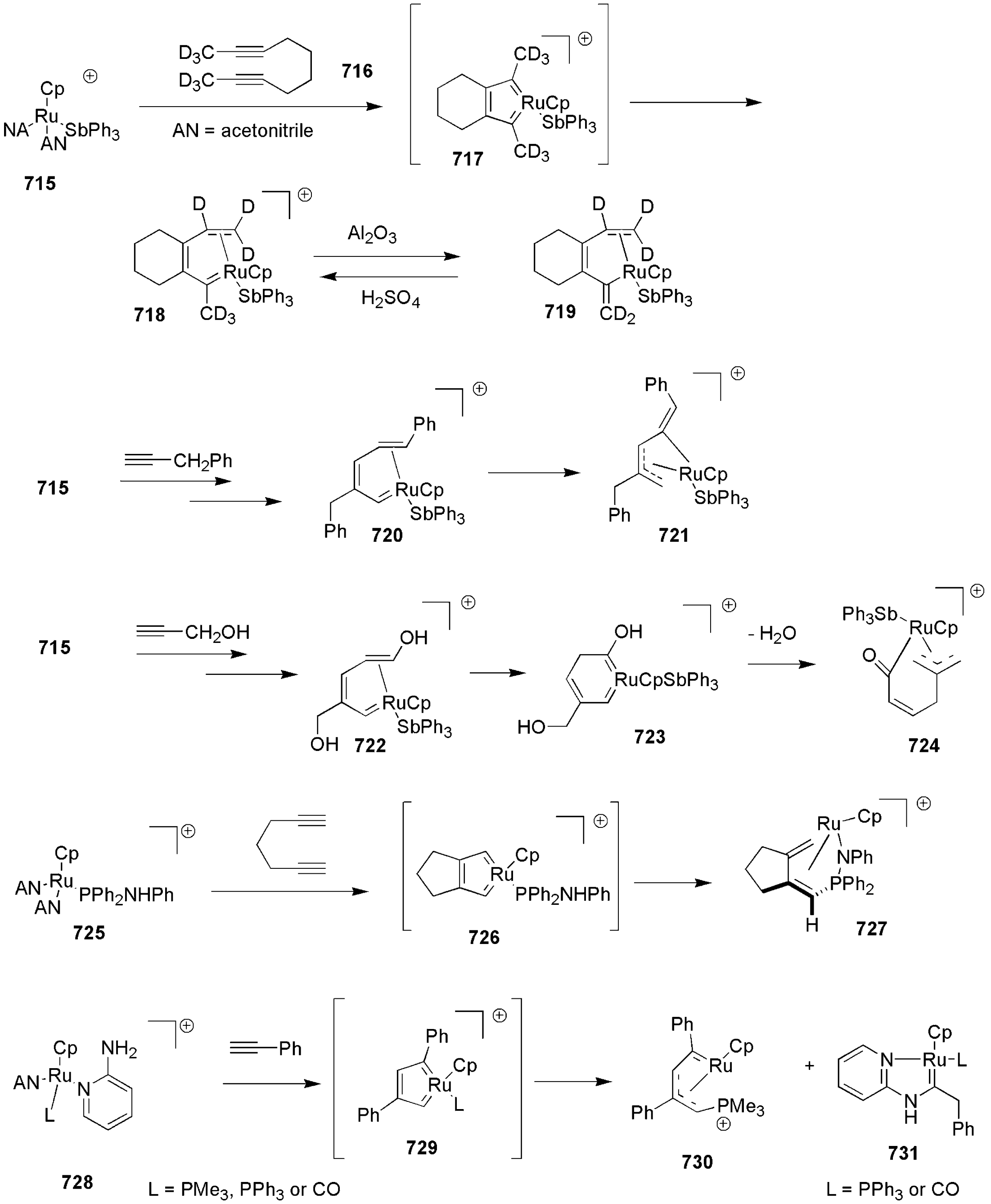
A mechanistic study of the formation of butadienylcarbene complexes (e.g. **718**, Scheme 75) from the coupling of ruthenium complex **715** with dialkynes was reported [566]. Bis(carbene)–ruthenium complex **717** is an important intermediate in this process as well as numerous other processes. The reaction using deuterium-labeled 2,8-decadiyne (**716**) led to dienylcarbene complex **718**, which led to the



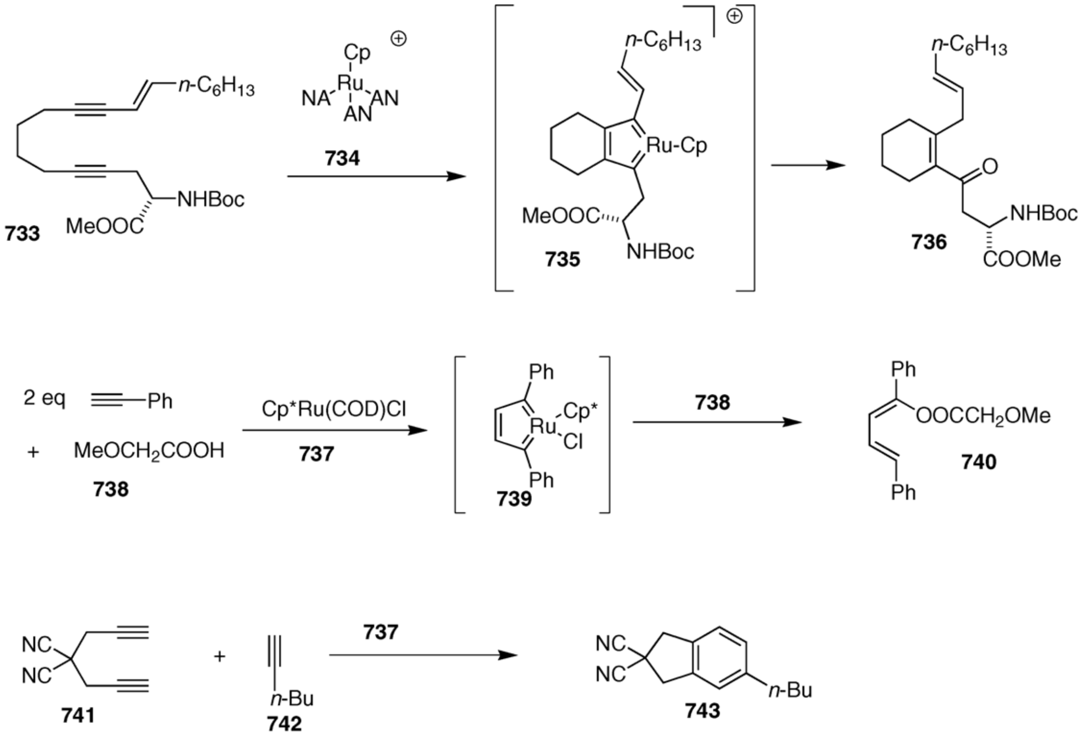
Scheme 73.



Scheme 74.



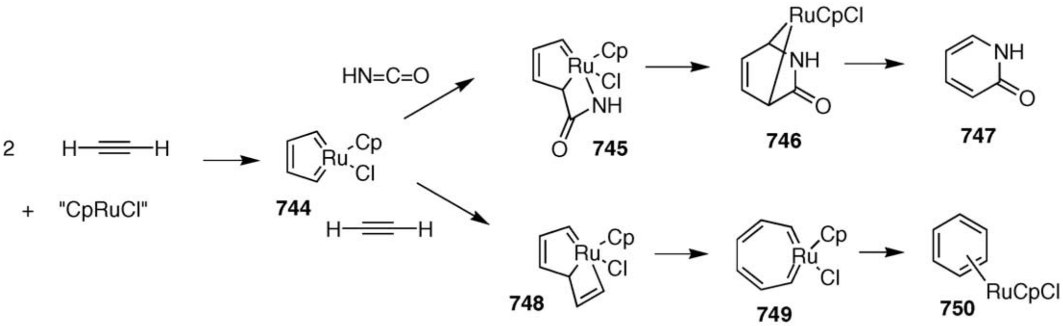
Scheme 75.



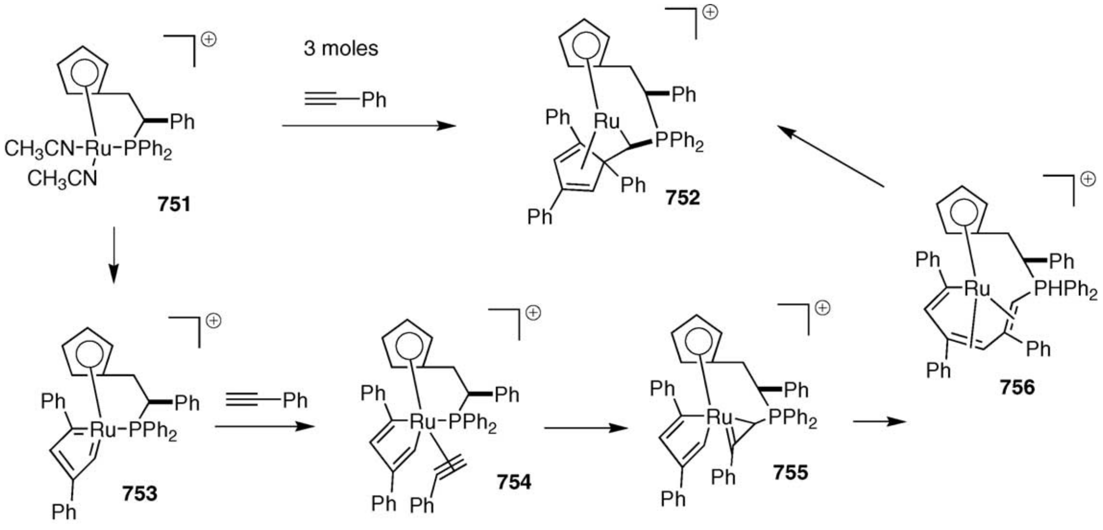
Scheme 76.

hexatrienylruthenium complex **719** upon treatment with aluminum oxide. Protonation of this species regenerated the dienylcarbene complex. A similar process was observed for monalkynes, however the intermediate dienylcarbene complexes underwent different reaction processes. Further reaction of dienylcarbene complex **720** afforded the π-allylruthenium complex **721**. A similar reaction using propargyl alcohol led to π-allyl-acyl complex **724** after proton transfer and elimination of $H_2O$. The proposed mechanisms are supported by DFT calculations. The reaction of the aminophosphine analog **725** led to the diene complex **727** [567]. A similar reaction process was observed using cationic aminopyridine–ruthenium complex **728** [568]. In addition to the expected product **730**, the aminocarbene complex **731** was obtained from CO or triphenylphosphine-ligated **728**. Formation of the carbene complex **731** likely occurs through the intermediacy of a vinylidene complex and does not involve the bis(carbene) complex intermediate **729**. Similar aminocarbene complexes were prepared from the coupling of 2-iminopyridine derivatives with cationic ruthenium–Cp complexes [569]. Polymeric bis(carbene)–ruthenium complexes were prepared from 1,4′-diethynylbiphenyl and found to undergo a reversible one-electron oxidation [570].

Several papers reported on the use of cationic bis(carbene)–ruthenium complex intermediates in synthetic organic chemistry. Ruthenium dicarbene complexes were suggested as intermediates in: (1) hydrative cyclization of diyne **733** (Scheme 76) to produce enone **736** [571]; (2) methanolic (or hydrative) cyclization reaction of diynes [572]; (3) formation of acyloxydienes (e.g. **740**) from 2 mol of a terminal alkyne and a carboxylic acid in the presence of neutral ruthenium complex **737** [573]; and (4) alkyne trimerization reactions (e.g. conversion of diyne **741** and 1-hexyne to indane **743**) [574,575]. Cycloaddition reactions involv-



Scheme 77.



Scheme 78.

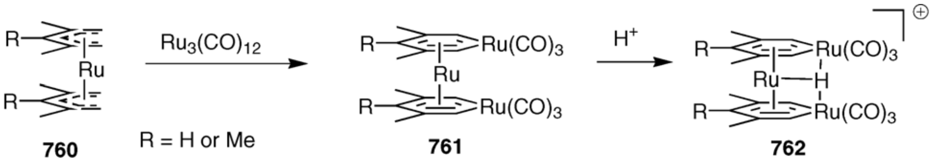
ing bis(carbene)–ruthenium complexes were studied theoretically (Scheme 77), with emphasis on either: (1) three-component synthesis of pyridones from 2 mol of an alkyne and an isocyanate (or isothiocyanate) [576] or (2) alkyne trimerizations [577]. Insertion of the third component to the bis(carbene)–ruthenium complex **744** was proposed to occur through [2 + 2]-cycloaddition with one of the carbene functional groups, resulting in intermediate **745** or **748**. The heterocyclic intermediate **745** converts to the pyridone **747** through migration of the heteroatom to the carbene carbon followed by decomplexation. The carbocyclic intermediate **748** converts to a benzene ring through ring opening to afford metallacycloheptatetraene **749**, followed by carbene coupling.

Alkyne trimerization using Cp-bridged ruthenium phosphine complex **751** (Scheme 78) led to $\eta^4$-cyclopentadiene complex **752** [578]. A mechanism involving formation of the bis(carbene) complex intermediate **753**, followed by ligation of a third alkyne unit and nucleophilic attack by phosphine to afford the $\eta^2$-alkenyl complex **755**, which affords the observed product after migration of a vinylic substituent to the carbene carbon. The energy profile for this reaction pathway was evaluated computationally.

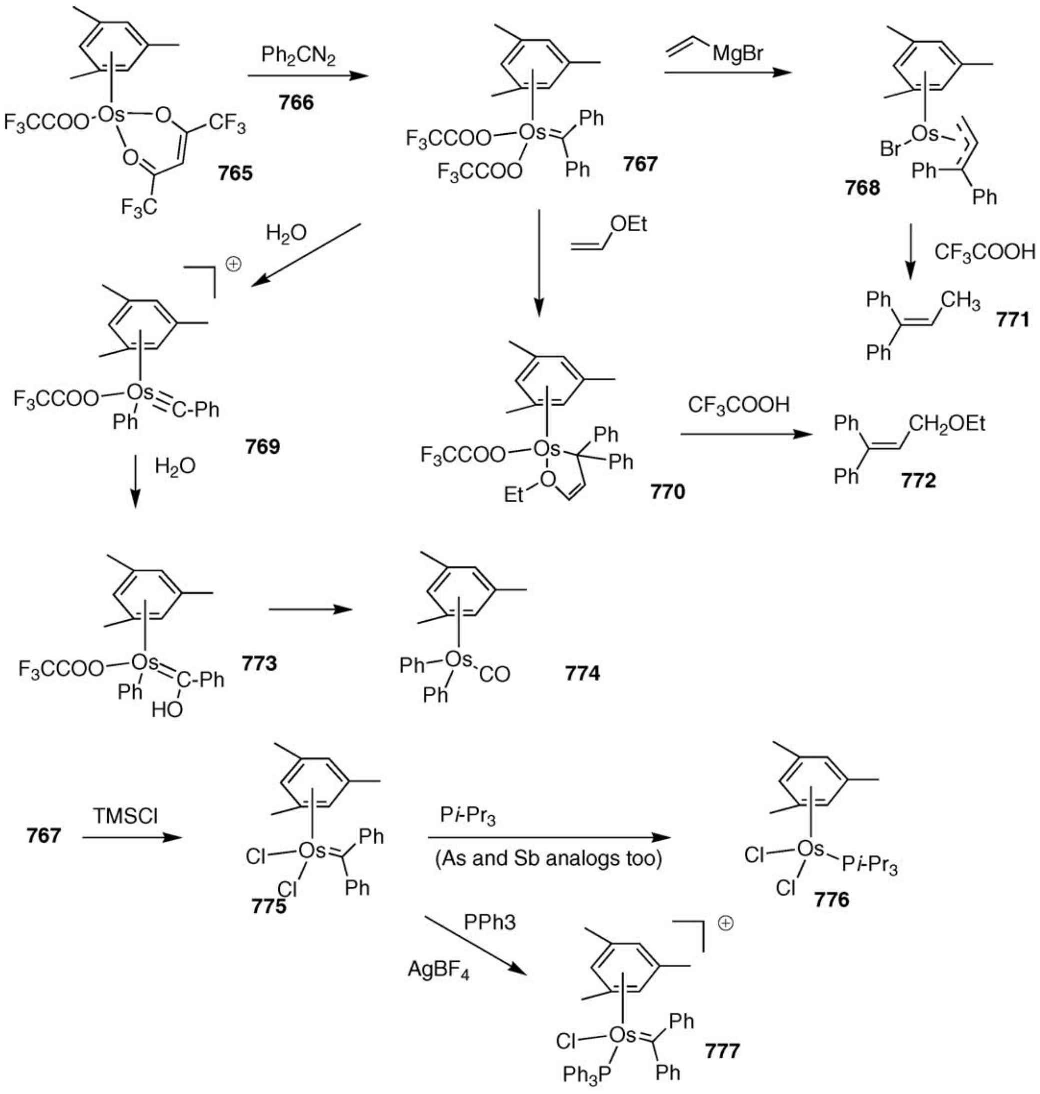
*2.3.5.3. Neutral nonheteroatom-substituted metal–carbene complexes that are not cumulenes.* Numerous additional examples of the synthesis and reactivity of this class of compounds have been presented in the alkene metathesis section. The Grubbs catalysts fall into this classification.

Ruthenabenzene derivatives (**761** and **762**, Scheme 79) were prepared from the reaction of bis(pentadienyl)ruthenium complex **760** with $Ru_3(CO)_{12}$ [579]. Protonation of complex **761** led to hydride-bridged complex **762**. Attempts to decomplex the aromatic ring using a variety of ligand additives was unsuccessful. The ruthenabenzene complexes were studied by DFT. A three-center bonding interaction among the ruthenium atoms of complex **761** was revealed by the electron localization function.

Several osmium carbene complexes (e.g. **767**, Scheme 80) were prepared by reaction of the half-sandwich osmium(II) species (e.g. **765**) with diazo compounds [580]. The analogous reaction with tosylate analogs of **765** led to carbene dimerization products. Several reactions exchanging the trifluoroacetate ligands were reported for complex **767**. Exchange of the halide ligands was also observed upon reaction of the complex with PhMgBr or MeMgI. Reaction with the vinylic Grignard reagent led to the π-allyl complex **768**, which led to the alkene **771** upon protonation. A C–C coupling reaction resulting in complex **770** was also effected by reaction of the carbene complex **767** with ethyl vinyl ether. Treatment of the adduct **770** with trifluoroacetic acid led to allylic ether **772**. The carbonyl diphenyl complex **774** was obtained from reaction of complex **767** with water. A mechanism involving migration of phenyl and displacement of trifluoroacetate was proposed, affording intermediate carbyne complex **769**. Addition of water to the carbyne ligand to afford the acylate **773** followed by migration of the other phenyl then affords complex **774**. Other reactions included displace-



Scheme 79.

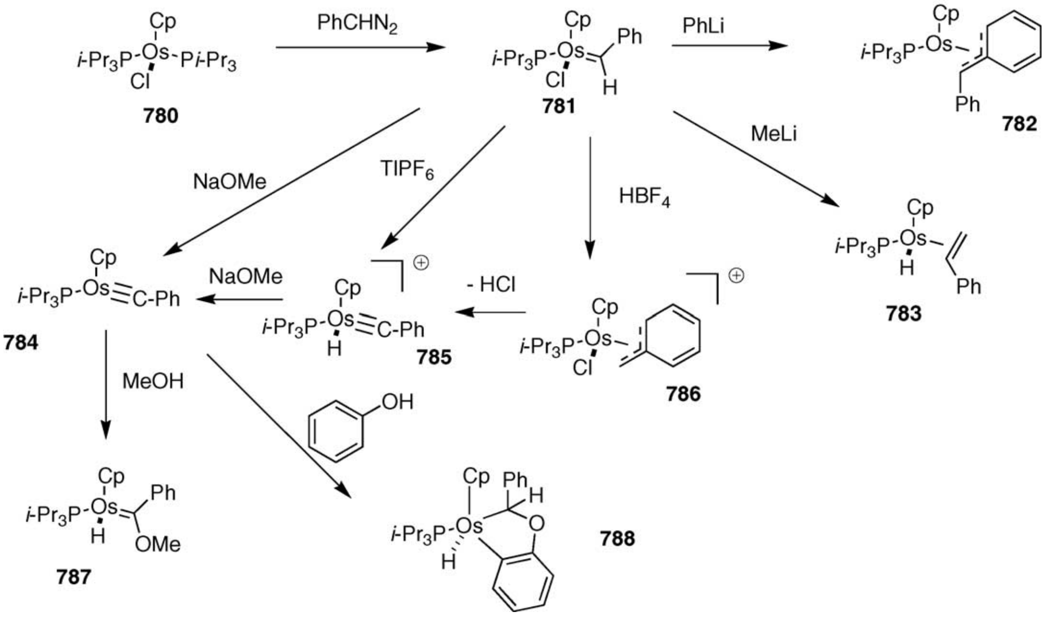


Scheme 80.

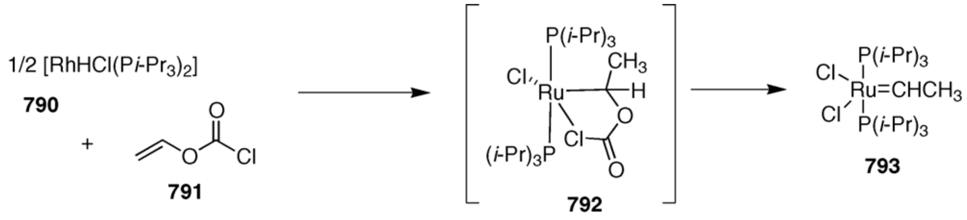
ment of the carbene ligand from the analogous dichloro compound **775** and formation of cationic carbene complex **777**. Related reactivity profile studies were reported other diazo-derived group VII metal complexes [581].

An ambiphilic osmium carbene complex (**781**, Scheme 81) was prepared through reaction of the bis(phosphine) complex **780** with phenyldiazomethane [582]. Reaction of this complex with nucleophilic and electrophilic substances was reported. Reaction with organolithium reagents initially affords adducts from addition of the nucleophilic carbon to the carbene carbon. The initially-formed adduct undergoes secondary processes (i.e. β-hydride elimination or complexation to alkene sites) to achieve coordinative saturation, resulting in **783** (from methyllithium) and **782** (from phenyllithium). Protonation of **781** afforded an $\eta^3$-benzyl complex (**786**), which eliminates HCl to form cationic carbyne complex **785**. Cationic carbyne complex **785** could also be generated through chloride abstraction from carbene complex **781**. A neutral carbyne complex (**784**) was afforded by treatment of complex **781** with sodium methoxide. Reaction of the neutral carbyne complex **784** with methanol led to Fischer carbene–hydride complex **787**. Reaction of the neutral carbyne complex **784** with phenol led to complex **788** via a formation of the Fischer carbene complex, followed by intramolecular C–H activation, followed by hydride migration.

Synthesis of carbene complexes (e.g. **793**, Scheme 82) through the coupling of ruthenium hydride **790** with vinyl ester derivatives was reported [583]. The reaction initially forms a carbene complex, which subsequently undergoes redistribution of the Cl and OOCR substituents. Vinyl chloroformate affords the ruthenium metathesis catalyst **793** and $CO_2$. Osmium analogs afford an alkene complex, which then decomposes to a carbyne complex by way of an observable carbene complex. These processes were evaluated computationally.



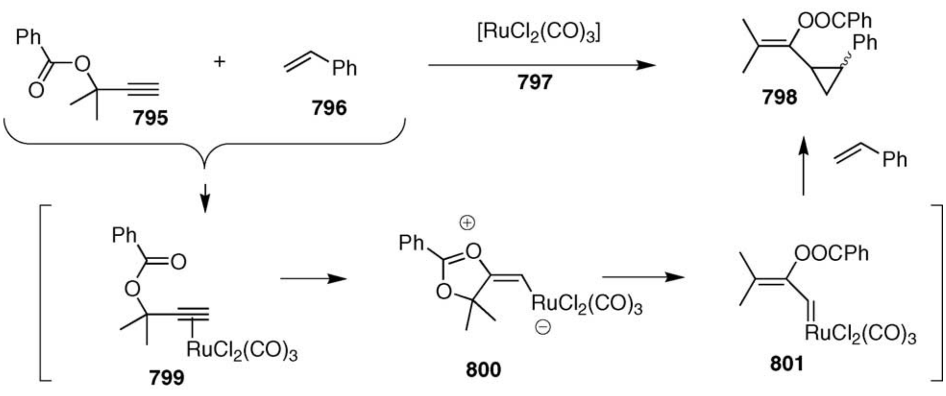
Scheme 81.



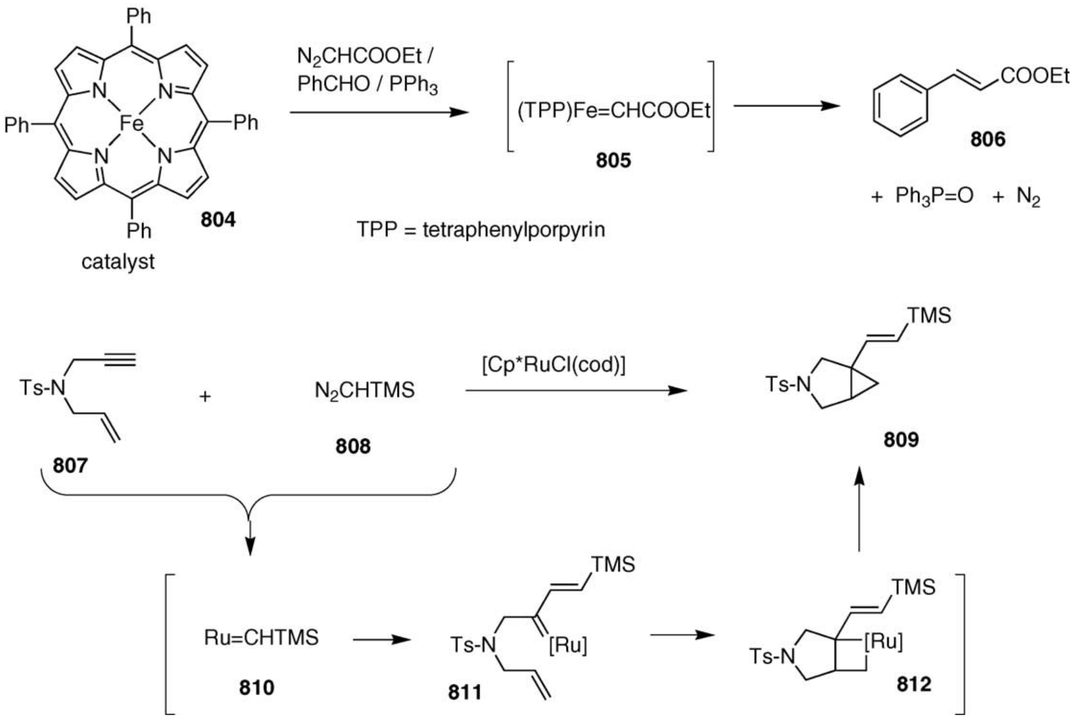
Scheme 82.

Ruthenium–carbene complexes were suggested as intermediates in the novel cyclopropanation reaction employing propargyl esters and alkenes in the presence of a ruthenium catalyst (**797**, Scheme 83) [584,585]. A mechanism involving alkyne complexation, intramolecular nucleophilic attack by the carbonyl oxygen, followed by elimination to afford the cationic alkenylcarbene–ruthenium complex intermediate **801** was proposed. Subsequent reaction of intermediate **801** with styrene lead to the cyclopropanation product **798**.

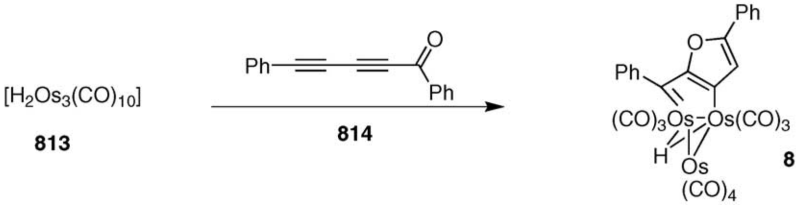
Several papers in 2003 reported on involvement of group VIII metal carbene complexes in metal-mediated reactions of diazo compounds. Coupling of iron porphyrin complex **804** (Scheme 84) with diazo compounds in the presence of triphenylphosphine and ketones or aldehydes led to carbonyl olefination products (e.g. **806**) [586]. A mechanism involving formation of a carbene complex, followed by [2 + 2]-cycloaddition of the carbonyl compound, followed by retro-[2 + 2]-cycloaddition resulting in formation of the alkene and



Scheme 83.

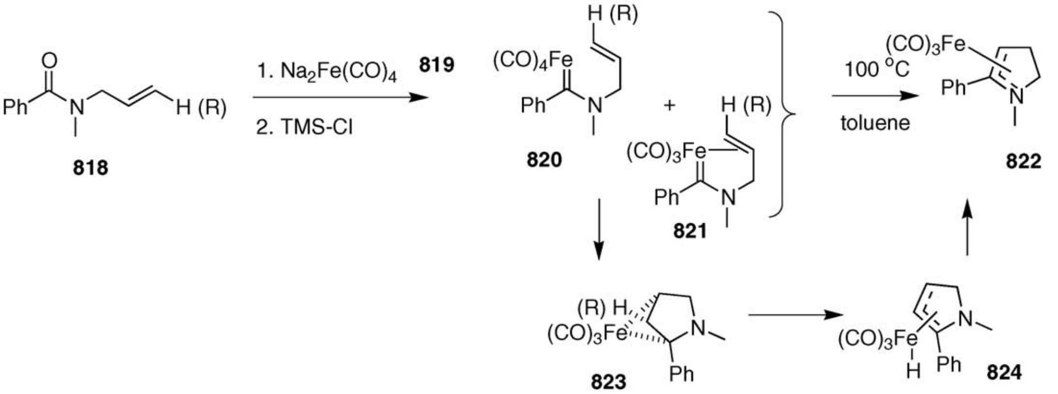


Scheme 84.

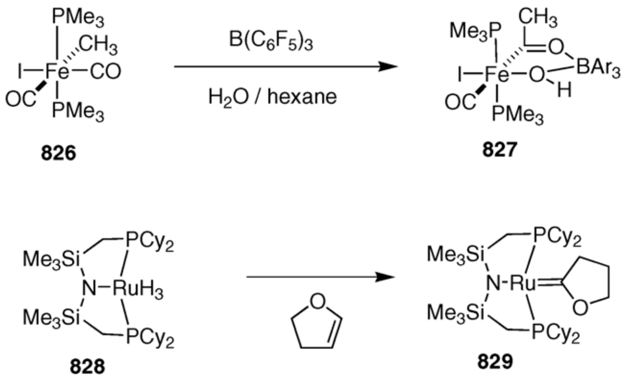


Scheme 85.

an iron oxide was proposed. Triphenylphosphine then deoxygenates the iron oxide to afford triphenylphosphine oxide and regenerate the original iron complex **804**. Formation of bis(carbene–osmium–porphyrin) complexes linked through an oxygen atom was reported [587]. These complexes serve as catalysts for cyclopropanation and C-H insertion reactions. Ruthenium–carbene complexes (e.g. **810** and **811**) were proposed as intermediates in the ruthenium-catalyzed addition/cyclization of enynes and diazo compounds [588]. Ruthenium–carbene complexes were proposed as intermediates in the formation of imine/amine mixtures from the coupling of amines with diazo compounds in the presence of



Scheme 86.



Scheme 87.

a ruthenium complex [589]. Ruthenium–carbene complexes were proposed as intermediates in the cyclopropanation and metathesis reactions observed in the coupling of styrene and diphenyldiazomethane in the presence of a ruthenium complex [590]. Iron(salen) complexes catalyze the cyclopropanation of alkenes by ethyl diazoacetate [591].

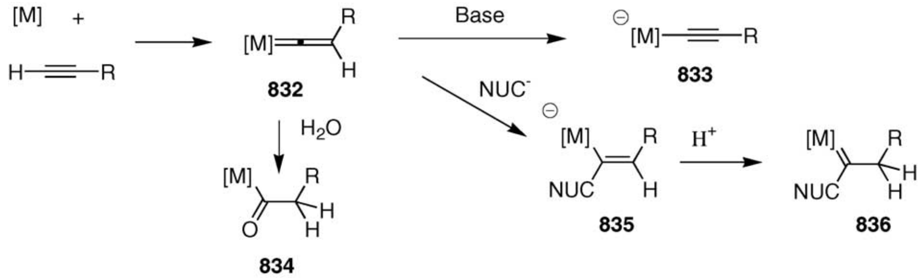
Other studies of carbene complexes in this category are depicted in Scheme 85, and include: (1) formation of osmium carbene complex **815** from osmium dihydride **813** and diyne **814** [592] and (2) X-ray structures for ruthenium porphyrin–carbene complexes [593,594].

*2.3.5.4. Heteroatom-substituted group VIII metal–carbene complexes.* The synthesis and reactivity of *N*-allylaminocarbene–iron complexes (e.g. **820** and **821**, Scheme 86) was reported [595]. Thermolysis of these complexes led to the $\eta^3$-dihydropyrrole complexes (e.g. **822**). A mechanism involving [2 + 2]-cycloaddition, followed by β-hydride elimination and reductive elimination was proposed. This mechanism was supported through deuterium labeling studies. Failure of the reaction for cases where the alkene has a *trans* substituent (*R*) was attributed to steric interaction with the iron group in intermediate alkene insertion product **823**. The reaction processes were evaluated computationally.

Additional examples of heteroatom-stabilized group VIII metal–carbene complexes are depicted in Scheme 87, and include: (1) formation of chelating boryloxycarbene iron complex (**827**) from the reaction of methyliron complex **826** with tris(pentafluorophenyl)borane in a water hexane suspension [596]; (2) direct formation of a carbene complex (**829**) from a ruthenium trihydride (**828**) and dihydrofuran [597]; (3) formation of bridging iron carbyne complexes featuring a bridging selenium ligand [598]; and (4) reaction of bridging aminocarbyne–diiron complexes with various nucleophiles [599,600].

*2.3.5.5. Group VIII metal–vinylidene complexes.* Many examples of the formation of metal vinylidene complexes (**832**, Scheme 88) via coupling of coordinatively unsaturated group VIII metal complexes with terminal or silylated alkynes were reported in 2003. Representative examples are depicted in Fig. 13. Common reaction pathways for these complexes include reaction with nucleophiles to form vinylmetal species (**835**), reaction with alcohols (or amines) to form Fischer carbene complexes (**836**) or water to form metal acyls (**834**), and deprotonation at the β-position to form alkynylmetal complexes (**833**). Other common synthetic routes to metal vinylidenes include addition of electrophiles to metal acetylide complexes (e.g. the reverse of the reaction synthesizing **833**), and treatment of acylmetal complexes with dehydrating agents (i.e. the reverse of the reaction synthesizing **834**).

Specific reports which highlight the reaction pathways of Scheme 88 are depicted in Fig. 13 and include: (1) formation of ruthenium vinylidenes, alkoxycarbene complexes (e.g. **839**), or carbonyl complexes through reaction of cationic ruthenium complex **838** with terminal alkynes [601]; (2) vinylidene complexes featuring vinyldiphenylphosphine ligands [602]; (3) generation of cyclic Fischer carbene complexes from the reaction of ruthenium complexes with 3-butyn-1-ol derivatives [603]; (4) formation of osmium–vinylidene complexes featuring an indenyl ligand (e.g. **840**) [604]; (5) thiophenylvinylidene–iron complexes and analogous binuclear complexes [605]; (6) tris(vinylidene–ruthenium) complexes [606]; (7) formation of and luminescence studies of ruthenium-aminocarbene chelates (e.g. **841**) from the coupling of ruthenium complexes with terminal alkynes in the presence of aniline (and subsequent intramolecular C–H activation to form the Ru-aryl linkage in **841**) [607]; (8) addition of allylic Grignard reagents to ruthenium vinylidene complexes that feature an



Scheme 88.

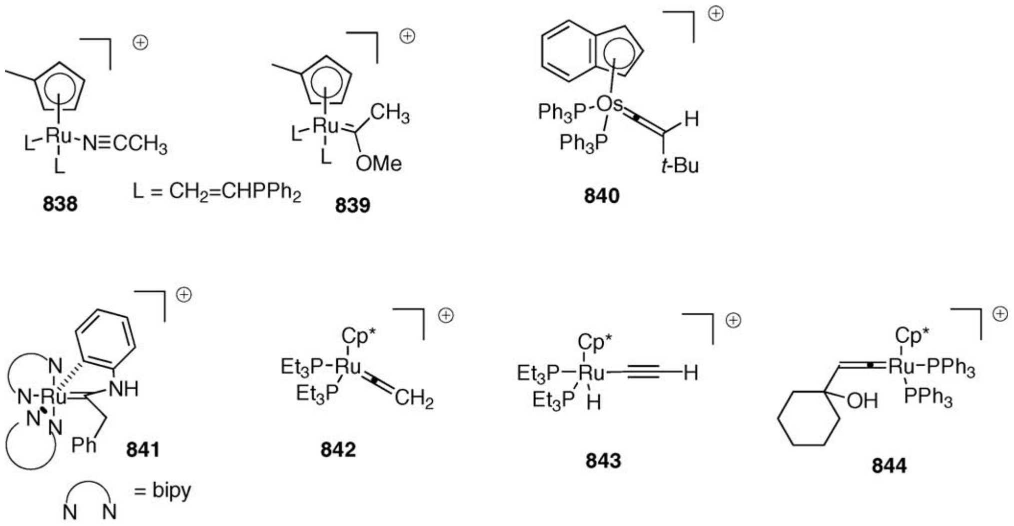
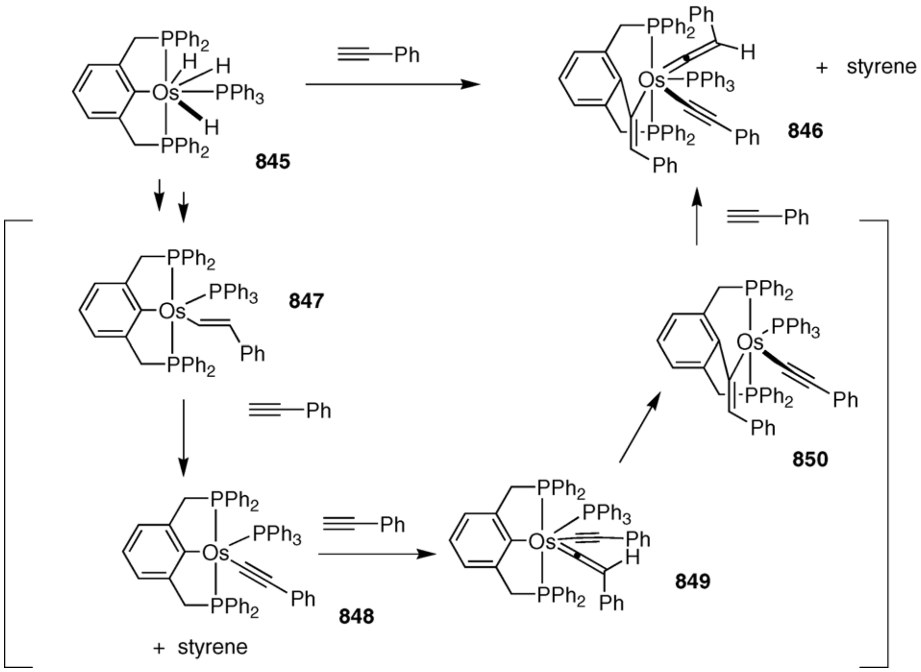


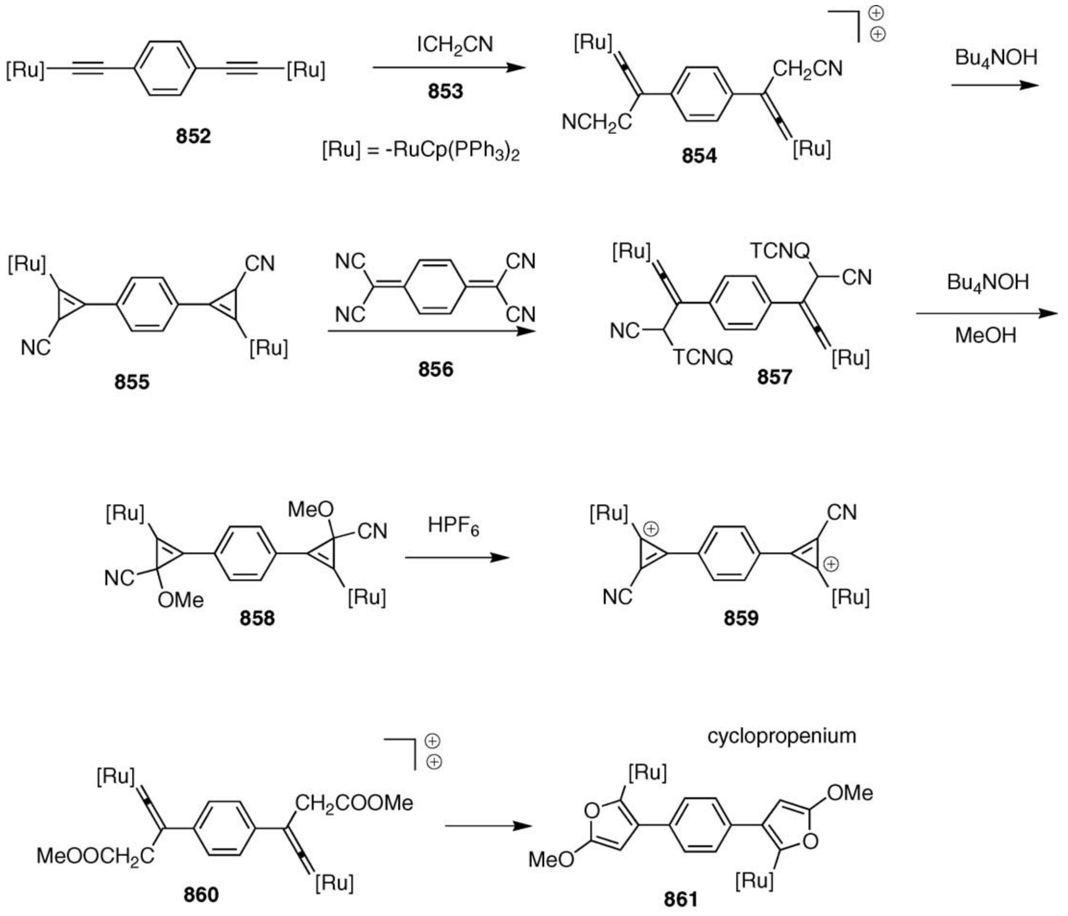
Fig. 13. Representative group VIII metal–vinylidene complexes reported in 2003.

indenyl ligand [608]; and (9) stepwise formation and X-ray characterization of vinylidene complex **842** and precursor hydrido–alkynyl complex **843** [609]. Many papers in 2003 invoke the processes in Scheme 88 for generation of vinylidene–metal complex reaction intermediates, including: (1) ruthenium-catalyzed conversion of propargyl alcohols to alkenylphosphines via nucleophilic addition of $Ph_2PH$ to an intermediate γ-hydroxyvinylidene complex (e.g. **844**) followed by protonolysis of the C-Ru bond [610] and (2) ruthenium-catalyzed addition of carboxylic acids to the triple bond of terminal alkynes [611].

The coupling of osmium trihydride complex **845** (Scheme 89) with terminal alkynes was reported [612]. The reaction with excess phenylacetylene led to the complex **846**. The proposed mechanism involves hydrogenation of 1 mol of phenylacetylene to provide styrene and a monohydride, which then adds another mole of phenylacetylene to provide the styryl complex **847**. Reaction of styryl complex **847** with another mole of phenylacetylene affords styrene and alkynyl complex **848**. Reaction of complex **848** with another mole of phenylacetylene affords the vinylidene complex **849**, which affords the observed product after aryl



Scheme 89.



Scheme 90.

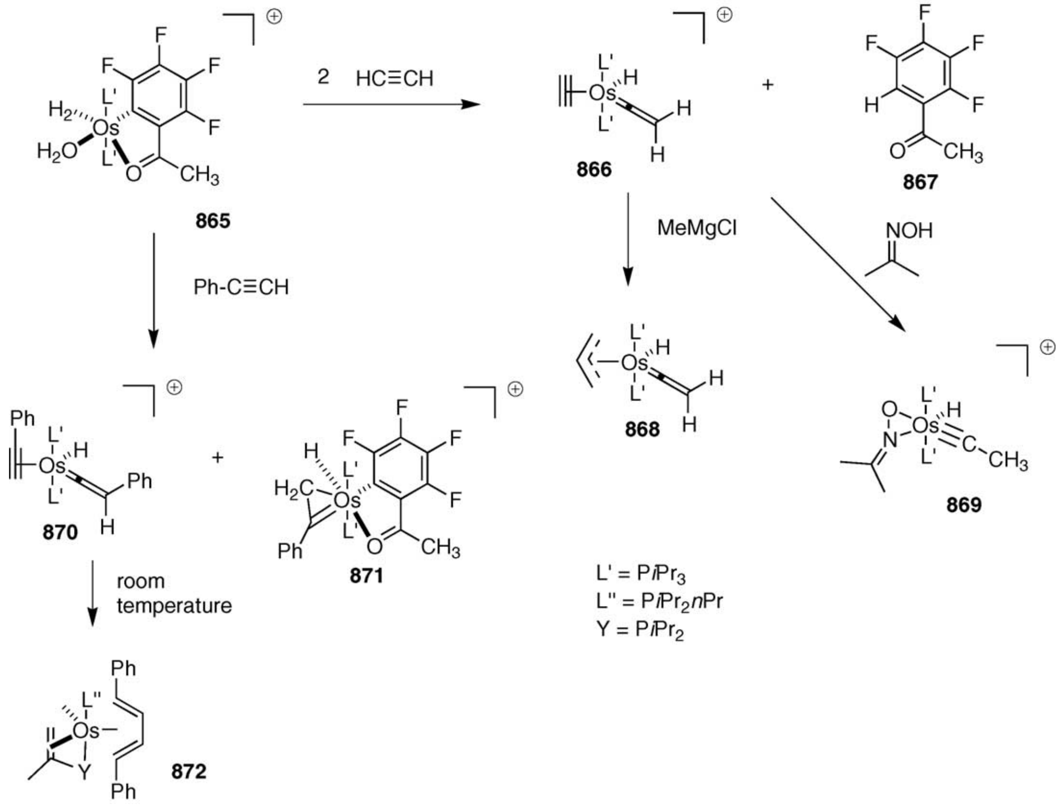
coupling and reaction with another mole of phenylacetylene.

The conversion of dicationic bis(ruthenium–vinylidenes) (e.g. **854**, Scheme 90) to the corresponding cyclopropenyl complexes (e.g. **855**) by deprotonation followed by cyclization was reported [613]. A net oxidation of the cyclopropenyl group was effected by treatment of the cyclopropenyl complex with tetracyanoquinonedimethane to afford the vinylidene complex **859**. Treatment with methanol and base effects ring closure and oxidation to afford the cyclopropenyl complex **858**, which affords the aromatic cation **859** upon treatment with acid. Trinuclear analogs of the compounds in Scheme 90 were also reported. Furylruthenium complexes (e.g. **861**) were obtained through a similar sequence using $\alpha$-haloesters–vinylidenes (e.g. **860**).

The reaction of chelated osmium dihydrogen complex **865** (Scheme 91) with alkynes was reported [614]. Reaction with acetylene afforded $\pi$-alkyne–vinylidene–hydride complex **866**. A mechanism involving reductive elimination from the dihydride tautomer to afford ketone **867** and $[OsH(H_2O)(PiPr_3)_2]^+$, followed by complexation of 2 mol of acetylene (one as a vinylidene) was proposed. Coupling of complex **865** with methylmagnesium chloride led to the $\pi$-allyl complex **868**. Reaction with acetone oxime led to the carbyne complex **869**. Reaction of complex **865** with phenylacetylene led to the vinylidene–alkyne complex **870** and the $\eta^2$-alkenyl complex **871**. The vinylidene complex decomposed to the $\eta^4$-diphenylbutadiene complex **872**, which features structural changes within the phosphine ligands.

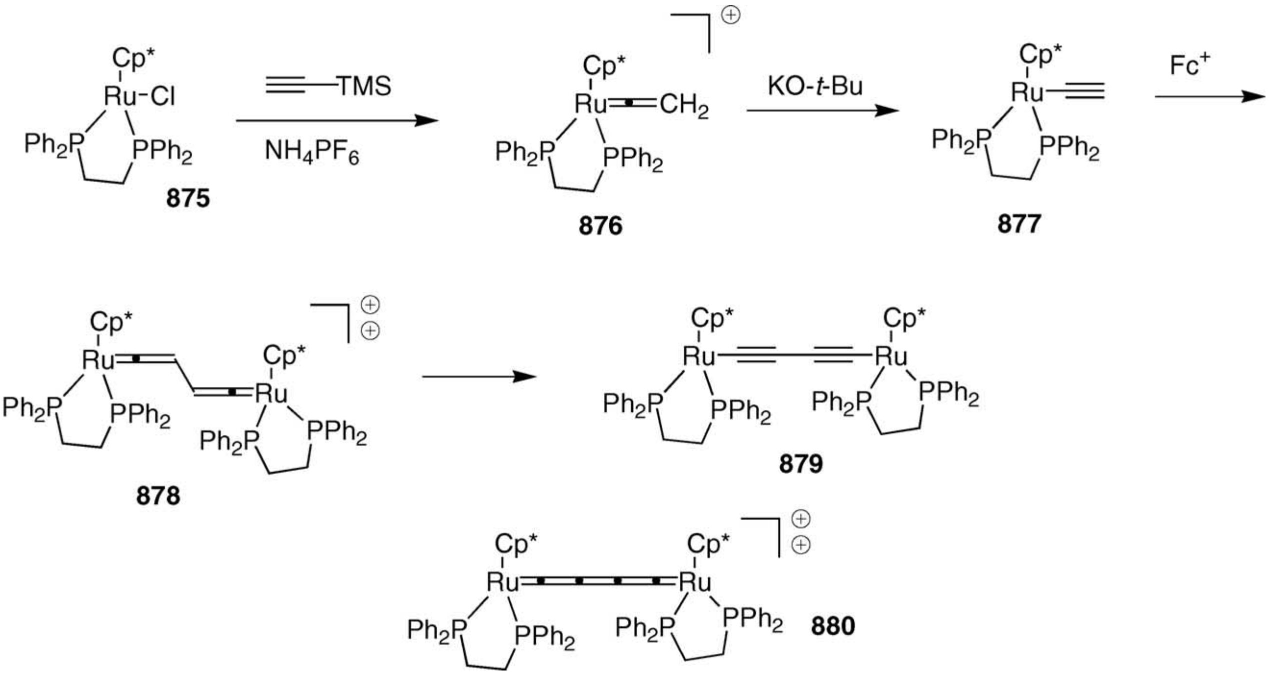
Butadiyne-bridged diruthenium compounds (e.g. **879**, Scheme 92) were prepared through a reaction sequence involving formation of a vinylidene complex (**876**), followed by deprotonation to afford an alkyne complex (**877**), followed by oxidative coupling to afford dicationic bis(vinylidene–ruthenium) complex (**878**), followed by treatment with base to afford all-carbon-bridged structure **879** [615]. The electrochemistry of diruthenium–dialkyne complex **879** was studied. Higher oxidized forms of **879** were formulated as ruthenium–carbon multiply-bonded structures (e.g. **880**).

Ruthenium–vinylidenes (e.g. **885** and **890**, Scheme 93) have also been proposed as intermediates in the conversion of alkynylstyrenes to the naphthalenes where the group on the alkene has migrated (e.g. **884** and **889**) [616]. The mechanisms depicted in Scheme 93 have been proposed for these transformations. Migration of the groups is due to 1,2-shifts in proposed carbocation intermediates.

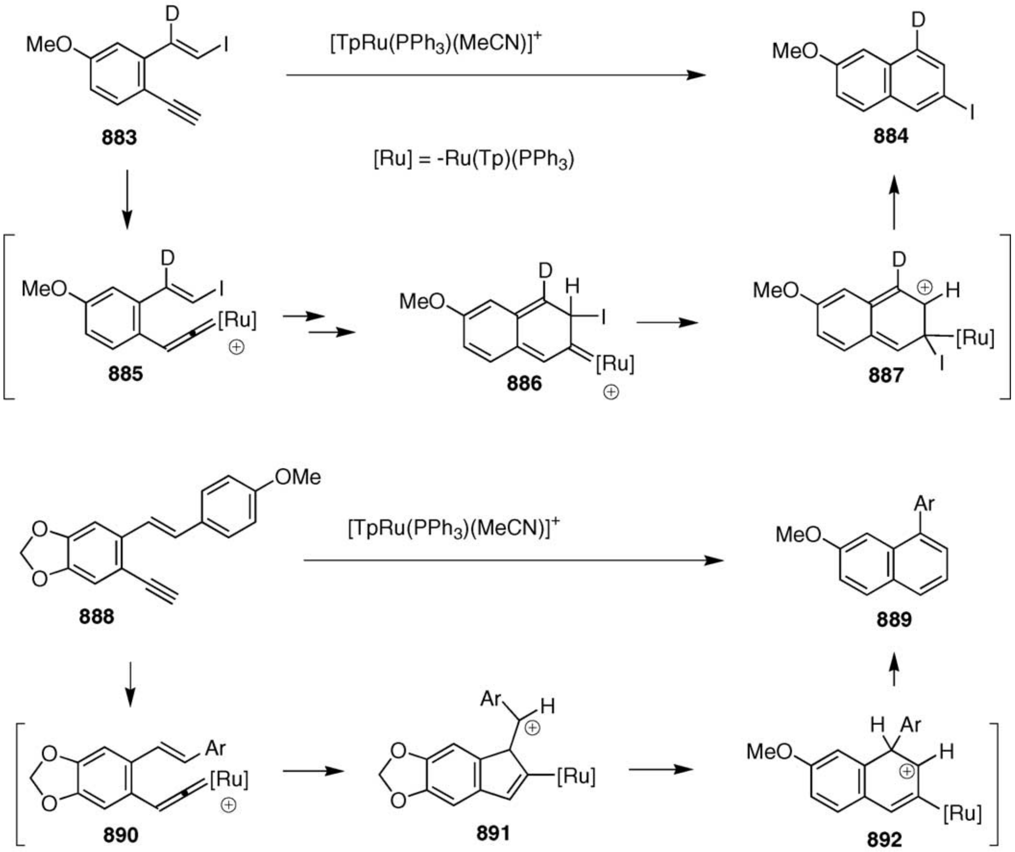


Scheme 91.

Additional reaction processes that involve metal vinylidenes are depicted in Scheme 94 and include: (1) formation of a [2 + 2]-cycloaddition product (**896**) through mild thermolysis of ruthenium–vinylidene complex **895** [617]; (2) ring expansion of complex **897** to **898** via ruthenium vinylidenes (e.g. **899**/**900**) [618]; (3) ruthenium-catalyzed alkenylation of pyridine by silylacetylenes, where [2 + 2]-cycloaddition involving a ruthenium vinylidene complex and the C–N dou-

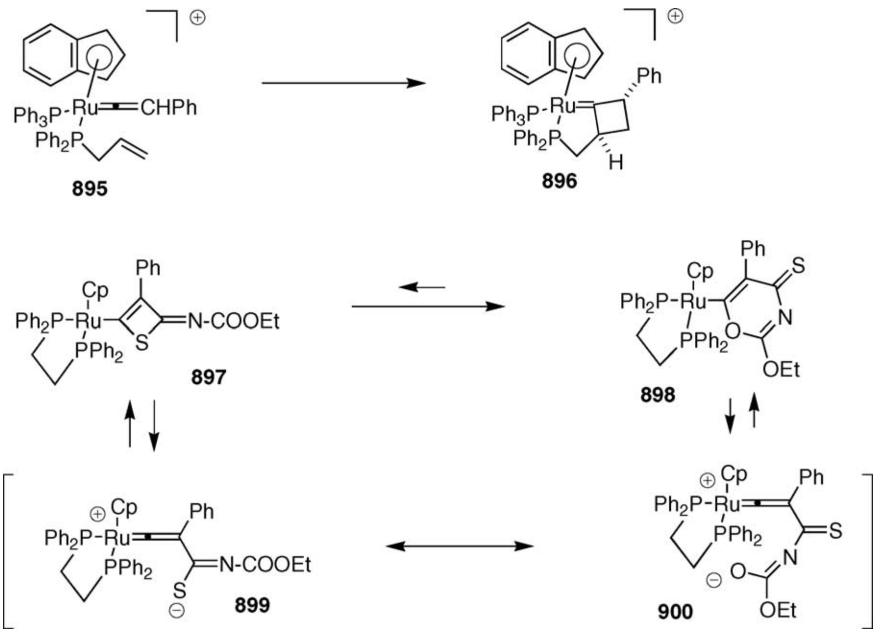


Scheme 92.

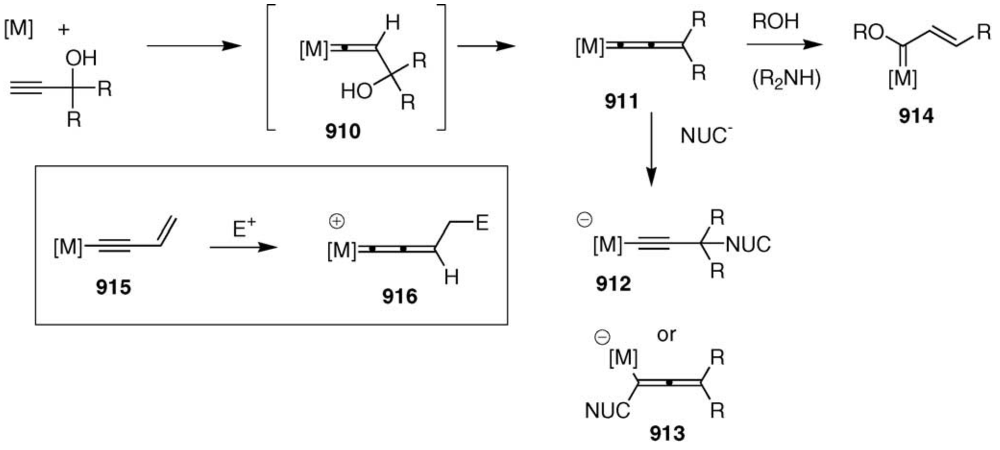


Scheme 93.

ble bond of pyridine is a key mechanistic event [619]; (4) hydration of alkynylruthenium complexes that feature nitrosyl ligands to form the metal-enolate derivative, which occurs via formation of a ruthenium–vinylidene followed by conversion to the π-alkyne complex, followed by Markovnikov hydration of the alkyne [620]; and (5) use of ruthenium–vinylidene complexes as catalysts for the addition of carboxylic acids to alkynes in competition with alkyne trimerization [621].



Scheme 94.



Scheme 95.

*2.3.5.6. Group VIII metal complexes of higher cumulenes.* Metal-higher cumulene complexes (**911**, **916**, Scheme 95) are produced from the coupling of coordinatively unsaturated group VIII metal complexes with propargyl alcohols (usually those that contain no hydrogens β- to the OH-group), or by addition of electrophiles to the δ-carbon of alkenylethynyl–metal complexes (**915**). A variety of reaction processes of Group VIII metal–cumulene complexes were reported in 2003. Common reaction pathways for these complexes include reaction with nucleophiles at the γ-position, resulting in alkynylmetal complexes (**912**), or attack at the γ-position, resulting in allenylmetal complexes (**913**). Reaction with alcohols or amines can lead to α,β-unsaturated Fischer carbene complexes (**914**). Representative examples of this class of compounds are depicted in Fig. 14.

Specific reports which highlight the reaction pathways depicted in Scheme 95 are depicted in Fig. 14, and include: (1) preparation of cationic iron allenylidene complexes (e.g. **917**) and addition of nucleophiles to the γ-carbon of the complexes [622]; (2) addition of chiral nucleophiles to cationic allenylidene–metal complexes [623]; (3) chiral and optically pure allenylidene–metal complexes (e.g. **918**) [624]; (4) preparation of cationic ruthenium allenylidene complexes followed by studies of their electrochemistry and spectroelectrochemistry [625]; (5) formation of cationic

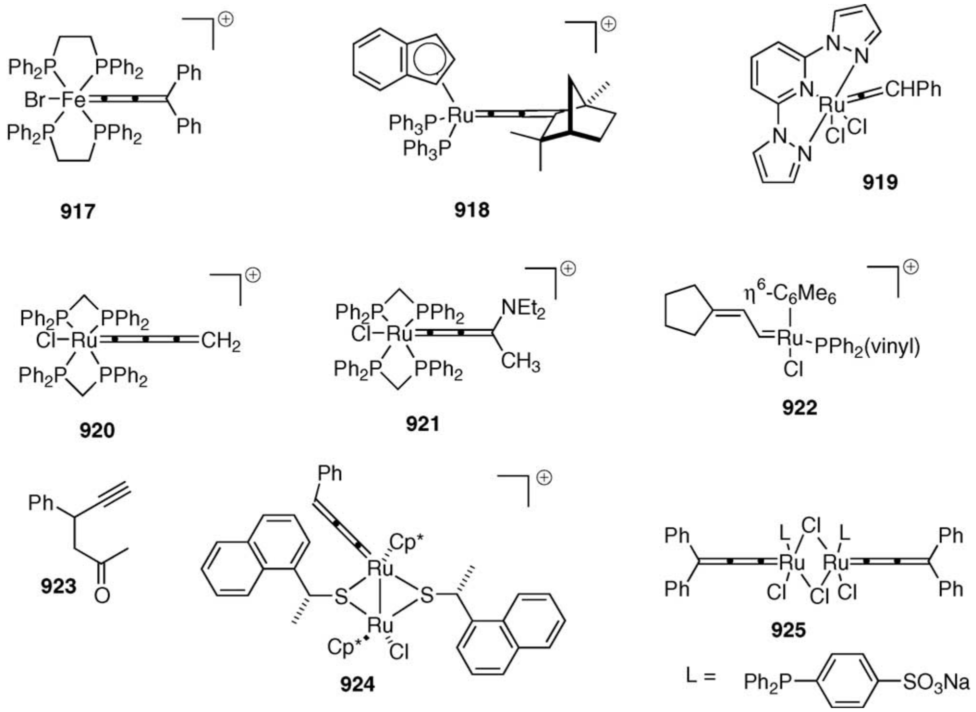
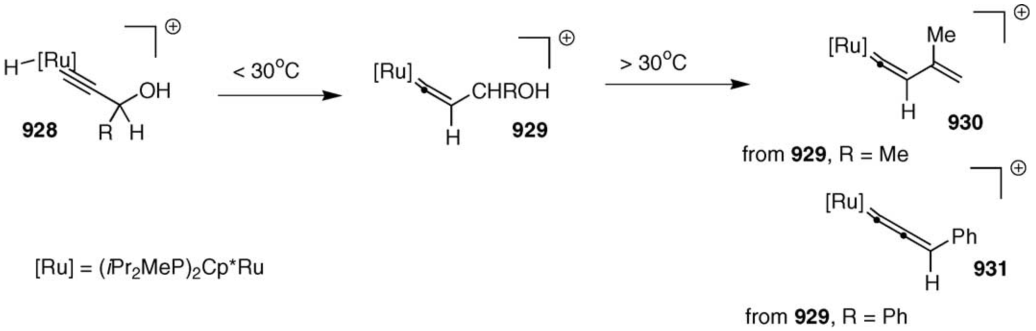


Fig. 14. Representative group VII metal-higher cumulene complexes and products derived therefrom reported in 2003.

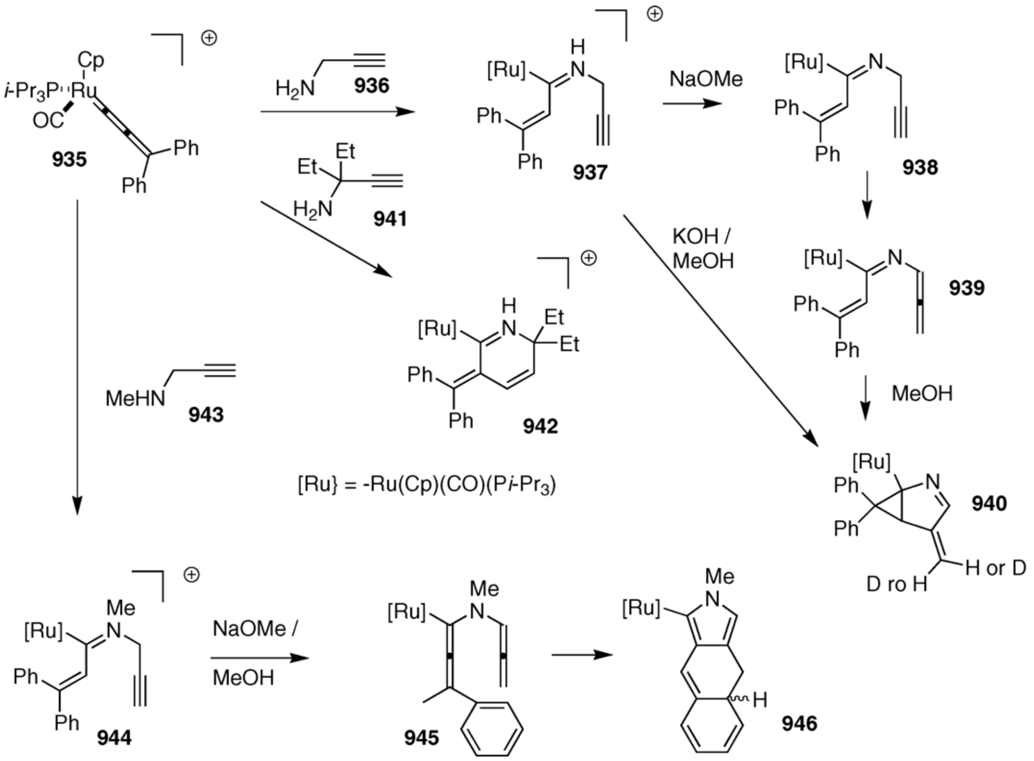


Scheme 96.

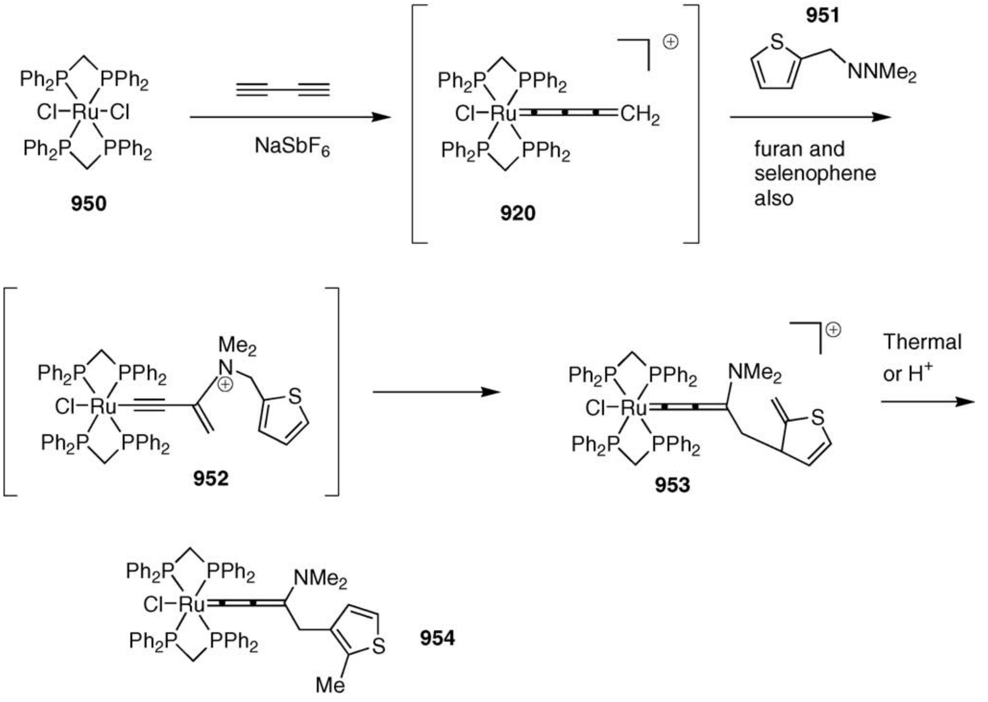
ruthenium allenylidenes (and vinylidenes) that feature chelating phosphine–pyrazole ligands [626]; (6) formation of ruthenium allenylidene and vinylidene complexes featuring 2,6-bis(pyrazolyl)pyridine ligands (e.g. **919**) [627]; (7) formation of ruthenium allenylidene complexes for luminescence studies [628]; (8) formation of iron–allenylidene complexes from 1-ethynylcyclohexanol and failure to form analogous complexes from propargyl alcohol or vinylidene complexes from homopropargyl alcohols [629]; (9) formation and Mössbauer studies of cationic iron allenylidene complexes [630]; and (10) reaction of butatrienylidene–ruthenium complex **920** with amines, which affords γ-aminoallenylidene complexes (e.g. **921**) through attack at the γ-position followed by proton transfer [631]. Several processes reported in 2003 invoke metal-higher cumulene complexes as intermediates, including: (1) formation of α,β-unsaturated Fischer carbene complexes (e.g. **922**) from a ruthenium complex and propargylic alcohols [632,633]; (2) moderately enantioselective synthesis of 4-alkyne–ketones (e.g. **923**) from propargyl alcohols and acetone through nucleophilic addition to chiral allenylidene complex intermediates (e.g. **924**) [634]; and (3) catalysis of enol ether exchange processes using binuclear allenylidene complex **925** [635].

Various unstable alkynylruthenium hydrides (e.g. **928**, Scheme 96) spontaneously transformed into either the vinylidene or hydroxyvinylidene (e.g. **929**) complexes at or below −30 °C [636]. The hydroxyvinylidene complexes could be transformed either to the corresponding alkenylvinylidene (e.g. **930**) or allenylidene (e.g. **931**) complexes upon further reaction at room temperature.

The coupling of ruthenium allenylidene complex **935** (Scheme 97) with various propargylamines followed by base-



Scheme 97.



Scheme 98.

induced cyclization processes was reported [637]. Treatment with primary propargylamines (e.g. **936**) led to the aminocarbene complex (**937**), which affords stable iminylruthenium complex **938** upon monodeprotonation. Subsequent treatment with methanol results in the cyclopropylruthenium complex **940**. Treatment of the initially-formed complex **937** directly with excess base lead to the cyclopropyl complex **940** directly. The analogous reaction employing propargylamine **941**, which features no propargyl hydrogens, affords the six-membered ring compound **942**. Reaction of allenylidene **935** with the secondary amine **943** led to the tricyclic pyrrole derivates **946** by a process involving conversion to the diallenyl complex **945** followed by intramolecular Diels–Alder reaction. Reaction of complex **935** with diallylamines was also reported [638].

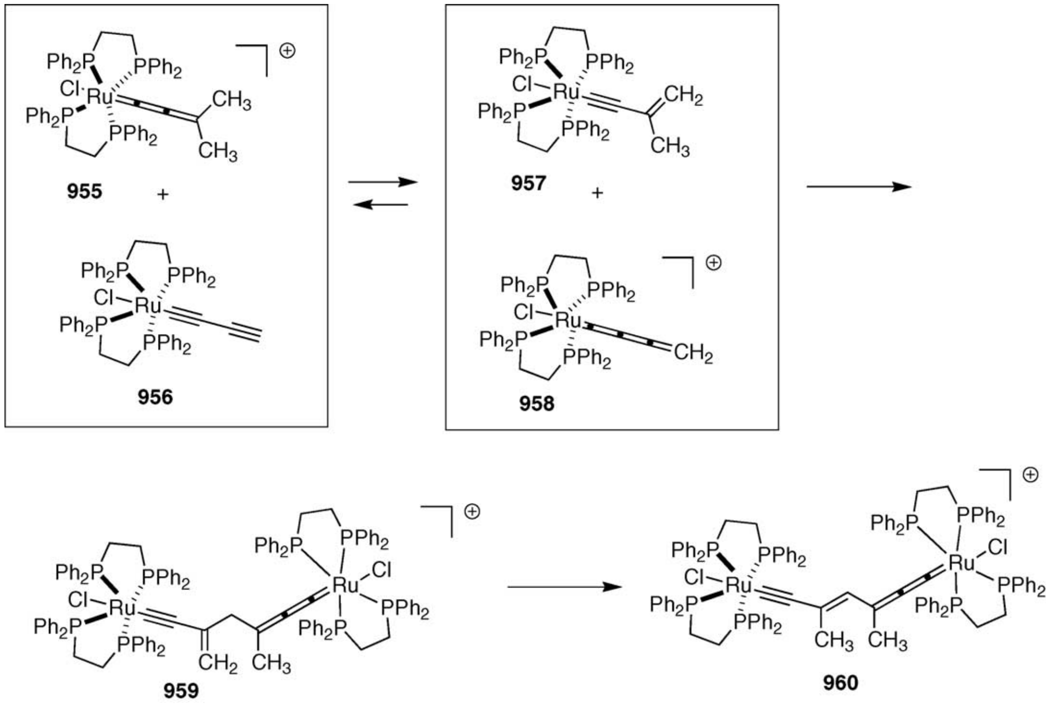
The coupling of in situ-generated butatrienylidene complex **920** (Scheme 98) with heteroarylamines (e.g. **951**) was reported [639]. Coupling of **920** with amine **951** affords a heterocycle-substituted allenylidene complex (**954**). A mechanism involving nucleophilic attack at the γ-position to afford enynylruthenium complex **952** followed by [3,3]-sigmatropic rearrangement was proposed. Thermolysis (85 °C) or exposure of unstable compound **953** to acid causes isomerization to the heteroaromatic ring system.

Coupling of allenylidene complex **955** (Scheme 99) and butadiynylruthenium complex **956** led to highly conjugated diruthenium complex **960** [640]. The proposed mechanism involves proton transfer followed by coupling of the alkenylalkynyl complex **957** at the γ-carbon of the resulting butatrienylidene complex **958** followed by double bond isomerization. Oxidation-induced isomerization of butadiynylruthenium complexes through [2 + 2]-cycloaddition was also reported.

Ruthenium–allenylidene complexes (e.g. **966**) were suggested as intermediates in the cycloisomerization of alkene–propargyl alcohols (e.g. **963**) catalyzed by diruthenium complex **964** [641]. The proposed mechanism of this reaction involves formation of an allenylidene complex (**966**) followed by nucleophilic attack of the alkene at the γ-position of the allenylidene ligand to afford a carbocation (**967**), followed by internal transfer of a proton to ruthenium to afford the observed product **965** (Scheme 100).

Cationic ruthenium allenylidene complexes (e.g. **973**) were proposed as intermediates in the conversion of propargyl alcohols (e.g. **970**) into the one-carbon depleted alkenes (e.g. **972**) catalyzed by ruthenium complex **971** [642]. The proposed mechanism involves formation of allenylidene complex **973**, followed by hydration to form the hydride-α,β-unsaturated acylruthenium complex **974**, followed by decarbonylation and reductive elimination (Scheme 101).

Cationic ruthenium cumulenylidene complexes of general structure $Cl(PH_3)_4Ru{=}C{=}C{=}C({=}C)_n{=}CH_2^+$ were studied by DFT [643]. The following features were noted. The complexes featuring an even number of carbons were generally less stable than those featuring an odd number of carbons. The charge distributions and MO's suggest that nucleophiles are most likely to attack at the odd numbered carbons excluding carbon 1. Electrophiles are most likely to attack the even numbered carbons except for the $CH_2$ at the end of the chain. The one- and two-electron reduction products were also examined. Theoretical studies of butadiyne-bridged diruthenium and diiron complexes were reported [644]. These studies sug-



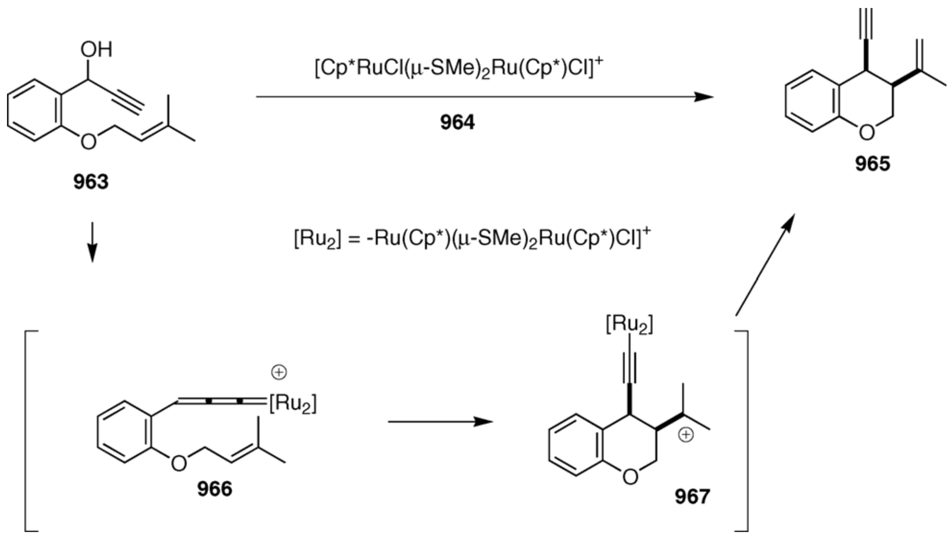
Scheme 99.

gest that the dications are cumulene-bridged structures, while the tetracations are bis(carbyne) complexes.

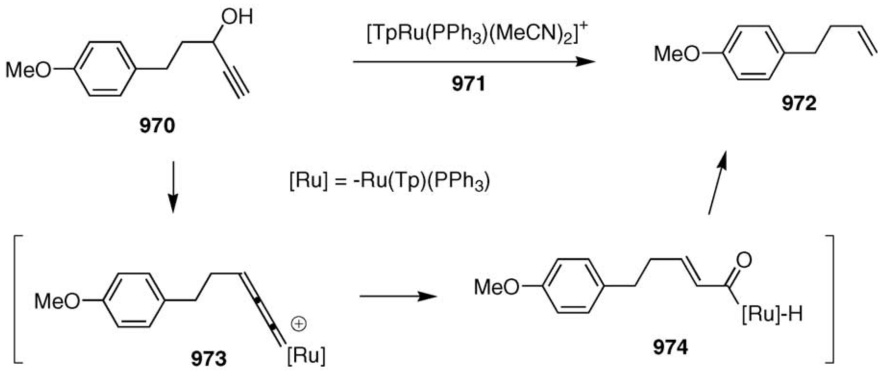
### *2.3.6. Group IX metal–carbene complexes*

*2.3.6.1. Simple carbene complexes.* Chelated iridium carbene complexes (e.g. **981** and **983**, Scheme 102) were prepared by the direct reaction of in situ-generated complex **979** with alkyl phenyl ethers or *N*,*N*-dimethylaniline [645]. This process involves initial C–H activation *ortho* to the alkoxy group, followed by intramolecular C–H activation α to the ether, reductive elimination of benzene, and α-hydride elimination. The reaction works for both anisole and ethyl phenyl ether, despite the presence of a β-hydrogen for elimination in the latter compound. Two carbene complexes, **983** and **984** were obtained from a similar reaction employing *N*,*N*-dimethylaniline.

The coupling of iridium complex **988** (Scheme 103) with the organolithium reagent derived from iodide **987** led to either iridabenzvalene **989**/**990** or iridabenzene **993** (or mixtures thereof), depending upon the phosphine ligand [646]. Complex **988** (L = $PEt_3$) led exclusively to the iridabenzvalene derivative, while analogous complex where L = $PPh_3$



Scheme 100.



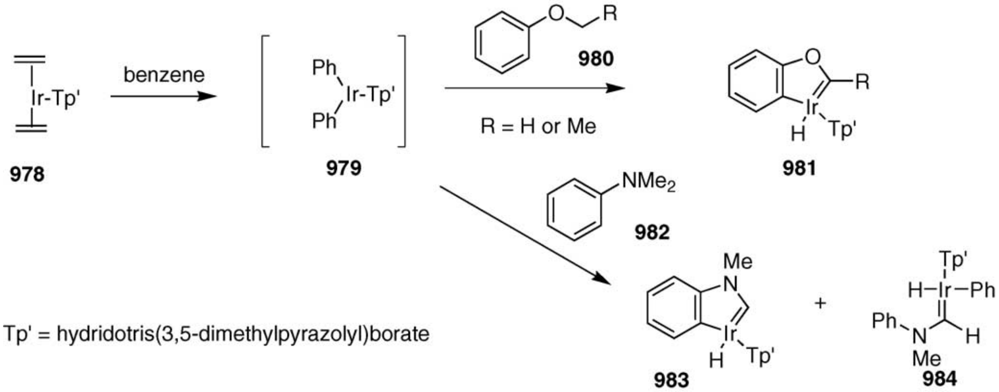
Scheme 101.

led exclusively to the iridabenzene derivative. Thermolysis of iridabenzvalene **989**/**990** (L = $PEt_3$) at 75 °C resulted in isomerization to iridabenzene derivative **993**. A mechanism involving decomplexation of the alkene ligand, followed by oxidative addition into the cyclopropane C–C bond to afford a metalla–Dewar benzene, followed by allylic isomerization was proposed for the conversion of iridabenzvalenes to iridabenzenes. Exposure of iridabenzene **993** (L = $PMe_3$) to oxygen led to the dioxygen-bridged structure **994**. An iridanaphthalene derivative (**996**) was produced from the reaction of iridium complex **995** with *t*-butyl hydroperoxide [647]. Formation of the iridanaphthalene was proposed to occur through Bayer–Villager reaction of the coordinated ester followed by elimination. Hydration resulting in **997** occurs upon treatment of the iridanaphthalene with silica gel, wet ether, or methyl chloroformate/pyridine. Several theoretical studies of iridabenzenes were reported in 2003. The [2 + 2]-cycloaddition reactions between iridabenzene derivatives (addition to the Ir–C double bond) and carbon–heteroatom double bonds were studied by DFT calculations [648]. A concerted cycloaddition pathway was favored for iridabenzenes, while heteroatom analogs were more prone to a stepwise mechanism. This was attributed to the cationic nature of the heteroatom analogs, which exhibit greater Lewis acidity. Conversions of metallabenzenes to the corresponding $\eta^5$-Cp complexes were evaluated computationally [649].

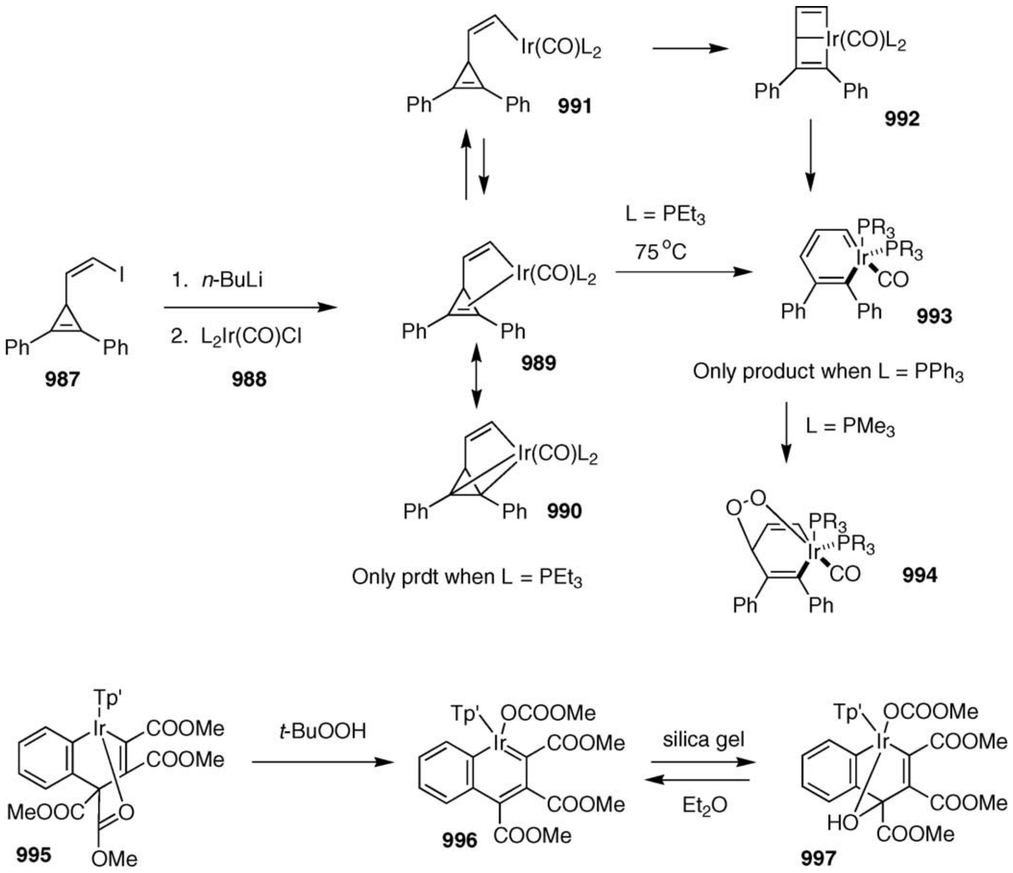
The chelating diphosphine complex **1002** (Scheme 104) was prepared from the reaction of the bis(stibine)complex **1000** with the chelating diphosphine ligand **1001** [650]. Coupling of this complex with ethylene led to the cyclopropane **1003** accompanied by small amounts of isomeric compounds **1004** and **1005**. The cyclopropanation reaction was unique to this complex. Previously prepared complexes featuring nonchelating phosphines and a *trans* disposition of phosphines reacted with ethylene to afford primarily **1004**. Formation of stable diazo complexes and not carbene complexes was noted in coupling of a variety of diazo compounds and *trans* $[RhCl(C_2H_4)(PiPr_3)_2]$ [651].

The reaction of chelating phosphinocarbene–iridium complex **1007** (Scheme 105) with electrophiles and chalcogens was reported [652]. Protonation afforded the phosphorus-protonated species **1008**, which was stable in the solid state. Compound **1008** transformed into the iridium–phosphine complex **1009** in dichloromethane solution. The phosphorus methylation product **1010** was formed upon treatment of complex **1007** with iodomethane. The phosphine sulfide (selenide) **1011** was obtained upon reaction with sulfur or selenium.

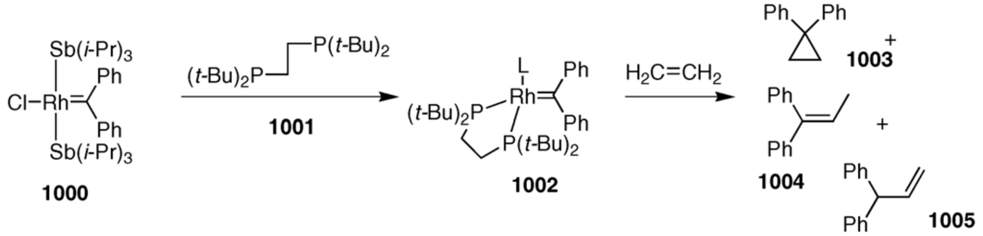
Other studies of group IX metal–carbene complexes (excluding cumulenes) are depicted in Scheme 106 and include: (1) formation of observable cationic carbenoid complex **1015** through protonation of cyclobutadiene-cobalt complex **1014**



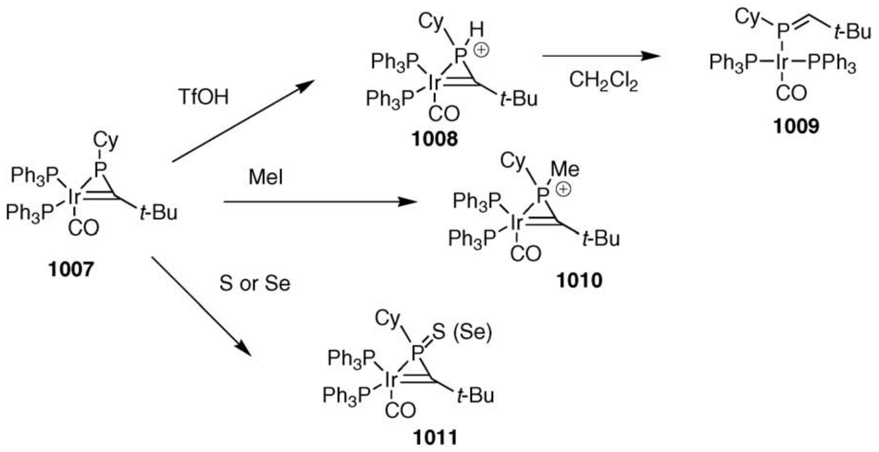
Scheme 102.



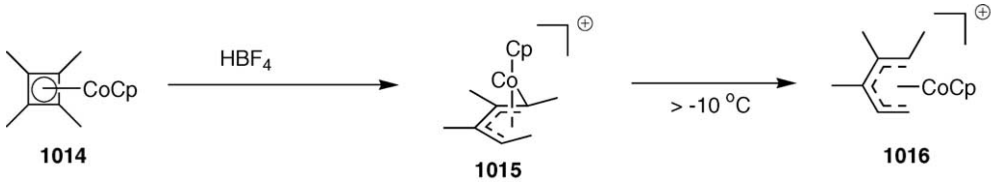
Scheme 103.



Scheme 104.



Scheme 105.

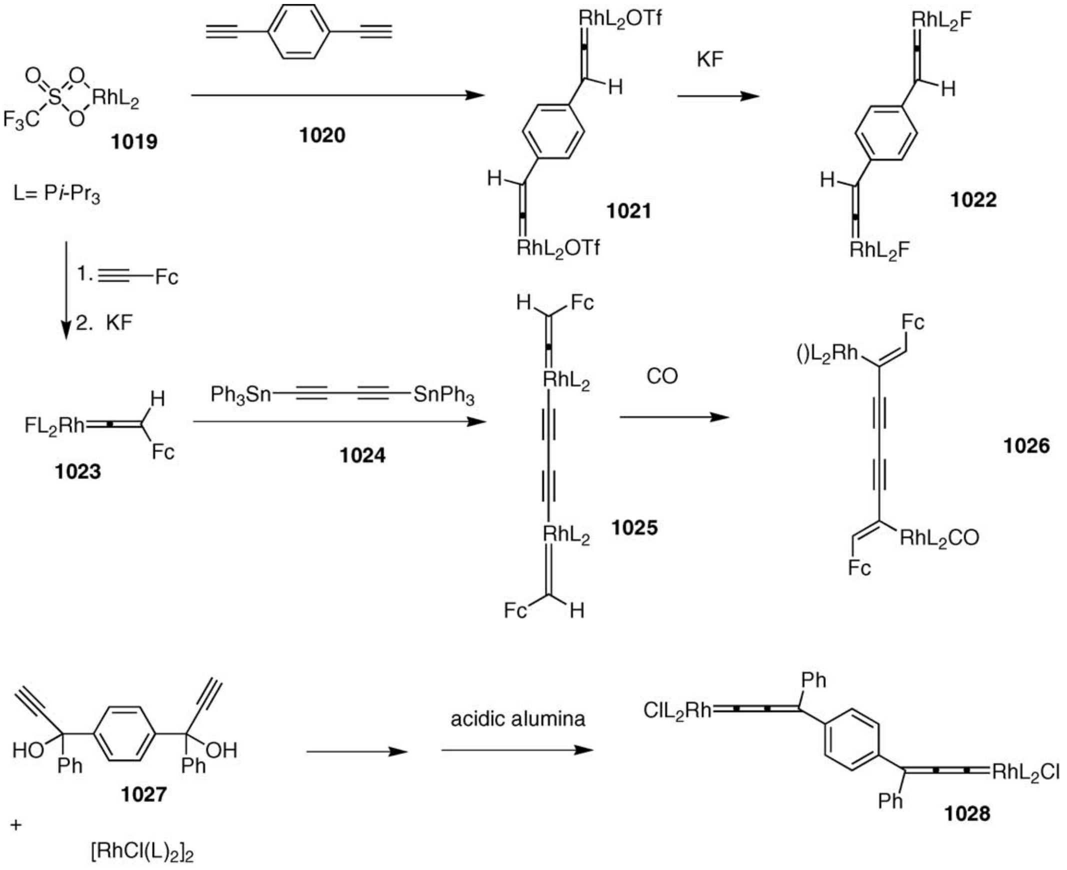


Scheme 106.

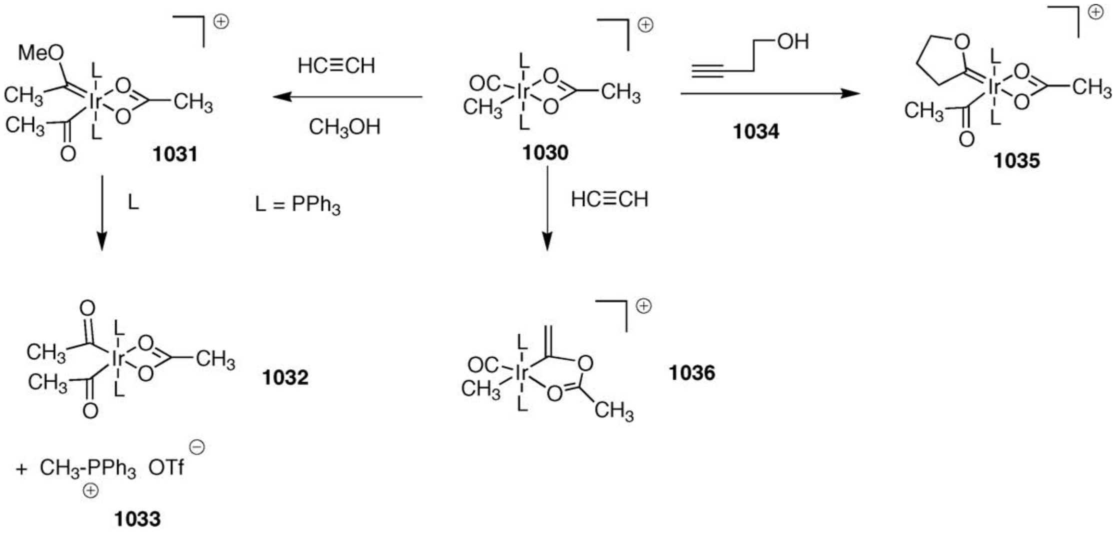
[653]; (2) possible involvement of cobalt carbene complexes in the conversion of propargyl alcohol–$Co_2(CO)_6$ complexes to bridging carbyne-tricobalt complexes [654]; (3) gas-phase reactions of diazoesters with $Rh_2(OAc)_4$ [655]; (4) a DFT study of the formation of rhodium–carbene complexes from diazo compounds and an experimental low-temperature study of this process [656]; (5) a theoretical study of C–H insertion reactions of rhodium(II) acetate-derived carbene complexes [657]; and (6) a theoretical study of several Bertrand-type carbene–rhodium complexes, which in most cases are ligated to the metal through ligation at both carbon and phosphorus [658].

*2.3.6.2. Cumulene complexes.* Similar synthetic procedures and reactivity patterns were generally observed for groups IX and VIII (Schemes 88 and 95) metal–cumulene complexes. Several dirhodium–cumulene-bridged complexes (e.g. **1021**–**1022**, **1025** and **1028**, Scheme 107) were prepared through coupling of terminal dialkynes with a rhodium–trifluoromethanesulfonate complex (e.g. **1019**) [659]. The bis(vinylidene) complex **1021** was prepared from direct reaction of **1019** with 1,4-diethynylbenzene. A ligand exchange reaction of vinylidene complex **1023** with 1,4-bis(triphenylstannyl)butadiyne led the dialkyne-bridged rhodium vinylidene complex **1025**. Treatment of complex **1025** with CO led to the diyne–diene–diylrhodium complex **1026**. An analogous allenylidene complex **1028** was prepared starting from bis(propargylic) alcohol **1027**.

The coupling of acetatoiridium complex **1030** (Scheme 108) with terminal alkynes was reported [660]. Reaction with acetylene in the presence of alcohols led to the CO-inserted alkoxycarbene–iridium derivatives **1031**. A



Scheme 107.



Scheme 108.

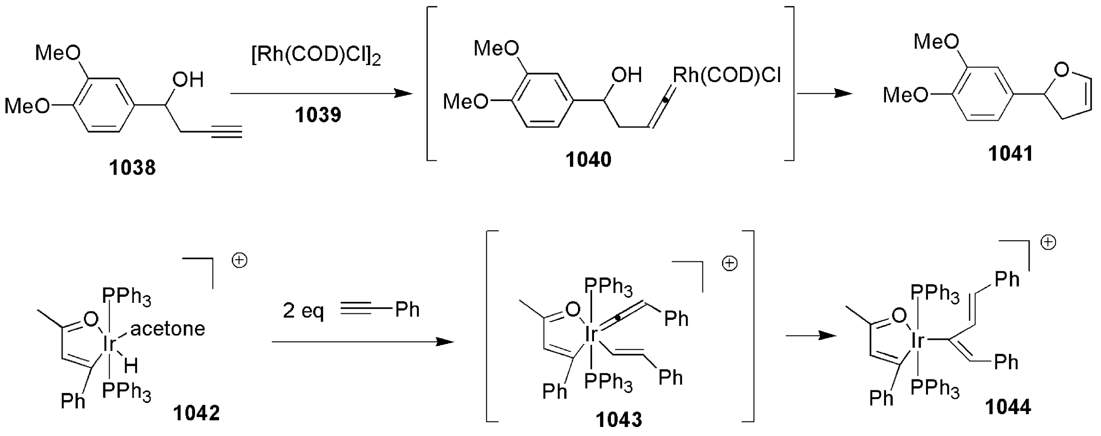
cyclic carbene complex **1035** was obtained from reaction of complex **1030** with 3-butyn-1-ol. These carbene complexes arise via formation of the vinylidene complex followed by attack of the alcohol at the vinylidene ligand. The methoxycarbene complex **1031** could be de-alkylated by treatment with triphenylphosphine. Vinyl acetate chelate **1036** was obtained from the reaction of complex **1030** with acetylene in the absence of an alcohol. Carbene complex **1036** arises via formation of the vinylidene complex followed by intramolecular attack of the acetate carbonyl group.

Several processes reported in 2003 proposed group IX metal–vinylidene complexes as intermediates (Scheme 109). These processes include: (1) involvement of ruthenium vinylidene complexes (e.g. **1040**) in the conversion of homopropargyl alcohols to dihydrofurans [661]; (2) involvement of iridium–vinylidenes (e.g. **1043**) in the reaction of hydride complex **1042** with two equivalents of a terminal alkyne to provide a dienyliridium complex (e.g. **1044**); (3) involvement of iridium–vinylidenes in the acid-induced conversion of complexes of general structure R–Ir–C≡CPh to the corresponding alkene RCH═CHPh [662]; (4) a failed attempt to detect vinylidene intermediates in the formation of an iridium carbonyl–benzyl complex from coupling of an iridium hydride, phenylacetylene, and water [663]; and (5) the synthesis of a compound depicted as an oxavinylidene–cobalt complex from complexing the oxygen of a carbonyl group of $Co_2(CO)_8$ with titanium [664].

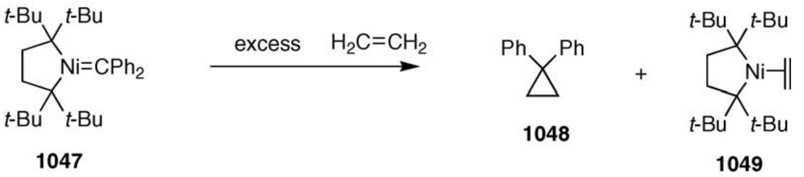
### 2.3.7. Group X metal–carbene complexes

The nickel–carbene complex **1047** (Scheme 110) was treated with ethylene to afford the corresponding cyclopropane **1048** and the ethylene-nickel complex **1049** [665]. Complex **1047** also served as a catalyst for the cyclopropanation of ethylene by diphenyl diazomethane. No intermediates or isomeric products were detected in the cyclopropanation reaction.

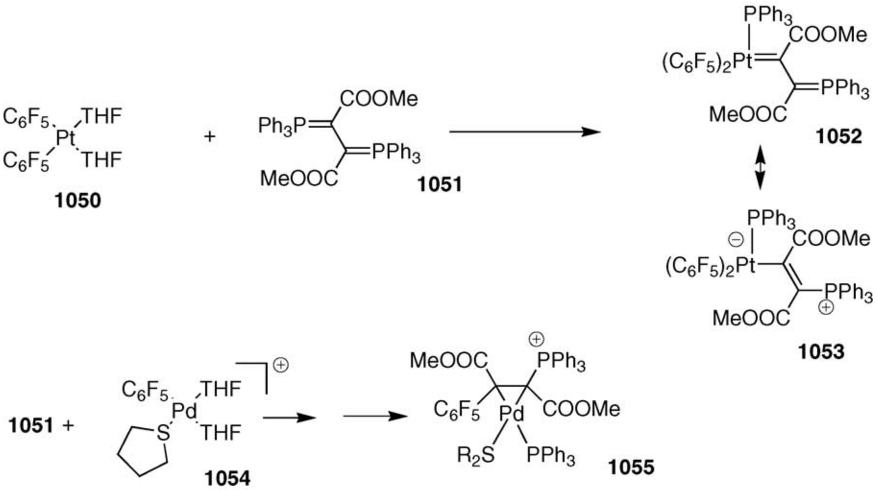
Platinum- and palladium–carbene complexes (e.g. **1052**/**1053**, Scheme 111) were prepared from the coupling of bis(ylide) reagent **1051** with various group X metal–bis(THF) complexes [666]. In the case of the sulfide–palladium com-



Scheme 109.



Scheme 110.

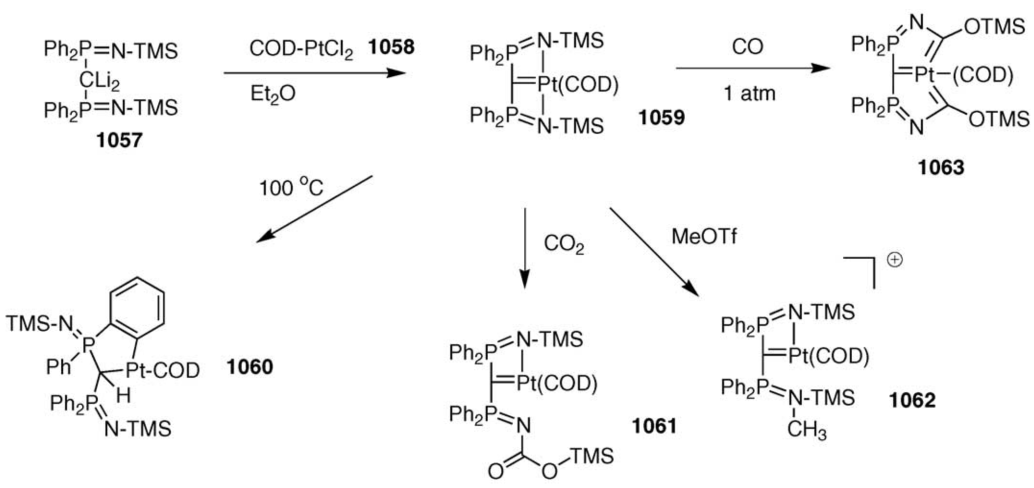


Scheme 111.

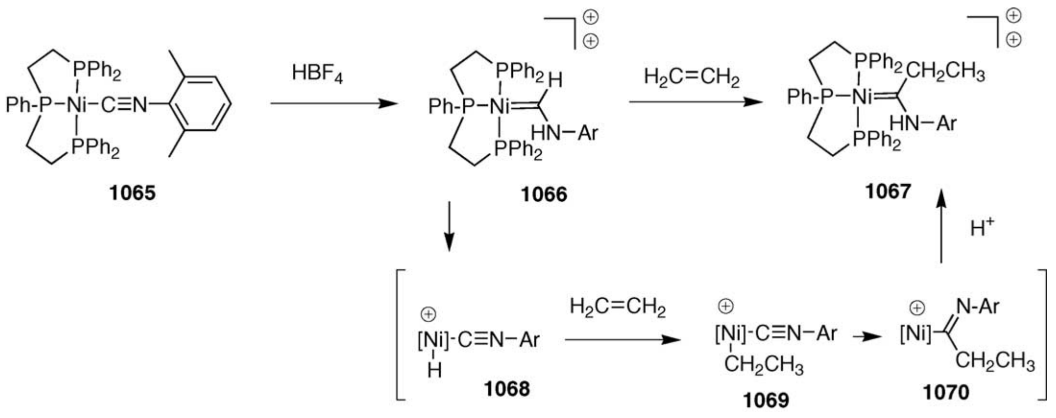
plex **1054**, the carbene complex could not be isolated, but was suggested as an intermediate in the formation of the alkene complex **1055**. Aryl ligand migration in the proposed carbene intermediate could lead to the observed alkene–palladium complex **1055**.

The preparation of platinum carbene complexes featuring pincer ligands (e.g. **1059**, Scheme 112) was reported [667]. These complexes were unreactive to ligands such as $PPh_3$ and ethylene, and to $H_2$. Complex **1059** was reactive to electrophiles, forming the 16-electron complex **1062** upon treatment with methyl triflate and complex **1061** upon treatment with $CO_2$. Thermolysis afforded the C–H oxidative addition product **1060**. This transformation was promoted by addition of water. The pincer carbene complex **1059** was obtained only when the reaction was conducted in ether. The tris(carbene) complex **1063** was obtained by treatment of the pincer carbene complex **1059** with CO [668].

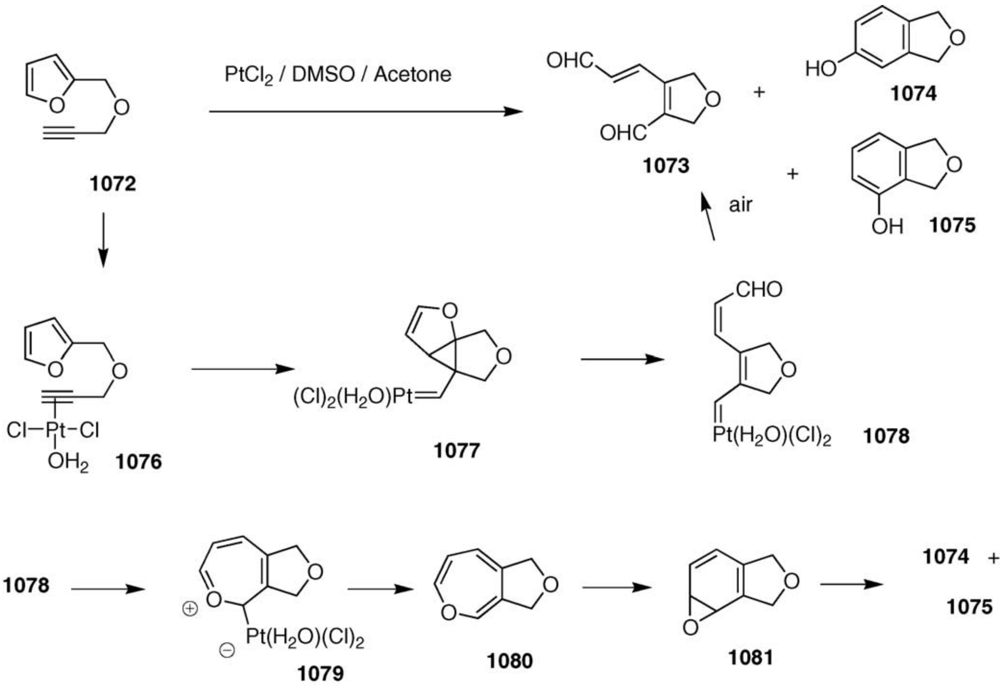
The synthesis of dicationic aminocarbene–nickel complexes (e.g. **1066**, Scheme 113) through double protonation of nickel isocyanide complex **1065** was reported [669].



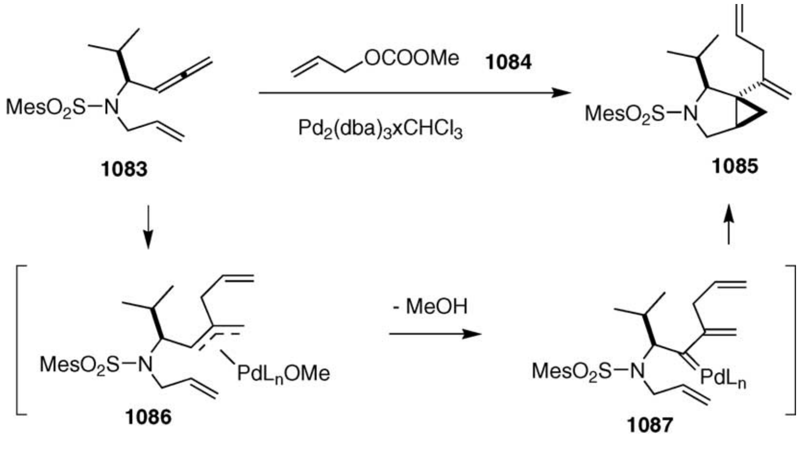
Scheme 112.



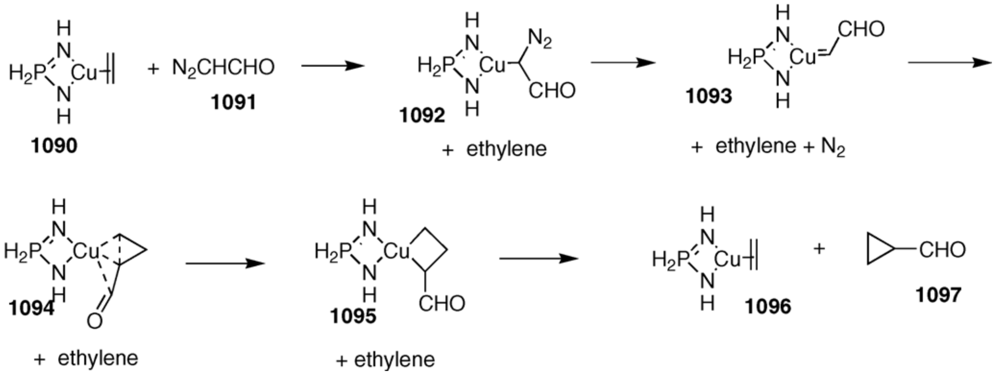
Scheme 113.



Scheme 114.



Scheme 115.



Scheme 116.

Hydrocarbation of alkenes, resulting in more highly substituted aminocarbene complex (e.g. **1067**), using these aminocarbene–nickel complexes was reported [670]. A mechanism involving deprotonation and hydrogen migration to afford a hydride/isonitrile complex (**1068**), followed by alkene insertion and isocyanide insertion, followed by reprotonation was proposed.

Platinum carbene complexes (e.g. **1077–1078**, Scheme 114) were proposed as intermediates in the isomerization of alkyne-furans to cyclic compounds **1073–1075** [671]. Mechanistic scenarios were evaluated using DFT calculations. The favored mechanistic pathway involves complexation of the alkyne, followed by cyclopropanation to generate a cyclopropylcarbene complex (**1077**), followed by ring opening to afford an aldehyde–carbene complex (**1078**), which reacts with air or water to afford the dihydrofuran product **1073**. In the absence of air or water, cyclization occurs to afford isomeric phenol derivatives **1074** and **1075**. These compounds form from intermediate **1078** via nucleophilic attack of the carbonyl oxygen at the carbene carbon to afford ylide **1079**, which affords the oxepin **1080**, which affords the observed products after cyclization and epoxide ring opening. Diels–Alder reaction of the platinum carbene complex **1076** was energetically disfavored. Related carbene complexes were proposed as intermediates in the cyclization of alkyne–enol ethers [672]. Additional mechanistic [673] and synthetic [674] studies of this reaction were also reported.

Palladium carbene complexes (e.g. **1087**, Scheme 115) were suggested as intermediates in the conversion of ene-allenes (e.g. **1083**) to bicyclo[3.1.0]hexane systems (e.g. **1085**) [675]. The proposed mechanism involves initial formation of the π-allyl palladium complex from the allylic carbonate, followed by insertion into the allene to afford π-allyl complex **1086**. Elimination of methanol from this complex affords the palladium carbene complex **1087**, which then undergoes an intramolecular cyclopropanation with the alkene to afford the observed product. Noncarbene-based mechanisms were also considered.

Additional studies of carbene complexes in this class include: (1) a study of the gas-phase reactivity of platinum–carbene clusters [676]; (2) a bimetallic bridging carbyne complex of tungsten and platinum is discussed in the group VI metal–carbene complex section [536]; and (3) a paper in the group VI carbene section involves transfer of carbene ligands from chromium to nickel [489].

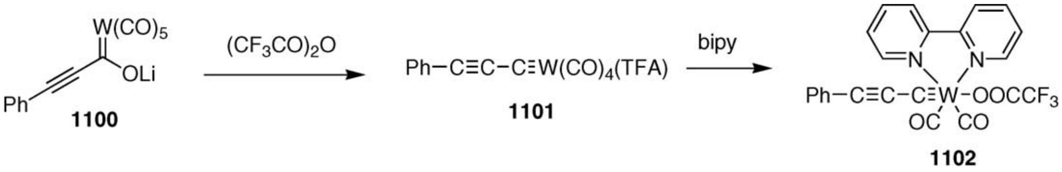
### 2.3.8. *Group XI carbene complexes*

The complete cycle of copper-catalyzed cyclopropanation of ethylene by diazoacetaldehyde (**1091**, Scheme 116) was studied by DFT calculations [677]. The favored mechanistic pathway for carbene complex generation and for cyclopropanation is depicted. The authors noted that carbene complex intermediate **1093** displays significant Cu–C double bond character. Fischer carbene–copper complexes were detected in the electrospray mass spectrum of diazomalonate/Cu(I) mixtures [678].

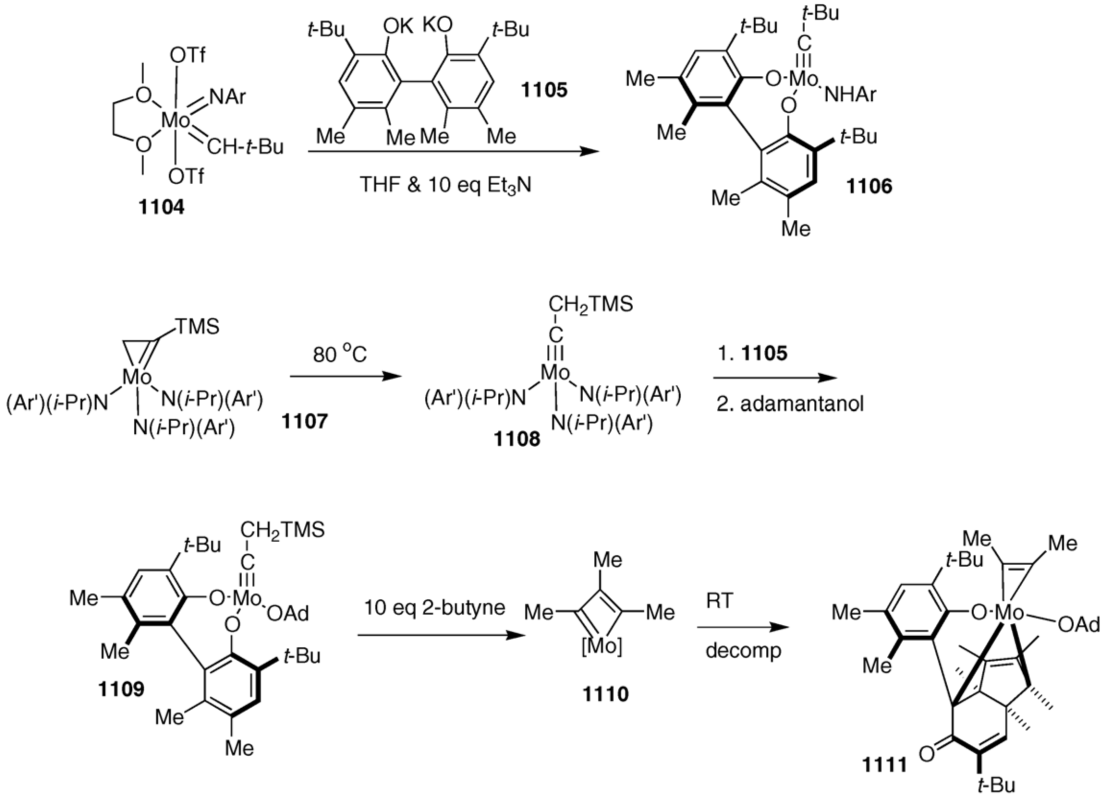
## 3. Metal–carbyne or metal–alkylidyne complexes

### 3.1. *Review articles*

Review articles featuring metal carbyne complexes which appeared in 2003 include: (1) a short review on the vibrational spectra of carbyne complexes [679]; (2) synthetic



Scheme 117.

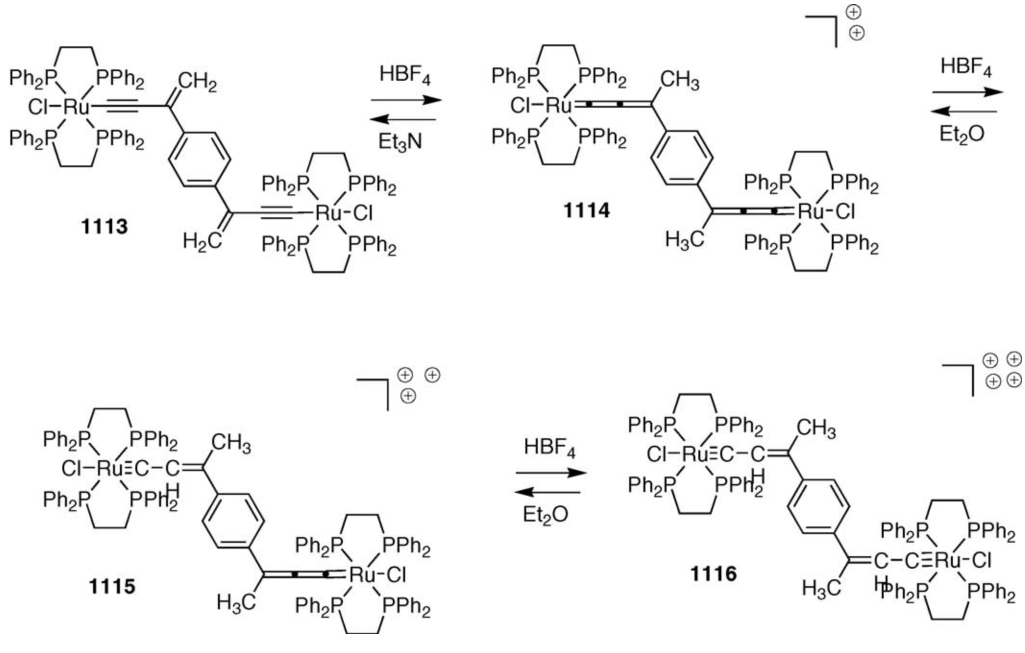


Scheme 118.

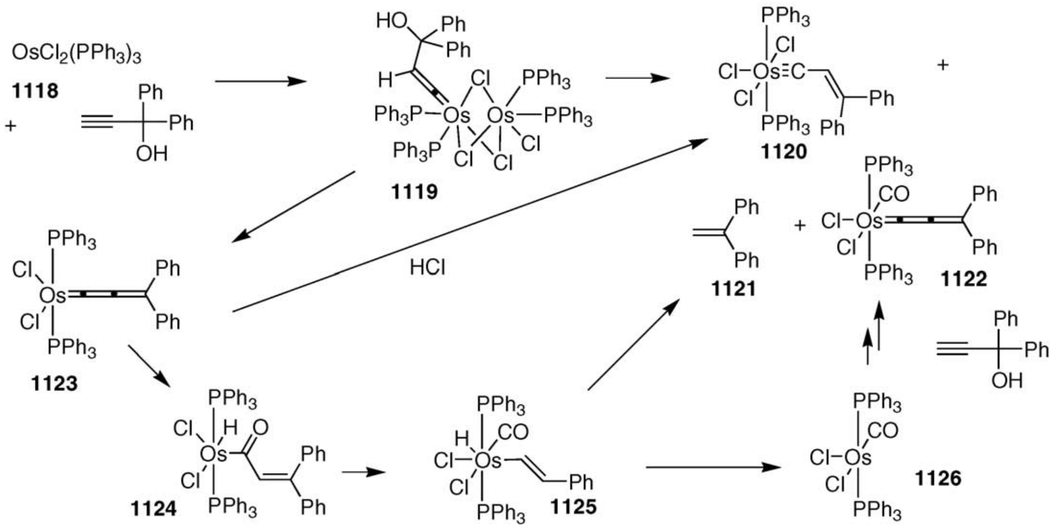
strategies for dehydrobenzannulenes, which features a brief section on alkyne metathesis approaches to this ring system [680]; (3) alkyne metathesis [681]; and (4) acyclic diyne metathesis condensation [682] and polymerization [683].

## 3.2. Synthesis and/or generation

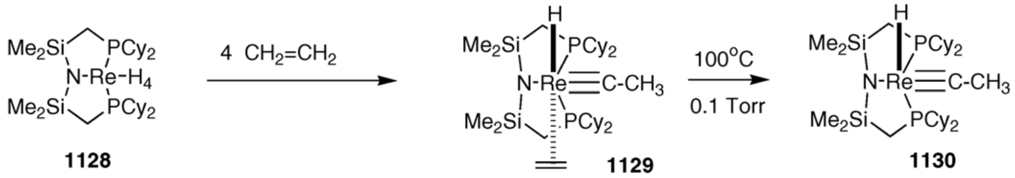
Alkynylcarbyne complexes (e.g. **1101**, Scheme 117) were generated through deoxygenation of the metal acylate complexes (**1100**) using trifluoroacetic anhydride [684]. Ligand



Scheme 119.



Scheme 120.



Scheme 121.

exchange reactions and examination of the IR spectra at various concentrations was also reported for these complexes. A similar method was employed to prepare various alkylcarbyne complexes, which could be converted to air-stable carbyne complexes through binding to a tridentate ligand.

Several examples of the preparation of molybdenum–carbyne complexes (e.g. **1106**, Scheme 118) from carbene–imido complex **1104** were reported [685]. Alternatively a related carbyne–molybdenum complex **1109** was prepared through thermolysis of the $\eta^2$-alkenylmolybdenum complex **1107**. Reaction of complex **1109** with 2-butyne led to the [2 + 2]-cycloadduct **1110**. This complex was only moderately stable in solution and led to the indenyl complex **1111** in low yield.

Formation of a bis(alkenylcarbyne)-bridged diruthenium complex (**1116**, Scheme 119) was reported [686]. Sequential protonation transforms bis(enyne)-bridged diruthenium complex **1113** into bis(allenylidene)-bridged diruthenium com-

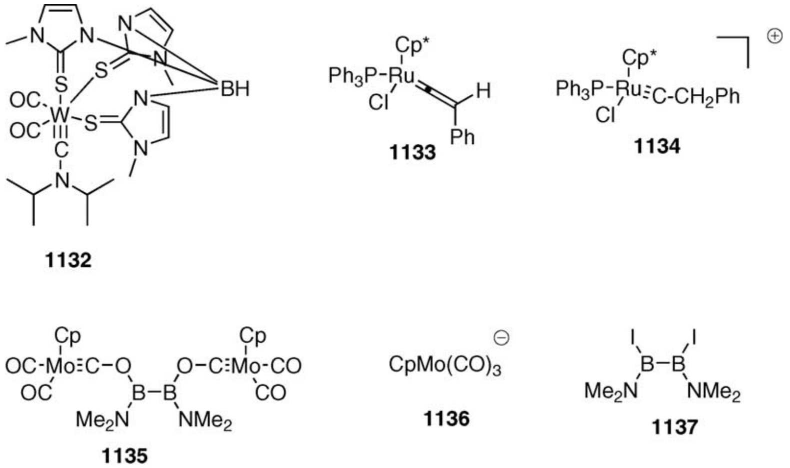
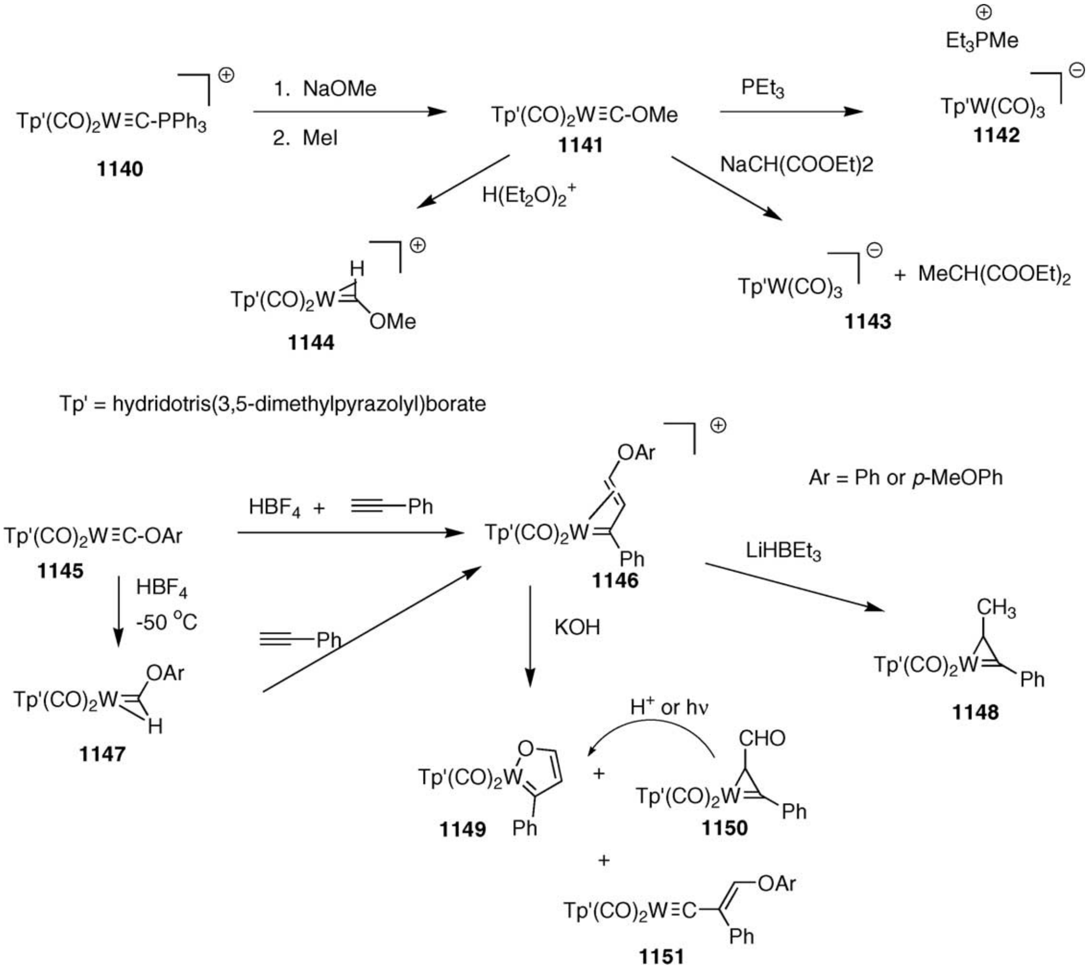


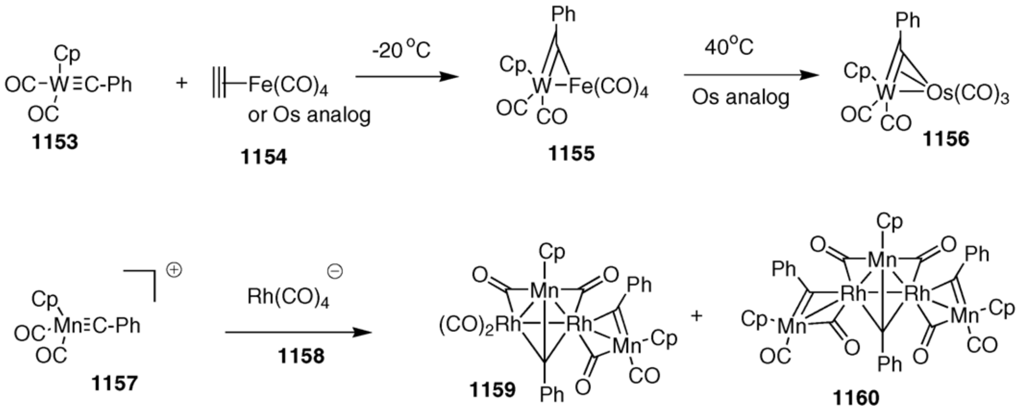
Fig. 15. Carbyne complexes and precursor complexes.



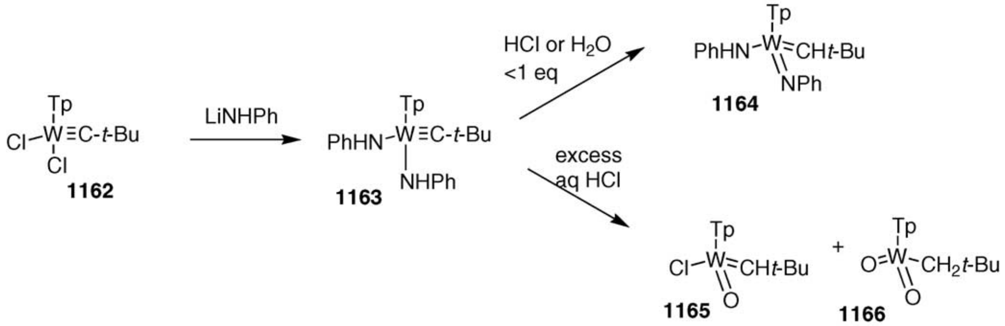
Scheme 122.

plex **1114**, allenylidene/carbyne-bridged diruthenium complex **1115**, and tetracationic bis(carbyne)-bridged diruthenium complex **1116**.

Synthesis of carbyne complexes from $OsCl_2(PPh_3)_3$ (**1118**, Scheme 120) and 1,1-diphenylpropargyl alcohol was reported [687]. Reaction of **1118** and diphenylpropargyl alcohol at room temperature afforded initially hydroxyvinylidene complex **1119**. Further reaction at room temperature led to the osmium carbyne complex **1120** and the carbonyl–allenylidene complex **1122**. Formation of carbyne complex **120** occurs through proptonation of allenylidene complex intermediate **1123**. Formation of the carbonyl allenylidene complex occurred through addition of water to allenylidene complex **1123** to form the hydrido-acyl complex



Scheme 123.



Scheme 124.

**1124**, followed by deinsertion of CO and reductive elimination to provide 1,1-diphenylethylene, followed by formation of the allenylidene from carbonyl complex **1126** and the starting alkynol. The carbyne complexes were the only products obtained when the reaction was conducted in the presence of HCl.

The coupling of rhenium tetrahydride complex **1128** (Scheme 121) with ethylene resulted in the carbyne complex **1129** [688]. Ethylene could be removed from the carbyne complex by heating in a vacuum at 100 °C. Mechanisms involving either oxidative addition into the ethylene C–H bond or hydrometallation of ethylene were suggested as possible reaction pathways for formation of the carbyne complexes.

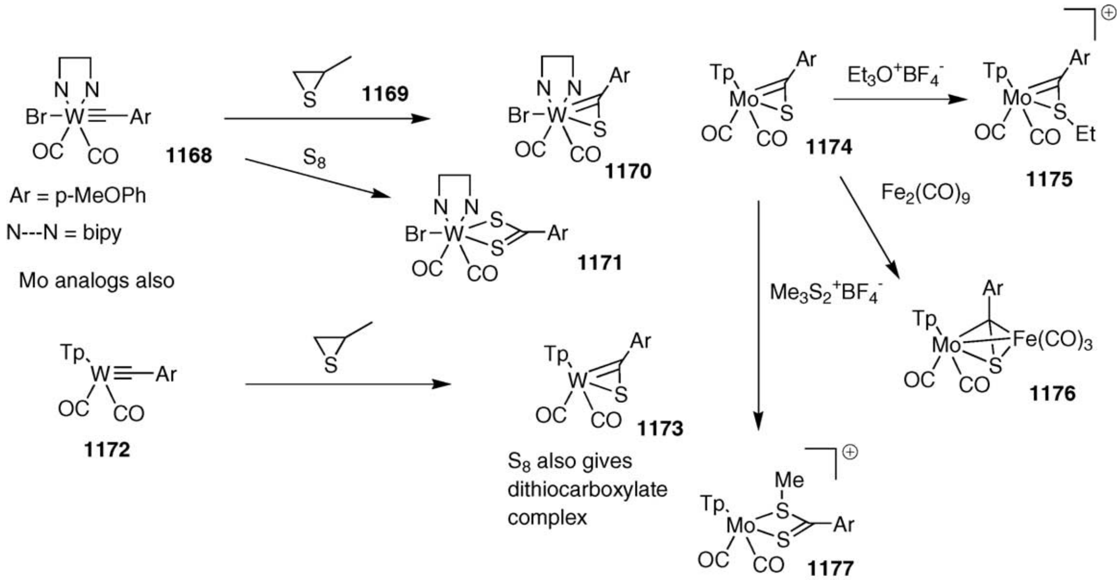
Additional carbyne complexes prepared in 2003 are depicted in Fig. 15 and include: (1) tungsten–carbyne complexes that feature a hydriotris(methimidazolyl)borate ligand (e.g. **1132**) [689]; (2) air stable tungsten carbyne complexes featuring the bulky Tp′ (hydridotris(3,5-dimethylpyrazolyl)borate) ligand [690]; (3) formation of a cationic carbyne complex (e.g. **1134**) via protonation of ruthenium vinylidene complex **1133** [691]; and (4) preparation of dicarbyne–dimolybdenum(and tungsten and chromium analogs) complexes (e.g. **1135**) from the reaction of diborane **1137** with metal carbonyl anions (e.g. **1136**) [692].

Some papers in the carbene section feature minor segments on carbyne chemistry. These studies include references [533,541,542,549,550,580–582,614].

## 3.3. Reactivity

### 3.3.1. Addition reactions of metal–carbyne complexes

Alkoxycarbyne complexes (e.g. **1141**, Scheme 122) were prepared from cationic carbyne–phosphonium salt **1140** [693]. The complex was unstable but could be stored at −35 °C if protected from air. The major decomposition reaction was demethylation to form the anionic tricarbonyl complex **1143**, however this process was suppressed by working up the synthesis of **1140** reaction with methyl iodide. Reaction with nucleophiles resulted in transfer of the methyl group to the nucleophile. Reaction with acid led to the agostically-bound carbene complex **1144**. The reactivity of aryloxycarbyne complex **1145** was also reported [694]. Protonation of this complex in the presence of phenylacetylene derivatives



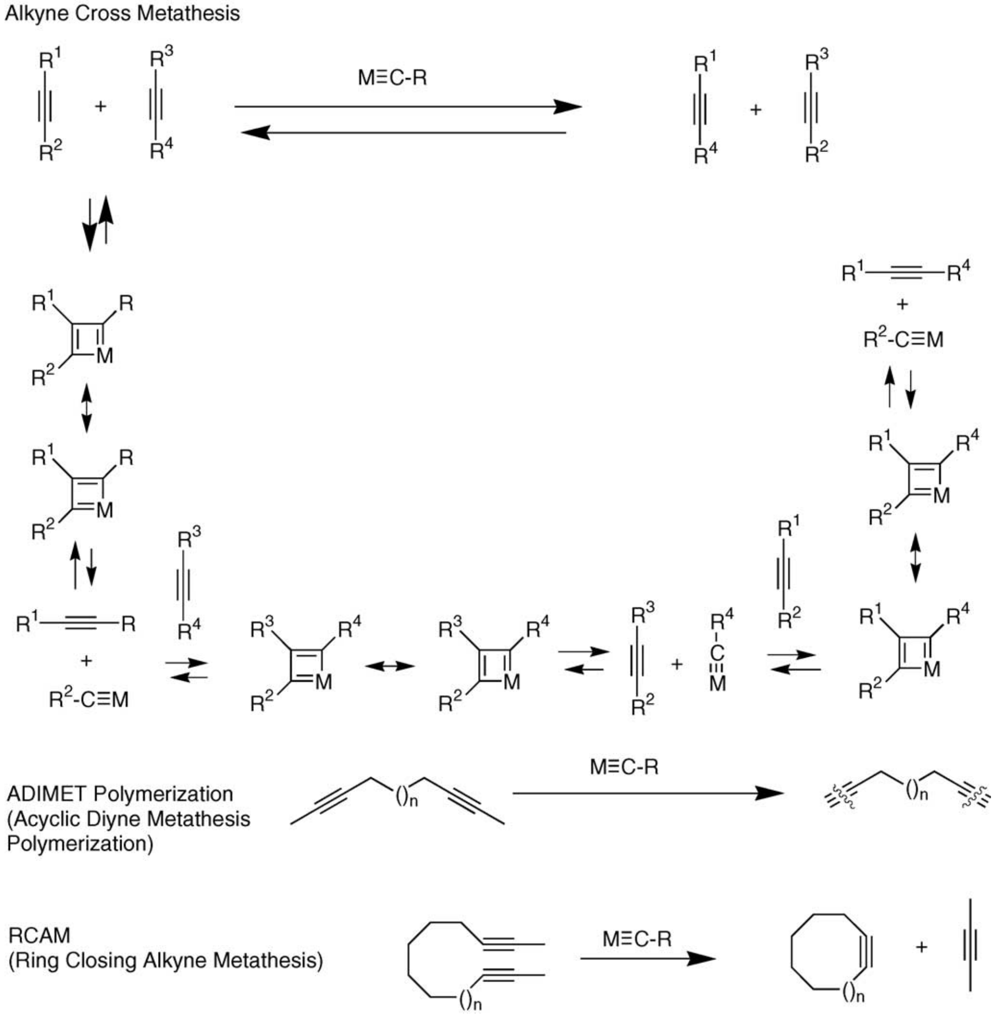
Scheme 125.

led to the $\eta^3$-β-aryloxyalkenylcarbene complexes **1146**. The reactions occurs by initial protonation of the carbyne complex to afford the agostically-bound Fischer carbene **1147**, which then reacts with the alkyne to form the insertion product. The intermediate carbene complex **1147** could be observed by low-temperature NMR. Reaction of the alkenylcarbene complex with $LiHBEt_3$ led to the $\eta^2$-alkenyl complex **1148**. Reaction with base led to a mixture of metallafuran **1149**, metallacyclopropene-aldehyde **1150**, and the carbyne complex **1151**. The aldehyde was transformed to the metallafuran upon treatment with acid or ultraviolet light.

Carbyne complexes have been frequently employed for the synthesis of polynuclear complexes (Scheme 123). The reaction of tungsten carbyne complex **1153** with iron- and osmium–acetylene complexes (e.g. **1154**) was reported [695]. This reaction led to the bridging bimetallic carbyne complexes **1155**. Mild thermolysis of the osmium complex led to the CO-dissociation product **1156**. The addition of tetracarbonylrhodium anion (e.g. **1158**) to manganese- and rhenium–carbyne complexes (e.g. **1157**) was reported [696]. Reaction of manganese carbyne complex **1157** with tetracarbonylrhodium anion led to a mixture of complexes **1159** and **1160**. The rhenium analog afforded the complex analogous to compound **1159** accompanied by a more complex polynuclear species.

The bis(amide)carbine–tungsten complex **1163** (Scheme 124) was prepared from the corresponding dichlortungsten–carbyne complex **1162** through a ligand exchange process [697]. Treatment with a substoichiometric amount of water or HCl led to the isomerization to the carbene(imido)tungsten complex **1164**. Treatment with excess water and acid led to the oxo-carbene complex **1165** and the bis(oxo)alkyltungsten complex **1166**.

The synthesis of group VI metal carbyne complexes (e.g. **1168** and **1172**, Scheme 125) and their reactions with sulfur sources was reported [698]. Coupling of carbyne complex with propylene sulfide led to the $\eta^2$-thioacyl complexes (e.g. **1170**, **1173**, and **1174**). Reaction with elemental sulfur led to the chelating dithiocarboxylate complexes **1171**. The reactivity of the molybdenum thioacyl complex **1174** was briefly explored. The bimetallic complex **1176** was obtained from the coupling with $Fe_2(CO)_9$. Alkylation afforded



Scheme 126.

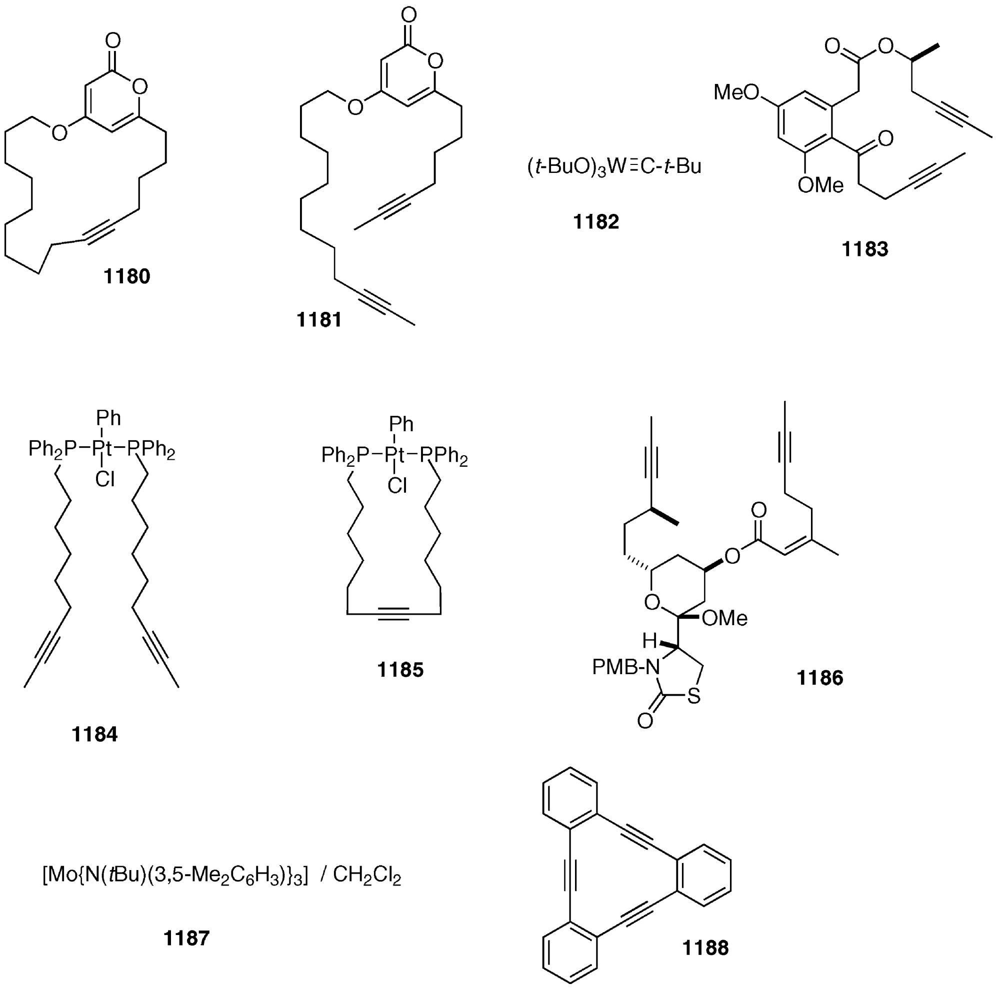


Fig. 16. Alkyne metathesis substrates, products, and catalysts.

the cationic Fischer carbene complex **1175**. Sulfenylation led to the dithioester complex **1177**, which was not isolated but treated with water to afford a monothioester complex.

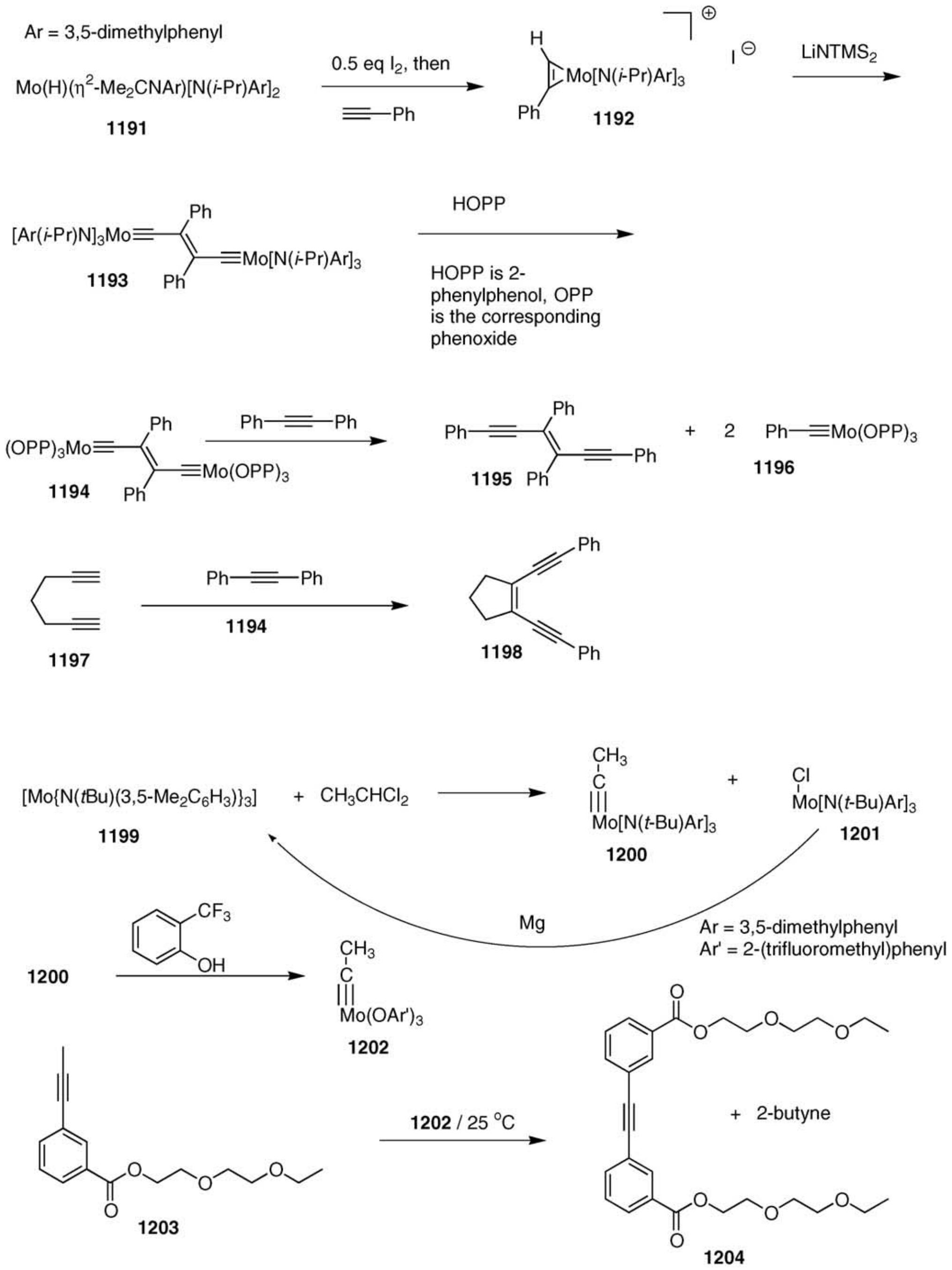
Theoretical studies of reversible hydrogen migration in hydrido tungsten carbyne complexes were reported [699]. A paper utilizing carbyne complexes to prepare anionic molybdenum carbene complexes is discussed in the group VI metal–carbene complex section [533].

### 3.3.2. *Alkyne metathesis*

Alkyne metathesis, which involves metal carbyne complexes as intermediates, has been covered comprehensively regardless of whether the initiator is a carbyne complex. General equations describing the mechanism and precedented modes are presented in Scheme 126. Several reports using alkyne metathesis for natural product synthesis and for polymer synthesis appeared in 2003; representative substrates and products are depicted in Fig. 16.

Several examples of RCAM (see Scheme 126) were published in 2003. Representative examples are depicted in Fig. 16. RCAM of dialkyne–pyrone **1181** (forming **1180**) was effected using a tungsten–carbyne complex catalyst **1182** [700]. Total synthesis of citreofuran employed RCAM of dialkyne **1183** as the key step [701]. RCAM of various 7-nonynylphosphine complexes (e.g. **1184**) using tungsten carbyne complex **1182** led to the macrocycle-bridged diphosphine complexes (e.g. **1185**) [702]. RCAM using substrate **1186** and molybdenum catalyst **1187** was employed for the total synthesis of latrunculin B [703]. The dehydrobenzannulene **1188** was formed upon treatment of 1,2-dipropynylbenzene with tungsten carbene complex **1182** [704].

A novel system for performing alkyne metathesis reactions was developed (Scheme 127) [705]. The bis(carbyne) complex **1193** was prepared by reaction of molybdenum hydride **1191** with iodine followed by a terminal alkyne (e.g. phenylacetylene). Ligand exchange with 2-phenylphenol (HOPP) led to the bis(carbyne) complex **1194**, which undergoes metathesis reactions with diphenylacetylene (and other symmetrical internal alkynes) to form **1195** and a new carbyne complex **1196**. Carbyne complex **1196** was capable of initiating alkyne metathesis. A cyclic *cis* enediyne (e.g. **1198**) was produced when a 1,6- or 1,7-diyne was used as the starting material. A similar alkyne metathesis cata-

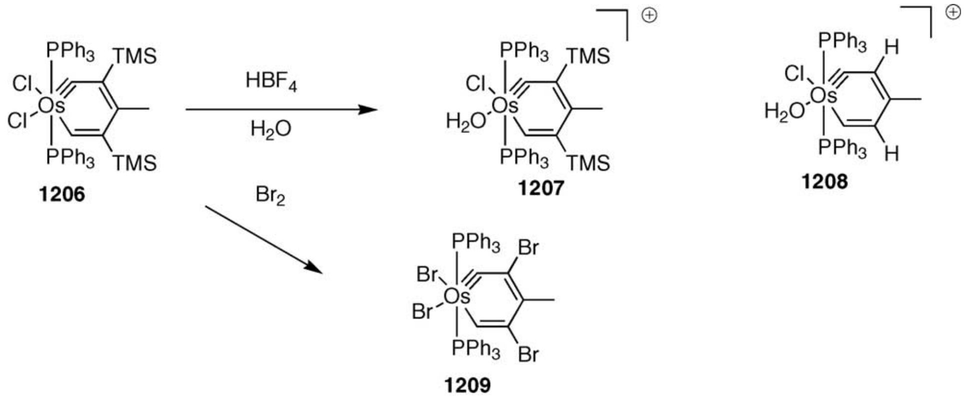


Scheme 127.

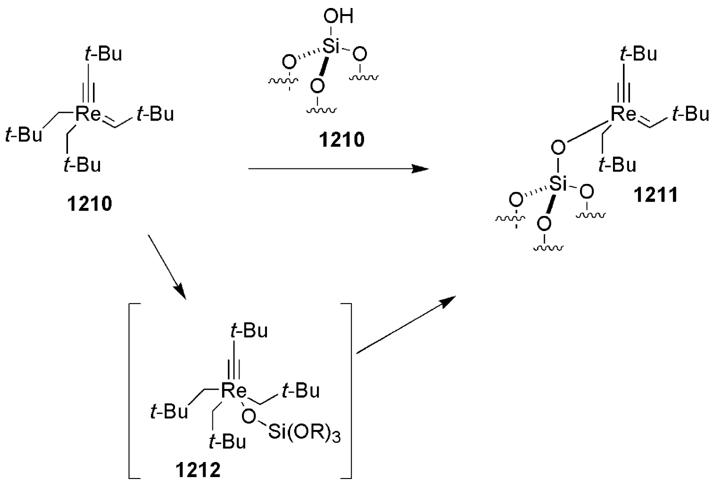
lyst (**1200**) was generated by reaction of molybdenum complex **1199** with 1,1-dichloroethane in the presence of magnesium [706]. Reaction in the absence of magnesium affords a mixture of carbyne complex **1200** and chloromolybdenum complex **1201**. The complex **1201** was reduced back to the starting material in the presence of magnesium. Higher homologs of carbene complex **1200** were similarly prepared, in addition to a lower homolog using dichloromethane in place of 1,1-dichloroethane. Carbyne complex **1202** was employed as a catalyst for metathesis of ester derivative **1203**. An active alkyne metathesis catalyst was generated from *p*-chlorophenol, Mo(CO)$_6$, molecular sieves, and a polyether [707]. This catalyst system catalyzes the metathesis of phenylpropyne at 50 °C.

### *3.3.3. Other processes involving metal–carbyne complexes*

The reactivity profile for osmabenzynes (e.g. **1206**, Scheme 128) was evaluated [708]. Treatment with electrophilic substances resulted in ligand substitution and desi-



Scheme 128.



Scheme 129.

lylation processes. Treatment with 1 mol of $HBF_4$ in $H_2O$ led to the cationic hydrate complex **1207**, while treatment with excess $HBF_4$ led to the desilylation product **1208**. Treatment with excess bromine led to the tetrabromo complex **1209**.

The binding of rhenium–carbene/carbyne complex **1210** (Scheme 129) to partially hydroxylated silica was reported [709]. Both syn- and anti-isomers with respect to the *t*-butyl group of the carbene ligand were detected. Two mechanisms were proposed: (1) protonolysis of a neopentyl ligand followed by addition of the siloxane and (2) addition of the OH group across the Re–C double bond followed by α-elimination and reductive elimination. Deuterium labeling studies supported the latter mechanism (depicted mechanism) involving intermediate **1212**.

The competitive binding of sodium ions to tungsten carbyne complex $[PhC{\equiv}W(Ot\text{-}Bu)_4]^-$ and crown ethers was reported [710].

### 3.4. Mechanistic/structural studies

Several mechanistically/structurally-oriented studies of the reactions of metal–carbyne complexes were reported in 2003. The origins of stability in osmabenzyne complexes were determined using DFT calculations, with emphasis on determination of the resonance and ring strain energies [711]. Ring strain was determined to be small because of the relatively small angle of bending at the carbyne carbon. The resonance stabilization was determined to be 44 kcal/mol, which is nearly identical to that for osmabenzene. Substituents at the 1- (*ortho* to carbyne carbon) and 3-positions that are π-electron accepting were stabilizing. The carbon metal double and triple bonds were studied through energy decomposition analysis [712]. The tungsten–carbon π-bonds in tungsten–carbyne complexes of general structure $(RX)_3M{\equiv}CH$ (X = O or S) were studied theoretically [713]. The bond energy is higher in oxygen analogs due to metal–oxygen π-antibonding interactions. Zirconium–carbyne and carbene complexes have been identified in gas-phase reaction of methane and $Zr^+$ ions, and have been studied theoretically [714].

## Acknowledgements

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

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