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Review

The chemistry of the carbon–transition metal double and triple bond: Annual survey covering the year 2005☆

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Abstract

This is a review of papers published in the year 2005 that focus on the synthesis, reactivity, or properties of compounds containing a carbon–transition metal double or triple bond.

Keywords: Synthesis; Carbon–transition metal; N-heterocycles

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. Several reviews in this area appeared in 2005 [1]. 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 usually minimal, there is no formal carbon metal multiple bond [2–7]. This area was reviewed several times in 2005 [8–10]. Another class of stable carbene complexes, amino/phosphine-stabilized or Bertrand carbenes, are less well developed and complexes to these carbenes have been included in this article [11]. A comparison of Arduengo and Bertrand carbene–metal complexes was reported [12]. This survey has been divided into two sections, metal carbene (or alkylidene)

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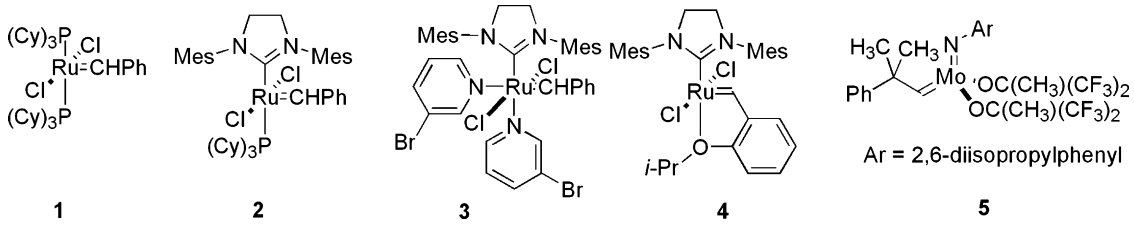


1 2 3 4 5

Fig. 1. Structures of alkene metathesis catalysts **1–5**.

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 [13] 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* [14]) (Fig. 1)

Grubbs catalyst I	Structure **1** (Fig. 1)
Grubbs catalyst II	Structure **2** (Fig. 1)
Grubbs catalyst III	Structure **3** (Fig. 1)
Hoveyda–Grubbs catalyst	Structure **4** (Fig. 1)
Schrock catalyst	Structure **5** (Fig. 1)
NHC	N-heterocyclic carbenes

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

1.1. Metal–carbene or metal–alkylidene complexes

1.1.1. Review articles and comments

Several reviews/comments covering aspects of metal–carbene complex chemistry appeared in 2005.

Many articles focusing on some aspect of carbene complex-initiated olefin metathesis were published, including the following specific subjects: (1) general carbene complex-initiated olefin metathesis [15–27]; (2) mechanism of metathesis reactions [28]; (3) recent developments in the design and synthesis of well-defined ruthenium metathesis catalysts [29]; (4) olefin metathesis focusing on catalyst development, microwave catalysis, and domino applications [30]; (5) olefin metathesis using tungsten(0) carbene complexes [31]; (6) relay metathesis [32]; (7) metathesis reactions in total synthesis [33,34]; (8) use of cross metathesis in the synthesis of biologically active natural products [35]; (9) use of cross metathesis for the formation of trisubstituted alkenes [36]; (10) use of RCM for the synthesis of various biologically important natural products [37]; (11) synthesis of N-heterocycles using ruthenium carbene complex-initiated metathesis and non-metathesis reactions also initiated by these complexes [38]; (12) metathesis strategies in nucleoside chemistry [39,40]; (13) use of RCM for the synthesis of peptidomimetics [41]; (14) use of RCM in carbohydrate chemistry [42]; (15) use of metathesis for the synthesis of biologically active macrocycles [43]; (16) use of metathesis for the synthesis of molecular gyroscopes [44]; (17) olefin metathesis polymerization using ruthenium carbene complexes [45]; (18) cyclopolymerization of α,ω-heptadiynes [46]; (19) living polymerization of substituted acetylenes [47]; (20) use of metathesis to link organic molecules to metal surfaces [48]; (21) group selective enyne metathesis [49].

Several review articles report on synthesis of various compound classes where carbene complex-initiated olefin metathesis is a commonly-employed synthetic route. Specific compound classes represented include: (1) unsaturated α-amino acids [50]; (2) molecules that contain quaternary centers [51]; (3) carbohydrate mimetics [52]; (4) dipeptide mimetics [53]; (5) propellanes [54]; (6) solid-phase carbohydrate synthesis and detachment from the solid support using metathesis [55]; (7) catenanes and rotaxanes [56,57]; (8) polyether toxins [58,59]; (9) epothilone analogs [60]; (10) taxol analogs [61]; (11) wortmannin [62]; (12) amphidinolide A [63]; (13) piperidine azasugars [64]; (14) zaragozic acids [65].

Additional review articles include some metathesis segments. Articles in this category focus on the following subjects: (1) dendritic catalysts [66]; (2) transition metal imido complexes as polymerization catalysts [67]; (3) carbon–carbon bond-forming reactions in aqueous media [68]; (4) ruthenium–Schiff base complexes in catalysis [69,70]; (5) N-heterocyclic carbene complexes, including metathesis catalysts [71,72]; (6) reactions of unsaturated organometallic reagents with trifluoroacetamides [73]; (7) organic reactions in ionic liquids [74,75]; (8) microwave activation of organic reactions [76]; (9) new synthetic methods based on organometallic complexes [77]; (10) formation of C=C bonds by condensation [78]; (11) diastereotopic group selection in the synthesis 1,4-cyclohexadienes [79]; (12) solid-phase synthesis using organometallic reagents [80]; (13) transition metal catalyzed reactions of heterocumulenes [81]; (14) carboxycarbene–iridium complexes obtained through C–H activation processes [82]; (15) chemical transformations of Baylis–Hillman adducts [83]; (16) structure and reactivity of tungsten(II) and molybdenum(II) compounds containing a metal-metal bond [84]; (17) synthesis of natural products by groups of Fürstner [85] and Nicolaou [86]; (18) application of interfacial organic reactions to nanobiotechnology [87]; (19) ion pairing in organometallic chemistry [88]; (20) production of neohexane [89].

Several reviews on carbene complex chemistry featuring some aspect other that metathesis appeared in 2005. These reviews include the following subjects: (1) high oxidation state alkylidene and alkylidyne complexes [90]; (2) new titanium carbene complexes and their application to organic synthesis

[91,92]; (3) half-sandwich complexes with non-Fischer carbene ligands [93]; (4) synthesis and reactivity of half-metallocene tantalum carbene complexes [94]; (5) reactivity of Group 6 Fischer carbene complexes [95]; (6) catalytic transformations using Group 6 Fischer carbene complexes [96]; (7) transition metal catalyzed reactions using alkynes as precursors of carbene and vinylidene complexes [97]; (8) organic synthesis using metal vinylidene complexes [98]; (9) diiron compounds featuring bridging carbene and carbyne ligands [99]; (10) phosphorus-substituted carbene complexes [100]; (11) synthesis of N-heterocyclic carbene complexes from isocyanides [101]; (12) ruthenium-salen catalyzed cyclopropanation [102]; (13) Fischer and Arduengo carbene complexes of various transition metals [103]; (14) gold-catalyzed enyne cycloisomerization [104].

Although not specifically focusing on metal–carbene complexes, some review articles place some emphasis on this subject. Subjects reviewed in this category include: (1) decomposition of transition metal alkyls [105]; (2) use of water in organic synthesis, which includes a section on alkyne hydration via vinylidenes [106]; (3) single electron transfer reactions in the synthetic organometallic chemistry of first row transition metals [107]; (4) metal catalyzed alkyne hydroarylation [108]; (5) chemistry of $CpOs(P\textit{i}\text{-}Pr_3)_2Cl$ complexes [109]; (6) parity violation in molecules (primarily osmium carbene complexes) [110]; (7) metal catalyzed enyne cycloisomerization [111]; (10) ruthenium-catalyzed reactions [112]; (11) gold-catalyzed reactions [113,114]; (12) properties of dialkylmolybdenum nitrosyl complexes [115]; (13) formation of molecules that contain organotransition metal groups (often Fischer carbene complexes) linked to nucleobases through peptide chains [116]; (15) platina-β-diketone complexes [117]; (16) ether dealkylation reactions (often accomplished through use of Grubbs catalyst I to effect alkene isomerization followed by enol ether hydrolysis) [118]; (17) alkynetrimerization [119]; (18) noble metal complexes [120]; (19) complexes of vanadium, niobium, and tantalum [121]; (20) complexes containing σ-bonds to the iron, cobalt, and nickel groups [122]; (21) complexes of groups 1 and 11 [123]; (22) noble metal complexes [124]; (23) synthesis of benzofuran natural products [125].

1.1.2. Alkene metathesis

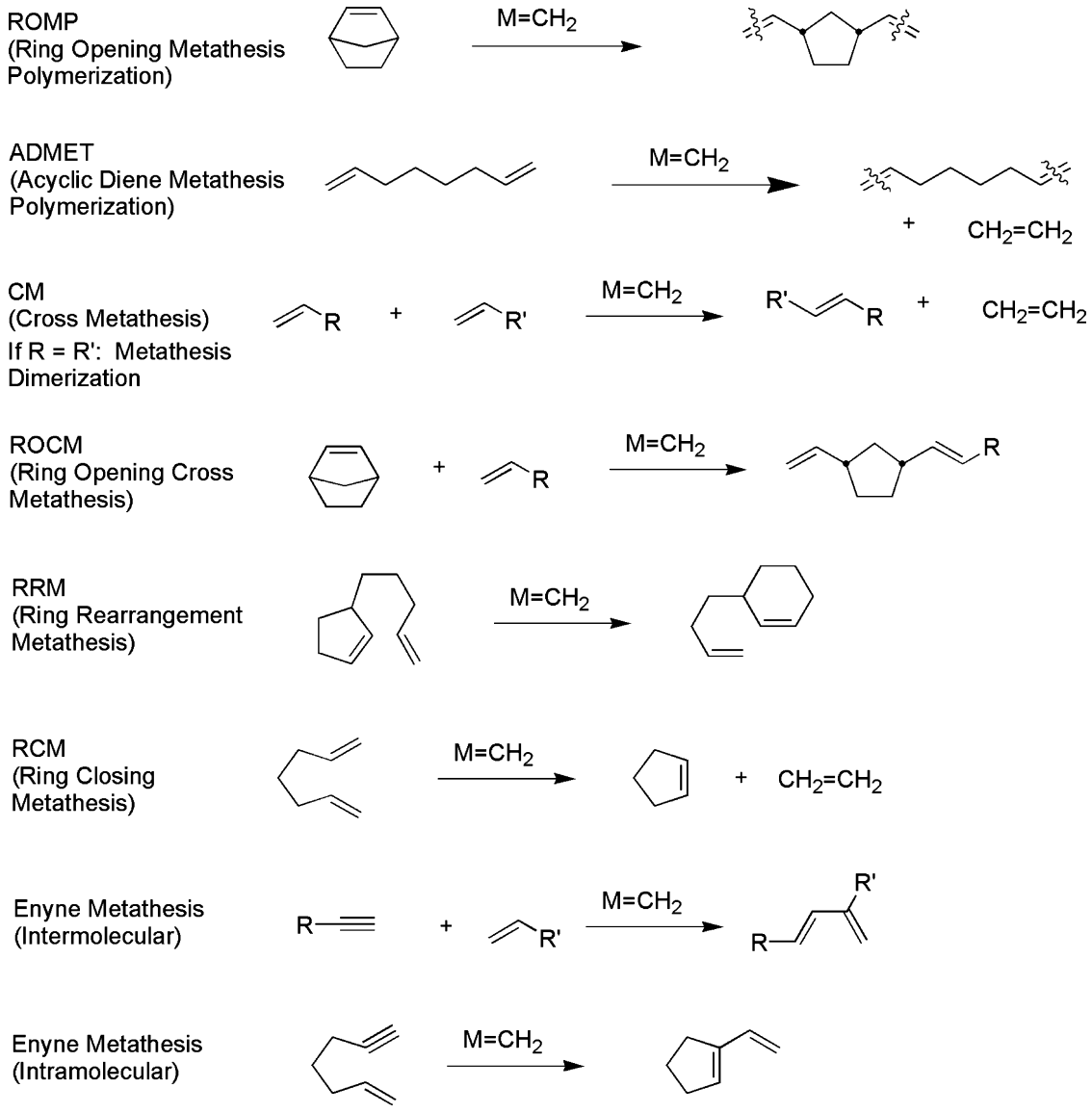
Alkene metathesis was the most common reaction process reported for metal–carbene complexes in 2005, and this special section is devoted to papers that focus on this process. Many examples of both polymerization [mostly ring opening metathesis polymerization (ROMP)] reactions and small-molecule syntheses appeared. Only metathesis reactions initiated by a discreet transition metal–carbene complex or metathesis reactions that offer significant discussion of the carbene complex intermediates of metathesis reactions have been included here. Distinct modes of alkene metathesis are depicted in Scheme 1.

The Nobel Prize in Chemistry for 2005 was awarded to Y. Chauvin, R.H. Grubbs, and R.R. Schrock for their seminal contributions to the understanding and advancement of olefin metathesis [126,127].

1.1.2.1. General studies of alkene metathesis catalysts.

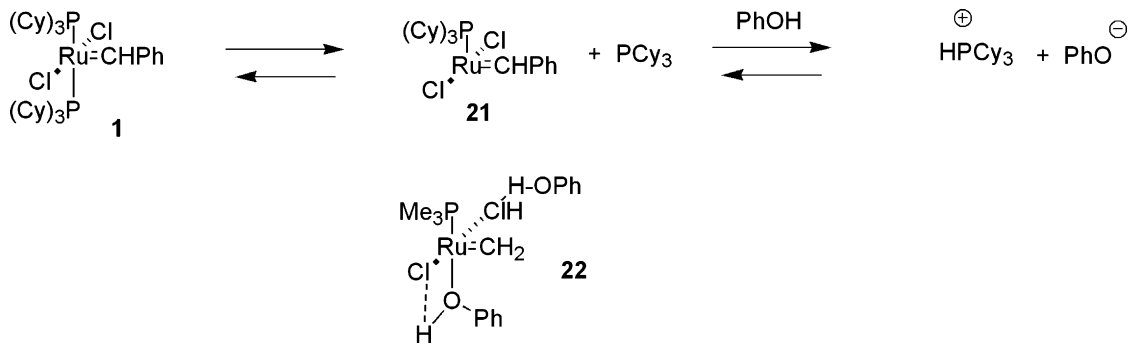
Numerous attempts to develop new catalysts for alkene metathesis were reported in 2005; some representative examples are depicted in Fig. 1. Several derivatives of the Grubbs and Schrock catalysts were synthesized and tested in their ability to undergo either ROMP or RCM processes, including: (1) chiral and chelated analogs of the Hoveyda–Grubbs catalyst (*e.g.* **6**) that effectively catalyze asymmetric RO-CM reactions [128]; (2) an analog of Grubbs catalyst I where the phenyl group is replaced by a ferrocenyl group [129]; (3) new dimethylvinylcarbene–ruthenium complexes [130]; (4) analogs of Grubbs catalyst II featuring pyridinecarboxylate ligands (**7**), which becomes an active catalyst upon treatment with HCl [131]; (6) ruthenium carbene complexes that feature chelating iminopyrollato ligands [132]; (7) highly active phenoxy analogs of Grubbs catalyst II (*e.g.* **8**) [133]; (8) ruthenium carbene complexes featuring four-membered ring N-heterocyclic carbene ligands (*e.g.* **9**) [134]; (9) ruthenium complex **10** featuring bromopyridine ligands and alkylcarbene ligands [135]; (10) a highly active ruthenium carbene complex featuring pyridine ligands [136]; (11) analogs of Grubbs catalyst II that feature a ring-fused N-heterocyclic carbene ligand (*e.g.* **11**) (prepared through an RCM reaction) [137]; (12) various analogs of the Hoveyda–Grubbs catalyst derived from alkyne insertion processes (*e.g.* **12**) [138]; (13) various imine analogs of the Hoveyda–Grubbs catalyst (*e.g.* **13**) [139]; (14) chiral ruthenium carbene complexes that feature chelating N-heterocyclic carbene ligands (*e.g.* **14**) [140]; (15) analogs of Grubbs ruthenium carbene complexes that feature pincer ligands (*e.g.* **15**) [141]; (16) analogs of the Hoveyda–Grubbs catalysts featuring an imidazolium salt substituent (*e.g.* **16**) for catalysis of metathesis reactions in ionic liquids [142,143]; (17) fluorous analogs of the Hoveyda–Grubbs catalyst (*e.g.* **17**) [144]; (18) water-soluble analogs of Grubbs-catalyst II [145]; (19) immobilized analogs of Grubbs catalyst III [146]; (20) analogs of the Hoveyda–Grubbs catalyst bound to functionalized polymer chips [147]; (21) silica bound analogs of the Hoveyda–Grubbs catalyst [148]; (22) ruthenium carbene complexes bound to mesopourous silica [149]; (23) monolith-supported ruthenium carbene complexes [150]; (24) polymer-bound trifluoroacetate analogs of Grubbs catalyst II [151]; (25) analogs of the Hoveyda–Grubbs catalyst bound to a gold surface [152]; (26) dendritic ruthenium carbene complexes [153]; (27) bis(carbene)bridged bimetallic analogs of the Schrock carbene complex prepared through stoichiometric metathesis of the Schrock catalyst [154]; (27) analogs of the Shrock catalyst featuring phenoxy ligands (*e.g.* **18**) [155]; (28) analogs of the Schrock catalyst immobilized on molecular sieves [156]; (29) vanadium carbene complexes (*e.g.* **19**) [157]; (30) an osmium carbene complex (**20**) [158]. Several patents were issued for the synthesis and development of metal–carbene containing olefin metathesis catalysts [159–171]. Theoretical studies of a hypothetic P-heterocyclic analog of Grubbs catalyst II were reported [172].

The role of phenol for enhancing the reactivity and loading of Grubbs catalyst I was investigated (Scheme 2) [173]. Several roles were attributed to phenol. Ability to protonate the free phosphine ligand likely suppresses the phosphine return in

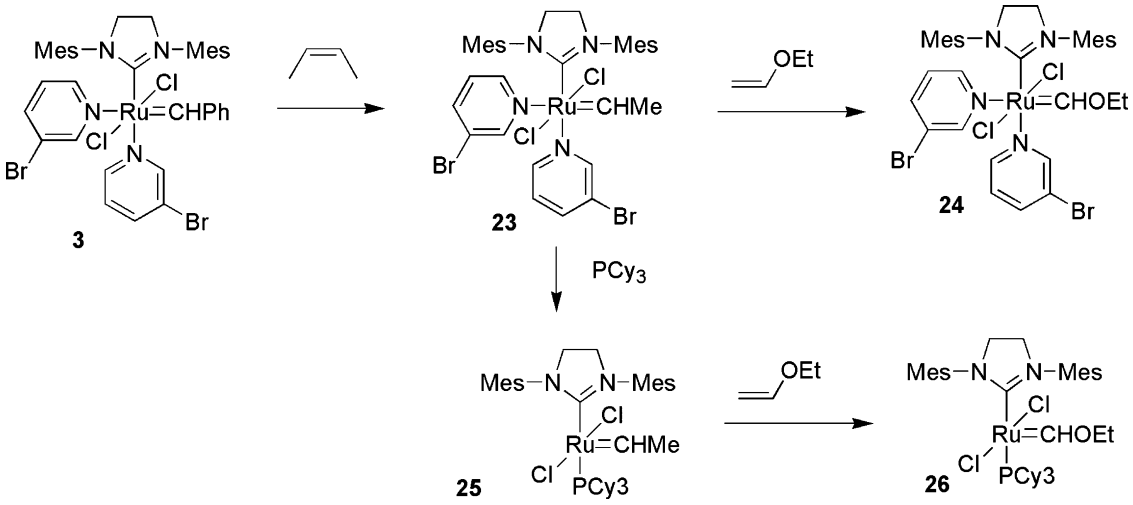


Scheme 1.

the initial dissociation step. In the DFT-optimized structure of the phenol complex (**22**), favorable hydrogen bonding effects can stabilize the chain-carrying methyleneruthenium species. Use of the phenolic compound *p*-cresol to improve the efficiency of cross metathesis reactions was also reported [174]. The additives acetic acid and benzoquinone were both effective in preventing alkene isomerization during alkene metathesis reactions [175]. Benzoquinone was more effective. The beneficial effect of benzoquinone was attributed to rapid reaction with any metal hydride intermediates to afford hydroquinone.



Scheme 2.

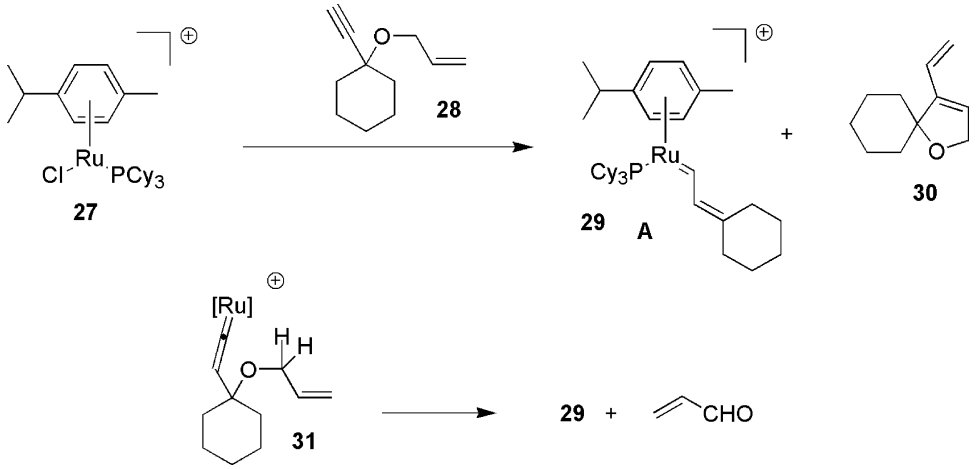


Scheme 3.

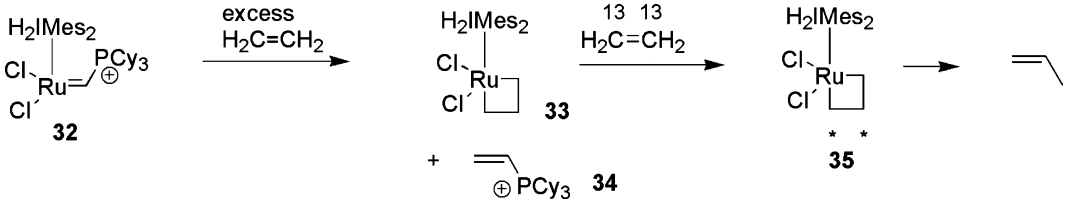
Stoichiometric metathesis reactions using Grubbs catalyst III were reported (Scheme 3) [176]. Reaction of Grubbs catalyst III (**3**) with symmetrical alkenes afforded the alkylcarbene analogs (*e.g.* **23**). Subsequent reaction with ethyl vinyl ether led to the Fischer carbene complex **24**. Conversion of alkylcarbene analogs of Grubbs catalyst II (*e.g.* **25**) was effected by treatment of **23** with tricyclohexylphosphine, which also afforded Fischer carbene complexes (*e.g.* **26**) upon treatment with ethyl vinyl ether. Alkylcarbene complex **25** was an effective initiator for ROMP but not RCM.

Generation of an alkene metathesis catalyst (**29**, Scheme 4) through reaction of ruthenium-*p*-cymene complex **27** with allyl propargyl ethers (*e.g.* **28**) was reported [177]. The reaction proceeds by generation of a vinylidene (*e.g.* **31**) followed by hydride shift/elimination to afford the carbene complex **29**, which catalyzes the enyne metathesis process. The catalyst **29** was of low activity for RCM but displayed high activity for intramolecular enyne metathesis.

The self-metathesis of ethylene using cationic 14-electron carbene complex **32** (Scheme 5) was investigated [178]. The



Scheme 4.



Scheme 5.

reaction with excess ethylene afforded an observable metallacyclobutane intermediate (**33**). Reaction with C-13 labeled ethylene led to the labeled metallacyclobutane. Eventually the carbene complex decomposed to propene and an unidentified ruthenium species.

A general study of the relationship between successful metathesis catalysts and metallacyclobutane structure was reported [179]. It was noted that metallacyclobutanes derived from successful alkene metathesis catalysts feature significant metal and C–C bond agostic interactions. This phenomenon was also investigated computationally using a variety of different metal–ligand systems [180]. All metallacyclobutanes derived from successful metathesis catalysts showed elongated C–C bonds, attributed to C–C bond-transition metal agostic interactions.

The interconversion of *cis* and *trans* pyridylruthenium carbene metathesis catalysts (*e.g.* Grubbs catalyst III) was studied by DFT calculations [181]. The most favorable pathway involves the dissociation of the pyridine followed by isomerization followed by reclosure. The position of equilibrium was highly dependent on solvent polarity. The complex with a *trans* pyridyl-NHC arrangement was favored in the gas phase however the *cis* isomer was favored in dichloromethane and for more polar solvents.

Other general studies of alkene metathesis where carbene complexes were discussed include the following subjects: (1) verification of the "release-return" mechanism for polymer-bound alkene metathesis catalysts using crossover experiments [182]; (2) examination of linear free energy relationships for the enyne metathesis reactions using *p*-substituted styrene derivatives and terminal or internal alkynes [183]; (3) switching of metathesis reaction processes on and off through redox processes [184]; (4) use of imidotungsten–ethylene complexes as alkene metathesis catalysts and discussion of possible methods for the initial generation of carbene complex intermediates [185]; (5) use of polymer-bound triphenylphosphine oxide for removal of ruthenium byproducts from metathesis reactions [186]; (6) catalysis of ROMP by bis(acetonitrile(allyl))-molybdenum- and -tungsten complexes activated by alkynes and a proposed mechanism involving norbonenylidene complex intermediates [187]; (7) rationalization of the effect of donor solvents on ROMP reactions catalyzed by ruthenium(II) complexes and ethyl diazoacetate [188]; (8) a comparison of silica supports (molecular and surface silanols) in molybdenum-catalyzed metathesis reactions [189]; (9) a comparison of turnover numbers for various ruthenium carbene complex catalysts in dilute solution [190]; (10) a computational study directed toward better understanding the superior reactivity of Grubbs catalyst II over Grubbs catalyst I (the better electron-donating N-heterocyclic carbene ligand can better the high formal oxidation state of the metallacyclobutane intermediate) [191]; (11) a computational study attributing the superior reactivity of Grubbs catalyst II to proper orientation of the alkene for metallacyclobutane formation and stabilization of the high oxidation state metallacyclobutane intermediate by the highly electron donating NHC ligand [192]; (12) a computational study of enyne metathesis focusing on the metallacyclobutene-vinylcarbene interconversion and defining the role for the beneficial effect of ethylene on the process, and favoring the "alkene-first" mechanism [193]; (13) metathesis versus cyclopropanation in the ruthenium-catalyzed reactions of ethyl diazoacetate with styrene [194]; (14) a computational study of rhenium carbene/carbyne complexes that function as alkene metathesis catalysts [195]; (15) a computational study delineating the origins of enantioselectivity using asymmetric alkene metathesis catalysts [196]. A computational study of the formation of a metathesis-active alkylidene complex from bis(ethylene)$W(CO)_4$ was reported [197]. The most favorable pathway identified involved two-electron oxidation prior to formation of a metallacyclopentane, followed by eventual conversion to $(CO)_4W{=}CHC_3H_7$. Patents were awarded for the removal of impurities in metathesis reactions [198,199] and for metathesis in ionic liquids [200].

1.1.2.2. 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 reactions involving a norbornene derivative and another alkene accounted for a large fraction of all reports of the ROMP reaction in 2005 (Fig. 3). Numerous substituted norbornenes have been subjected to ROMP using metal carbene complexes, including those possessing the following structural features: (1) norbornene [201]; (2) norbornene in a microemulsion [202]; (3) 5-alkylnorbornenes [203]; (4) norbornenecarboxylate esters [204]; (5) norbornenes connected to diazenes (*e.g.* **36**) [205]; (6) norbornenes connected to magnesium porphyrins [206,207]; (7) norbornenes linked to carbazoles and isoquinolines (*e.g.* **37**) [208]; (8) norbornenes linked to cyanuric acid and pyrimidine derivatives [209]; (9) glycosylated norbornenes [210]; (10) norbornenes linked to carbohydrates (*e.g.* **38**) [211,212]; (11) norbornenes linked to iminyl fluorides (*e.g.* **39**) [213]; (12) norbornenes linked to sulfonyl chlorides (*e.g.* **40**) [214]; (13) norbornenes linked to polystyrenes [215]. The formation of block copolymers through ROMP reactions was reported using: (1) norbornenes containing *N*-hydroxysuccinate esters (*e.g.* **41**) and maleimide groups (*e.g.* **42**) [216]; (2) block copolymers from norbornene derivatives attached to the anticancer drug doxorubicin [217].

Other ring systems that have been subjected to ROMP reactions include: (1) cyclooctenes followed by termination with allylpolythiophene derivatives [218]; (2) protected dihydroxycyclooctenes (*e.g.* **43**) [219]; (3) cyclooctenes linked to phosphazenes (*e.g.* **44**) [220]; (4) cyclooctadiene followed by termination with an alkene containing a dithioester group [221]; (5) moderately strained alkenes (*e.g.* cyclopentene and cycloheptene) [222]; (6) cometathesis of cyclooctene and disubstituted alkenes featuring pyridinecarboxylate esters at the ends of the chain [223]; (7) cyclooctenes and dendrimeric alkenes [224]. Identification of an oxygen coordinated carbene complex (**46**, Scheme 6) as the propagating carbene species in ROMP reactions of 7-alkoxynorbonadiene derivatives was reported [225]. Hypothetical formation of rhenium carbene complexes in the ROMP of cyclooctene using supported methyltrioxorhenium was discussed [226]. Formation of surface bound ruthenium car-

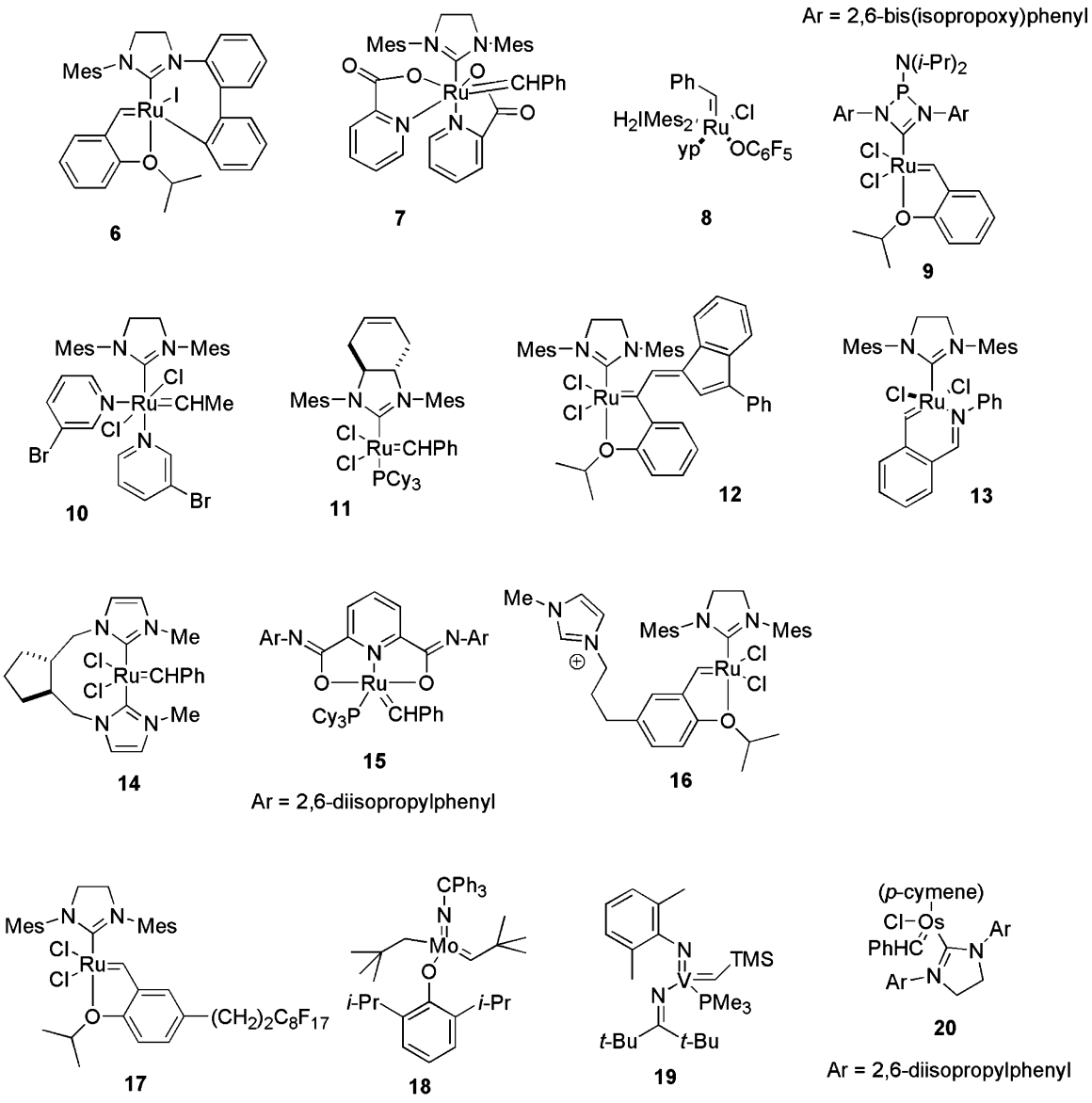
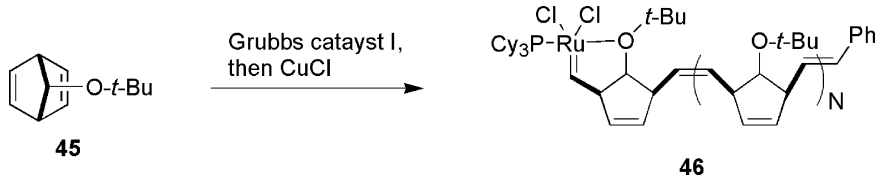


Fig. 2. Representative examples of new catalysts for alkene metathesis.

bene complexes from reaction of a ruthenium surface with diazo compounds followed by ROMP and cross metathesis reactions was reported [227]. Related studies were reported for the carbenes generated through the interaction of molybdenum carbide surfaces and various simple alkenes, followed by ROMP of norbornene [228]. Several patents were awarded for various aspects of carbene complex-initiated ROMP reactions [229–235].

Several examples using carbene complexes to initiate acyclic diene metathesis (ADMET, see Scheme 1) were reported in 2005. Substrates subjected to ADMET polymerization are depicted in Fig. 4 and include: (1) alkenes linked through polyaromatic compounds (*e.g.* **47**) [236]; (2) all carbon-linked alkenes featuring ether substituents (*e.g.* **48**) [237]; (3) alkene isomerization during ADMET polymerization of all carbon linked alkenes containing amino acid functionality (*e.g.* **49**) [238]. Solid state ADMET and RCM reactions were reported [239]. These processes involve the addition of Grubbs catalyst II to the solid or molten monomer, followed by cooling of the



Scheme 6.

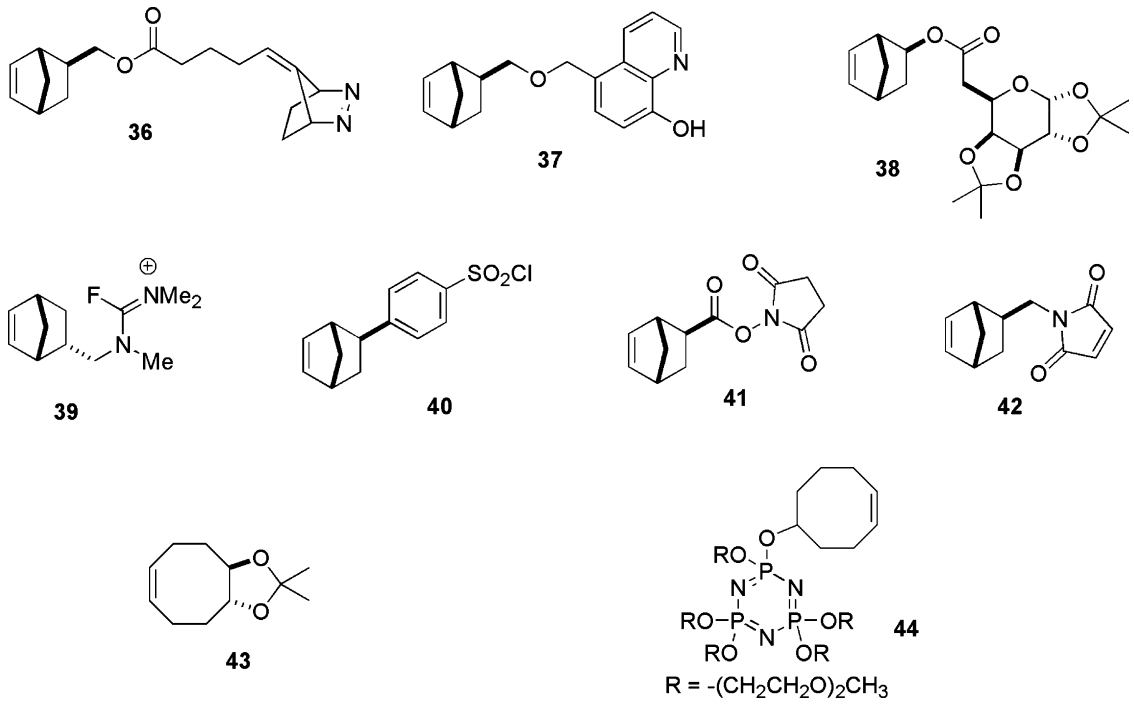


Fig. 3. Representative substrates for the ROMP reaction.

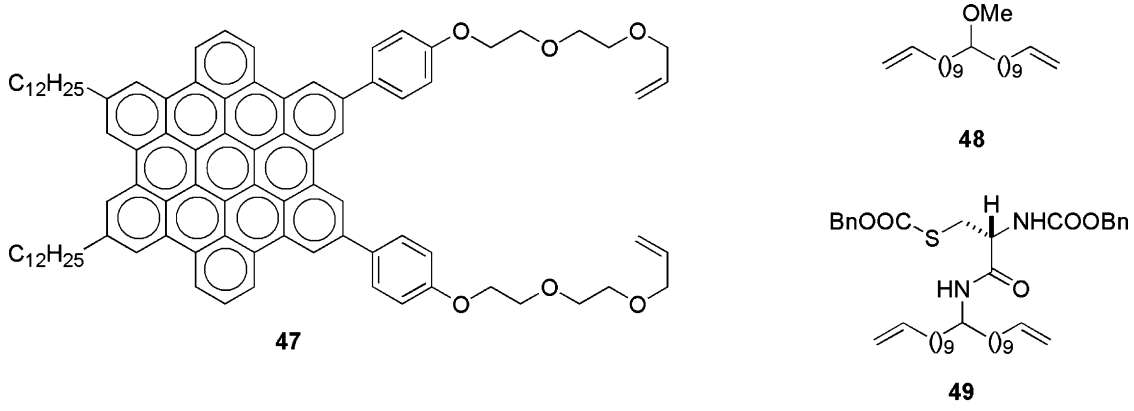
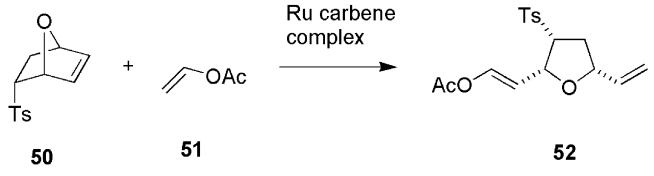


Fig. 4. Representative substrates for ADMET polymerization.

mixture to the solid state and monitoring the progress of the polymerization/RCM reaction.

1.1.2.3. Nonpolymer-forming ring opening metathesis reactions. Several examples of RO-CM (see Scheme 1) were reported in 2005. A representative example is depicted in Scheme 7. Co metathesis of norbornene derivative **50** and various monosubstituted alkenes proceeded with a high degree of regioselectivity to form the regioisomer depicted by **52** as the major product [240,241].



Scheme 7.

1.1.2.4. 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 2005. Representative examples are depicted in Fig. 5. Specific pairs of compounds subjected to cross metathesis include: (1) end-of-chain alkene aldehydes (*e.g.* **53**) and allylic acetates [242]; (2) monosubstituted alkenes and α,β-unsaturated ketone derivatives [243]; (3) alkene-alcohols and alkene-nitriles [244]; (4) diester-cyclic carbonate **55** and ketone-alkene **56** for total synthesis of viridofungin [245]; (5) complex reacting partners (**57** and **58**) for total synthesis of apoptolidinone [246]; (6) allylic alcohols and allylic acetates for mucocin total synthesis [247]; (7) natural unsaturated triacylglycerides

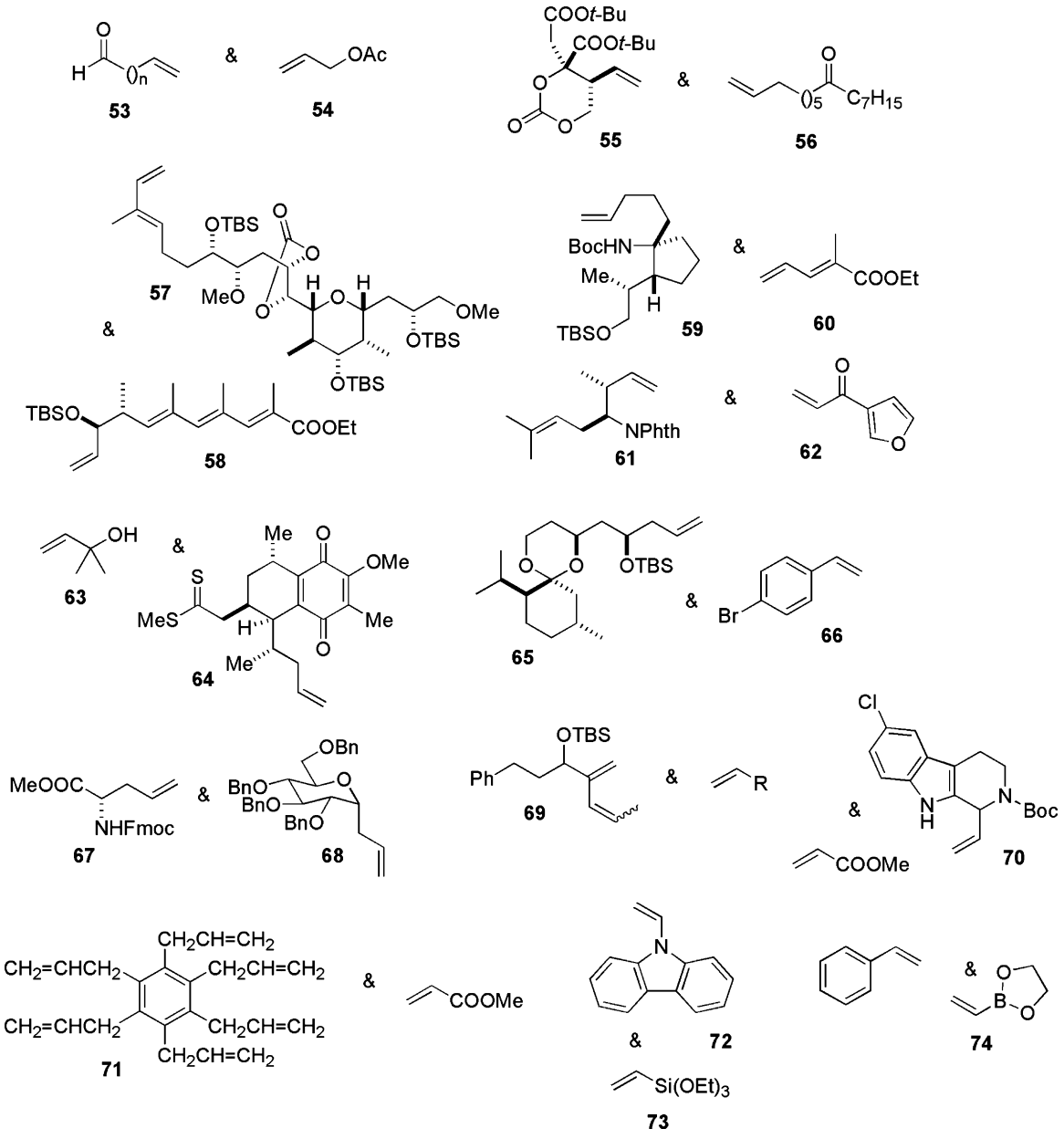


Fig. 5. Represent pairs of alkenes subjected to cross metathesis.

and *cis* 2-butene [248]; (8) allylic ethers and *N*-allylpyrimidines [249]; (9) ginkgolide acrylate esters with styrene [250]; (10) *C*-allyl glucoside or *C*-homoallyl glucosides with allylglycine derivatives [251]; (11) chemoselective cross metathesis of monoprotected 1,5-cyclohexadien-3,4-diol derivatives and α,β-unsaturated ketones for total synthesis of phomopsolide C (a later step employs an RCM reaction) [252]; (12) polyoxygenated compounds that feature an alkene at the end of the chain with allylglycines [253]; (13) allylglycine derivatives and alkene-containing esters [254]; (14) *N*-allylphthalimide derivatives and analogous carbamates with various monosubstituted alkenes [255]; (15) a complex amide (**59**) and a diene-ester (**60**) for halichlorine total synthesis [256]; (16) dissimilar allylamine and homoallylamine derivatives [257]; (17) homoallylic amine derivatives with α,β-unsaturated ketones for total synthesis of indolizidines [258]; (18) a complex pentenyl pyrrole derivative and allyltrimethylsilane for total synthesis of anatoxin A [259]; (19) a methylenetetrahydrofuran derivative with a vinylboronic ester for total synthesis of aureothin [260]; (20) allylic ether derivatives and monosubstituted alkenes for synthesis of bengamide derivatives [261,262]; (21) a complex carbohydrate derivative and an allylamino acid derivative followed by hydrogenation [263]; (22) *O*-glycosyl-linked carbohydrates and various amino aid derivatives [264]; (23) a homoallylic acetate derivative and methyl acrylate for total synthesis of colletodiol [265]; (24) *N*-pentenylphthalimide and allyltrimethylsilane for tashiromine total synthesis [266]; (25) an alkene-ester and acrolein for octalactin synthesis [267]; (26) a homoallylamine derivative (**61**) and acryloylfuran (**62**) for nupharamine total synthesis [268]; (27) conjugated diene-esters

and monosubstituted alkenes (metathesis occurs at the alkene distant from the ester group) [269]; (28) conjugated dienes and α,β-unsaturated ketones [270]; (29) double CM of bis(allylic alcohol) derivatives and 2-butene-1,4-diol diacetate [271]; (30) highly oxygenated 1-hexene derivatives and monosubstituted alkenes [272]; (31) dissimilar alkoxystyrene derivatives [273]; (32) 2-methyl-3-propen-1-ol and a complex alkene (*e.g.* **64**) for total synthesis of colombiasin A and elisapterosin B [274]; (33) monoprotected alkene-diols and ethyl acrylate for preparation of amphidinolide segments [275]; (34) a complex homoallylic ether (**65**) and styrene derivatives (*e.g.* **66**) for total synthesis of bryostatin analogs [276]; (35) *C*-allyl glycosides (*e.g.* **68**) and homoallylamine derivatives (*e.g.* **67**) [277]; (36) *C*-allylglycosides and various electron deficient monosubstituted alkenes [278]; (37) allylated carboline derivatives and monosubstituted alkenes [279]; (38) conjugated dienes (*e.g.* **69**) and monosubstituted alkenes as part of an investigation to determine the origin of *E* selectivity in enyne metathesis reactions (only the *Z* isomer readily undergoes CM reactions) [280]; (39) an azidoribose derivative and 1-nonene for sphingosine total synthesis [281]; (40) iminosugars with allylic amine derivatives [282]; (41) homoallylic amine derivatives with allylglycine derivatives [283]; (42) an allylglycine derivative and a γ,δ-unsaturated ketone for total synthesis of FR 235222 [284]; (43) indole derivative **70** with methyl acrylate [285]; (44) preparation of sphingosine derivatives through cross metathesis [286]; (45) sphingosine derivatives and fluorescent tags that contain remote monosubstituted alkene functionality [287]; (46) discodermolide derivatives and monosubstituted alkenes connected to fluorescent species [288]; (47) hexaallylbenzene (**71**) (and iron-complexed arene analogs) and methyl acrylate [289]; (48) vinylsilanes and monosubstituted alkenes [290]; (49) *N*-vinylcarbazoles (*e.g.* **72**) and vinylsiloxanes (*e.g.* **73**) [291]; (50) polymer-bound allylsilanes and homoallyltyrosine derivatives [292]; (51) vinylphosphine oxides and various monosubstituted alkenes [293]; (52) Hoogsteen-paired polyamides containing remote alkene functionality. Cross metathesis was frequently employed for the crosslinking of polymers and scrambling of polymers [294,295]. Cross metathesis of vinylboranes (*e.g.* **74**) and styrene was reported [296]. In this case the apparent CM product can be obtained through CM or through a hydroboration mechanism. The cross metathesis product was also obtained using a ruthenium hydride complex, however D labeling studies showed that only the ruthenium–carbene complex catalyzed process proceeded through a metathesis mechanism. Microwave cross metathesis was reported [297]. The difficulty in cross metathesis of cyclic compounds with haloalkenes was studied computationally [298,299]. Patents were awarded for the preparation of various compounds via cross metathesis [300–304].

Several examples of dimerization via metathesis (see Scheme 1) were reported in 2005. Compounds subjected to metathesis dimerization are depicted in Fig. 6, and include: (1) alkene-containing amino acid derivatives (*e.g.* **75**) [305]; (2) moderately efficient dimerization of acrylonitrile in the presence of titanium isopropoxide [306]; (3) allylamine and homoallylamine esters [307]; (4) microwave metathesis dimerization and cross metathesis of allylamine derivatives (*e.g.* **76**) [308]; (5) *O*-allylnucleosides [309]; (6) alkene-esters connected to dibenzo crown ethers [310]; (7) artemisinin derivatives (*e.g.* **77**) [311]; (8) allylCp–$TiCl_2$ complexes [312]; (9) dimerization of various alkene-containing zirconacene derivatives (*e.g.* **78**) [313]; (10) acrylamides [314]; (10) dimerization of vinylsiyl chlorides (*e.g.* **79**) [315].

Additional examples feature cross metathesis in tandem with some other metathesis mode. A representative example is depicted in Scheme 8. Tandem metathesis trimerization-RCM was observed in the treatment of diene **80** with Grubbs catalyst II [316]. None of the desired RCM product **82** was observed in this reaction. Cyclic tetrameric porphyrins were formed in a similar tandem CM-RCM sequence [317].

1.1.2.5. 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 2005, 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) formation of simple five-membered rings [318]; (2) formation of spirocyclic cyclopentenes [319]; (3) moderately selective formation of a spirocyclic cyclopentene derivative from a tetraene derivative [320]; (4) formation of cyclopentenes for total synthesis of the proposed structure of agardhilactone [321] and herbertene-1,13-diol [322]; (5) formation of cyclopentenols for synthesis of aminopeptidase-2 inhibitor total syntheses [323]; (6) formation of cyclopentenenitriles [324]; (7) formation of cyclopentenediol derivatives for prostanoid synthesis [325]; (8) formation of cyclopentene esters [326], spirocyclic lactone analogs [327], and application to HM-1 and HM-2 total syntheses [328]; (9) formation of cyclopentenes for carbocyclic

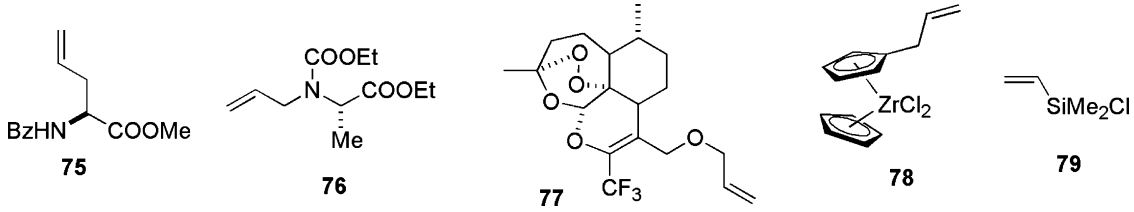
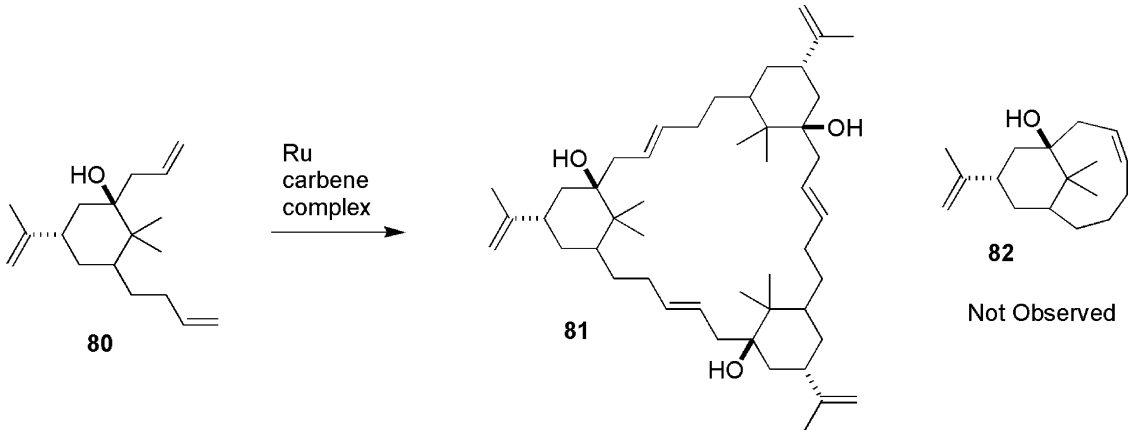


Fig. 6. Representative alkenes subjected to metathesis dimerization.



Scheme 8.

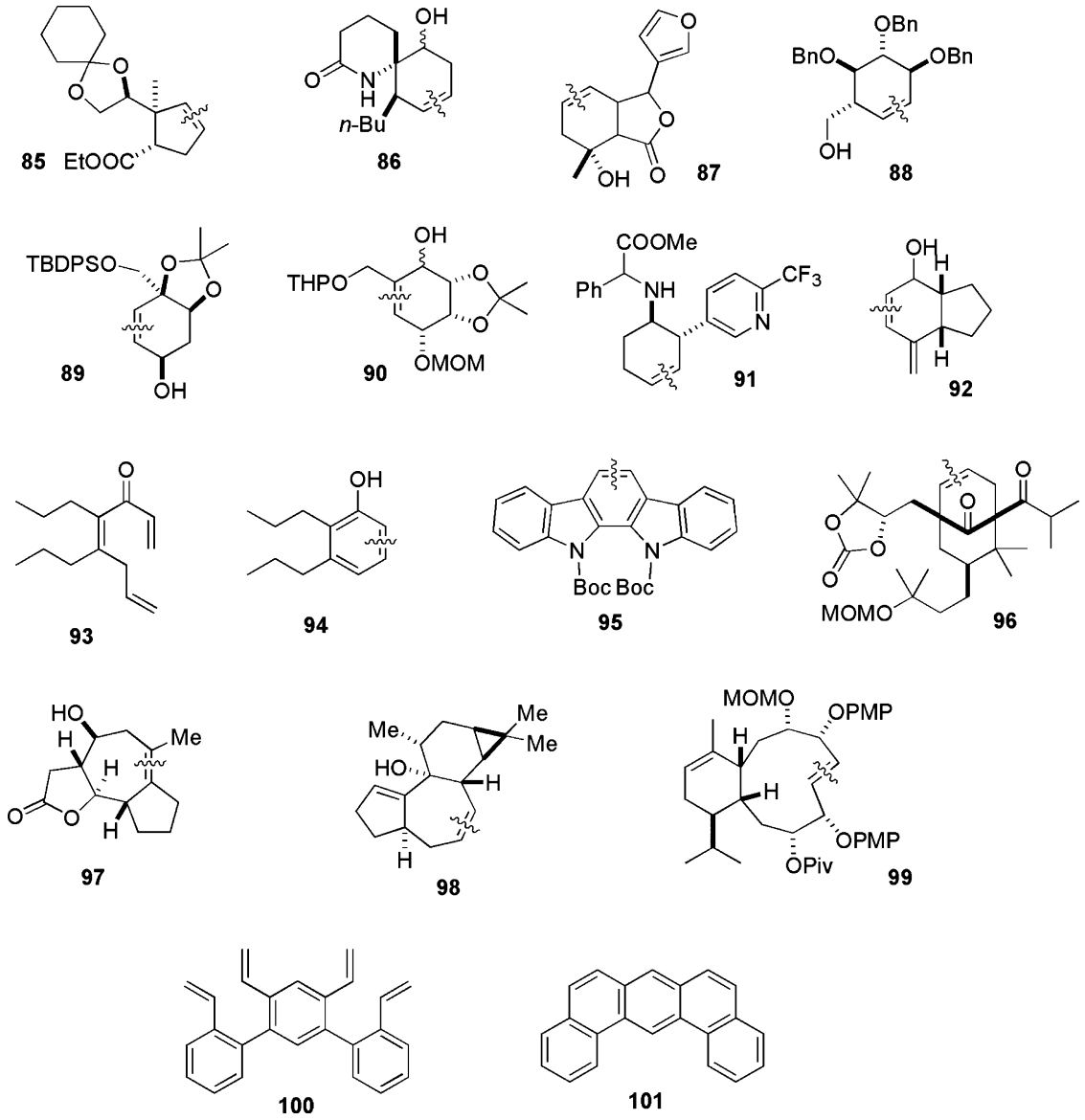


Fig. 7. Representative carbocycles produced through an RCM reaction (bond constructed through RCM indicated).

nucleoside synthesis (*e.g.* **85**) [329–332]; (10) formation of cyclopentenes spiro fused to five-membered ring ketolactones [333]; (11) formation of cyclopentenols for utenone A total synthesis [334]; (12) formation of cyclopentenones for oleocanthol total synthesis [335]; (13) formation of indenols and indenones [336]; (14) formation of decalin derivatives [337]; (15) formation of spirocyclic barbituric acid derivatives [338]; (16) formation of a spirocyclic cyclohexene (**86**) for histrionicotoxin total synthesis [339]; (17) formation of spirocyclic cyclohexenones [340]; (18) formation of a cyclohexene fused to a γ-lactone (**87**) for fraxinellone liminoids total synthesis [341]; (19) formation of a cyclohexene ring for tenuifolene total synthesis [342]; (20) formation of highly oxygenated cyclohexenes for total synthesis of cyclophellitols (*e.g.* **88**) [343,344], conditurols [345], valienamine [346,347], halichondrin B [348], ovalicin (*e.g.* **89**) [349], and gabosine C (*e.g.* **90**) [350]; (21) formation of an aminocyclohexene (**91**) for total synthesis of epibatidine [351]; (22) diastereoselective formation of cyclohexenes [352]; (23) formation of cyclohexene rings fused to piperidine rings [353]; (24) formation of methylenecyclohexenols (*e.g.* **92**) for total synthesis of otteliones [354]; (25) formation of phenols (*e.g.* **94**) through RCM of trienones (*e.g.* **93**) [355]; (26) formation of the middle ring of phenanthrenes [356]; (27) formation of indolocarbazoles (*e.g.* **95**) [357]; (28) formation of the bicyclo[3.3.1]nonenone ring system of **96** for total synthesis of garsubellin A [358]; (29) formation of a cycloheptenes featuring a tetrasubstituted alkene (*e.g.* **97**) using microwave irradiation and nitrogen sparging [359]; (30) formation of seven- and eight-membered rings fused to cyclopentenone rings [360]; (31) formation of eight-membered ring cyclic Vitamin D analogs [361]; (32) formation of highly oxygenated eight-membered rings [362]; (33) formation of fluorinated eight-membered rings [363]; (34) failed attempts to bridge the *cis* decalin ring system [364]; (35) synthesis of the ingenane skeleton of **98** [365]; (36) synthesis of a 10-membered rings (*e.g.* **99**) for total synthesis of eleutherobin [366] and eleutherobin analogs [367]; (37) formation of a pyrrolidine-bridged 10-membered ring for streptorubin synthesis [368]. Double carbocyclic RCM was employed for total synthesis of polynuclear aromatic systems (*e.g.* formation of **101** from **100**) [369].

Numerous examples of the formation of nitrogen heterocycles using the RCM reaction (Fig. 8) were reported in

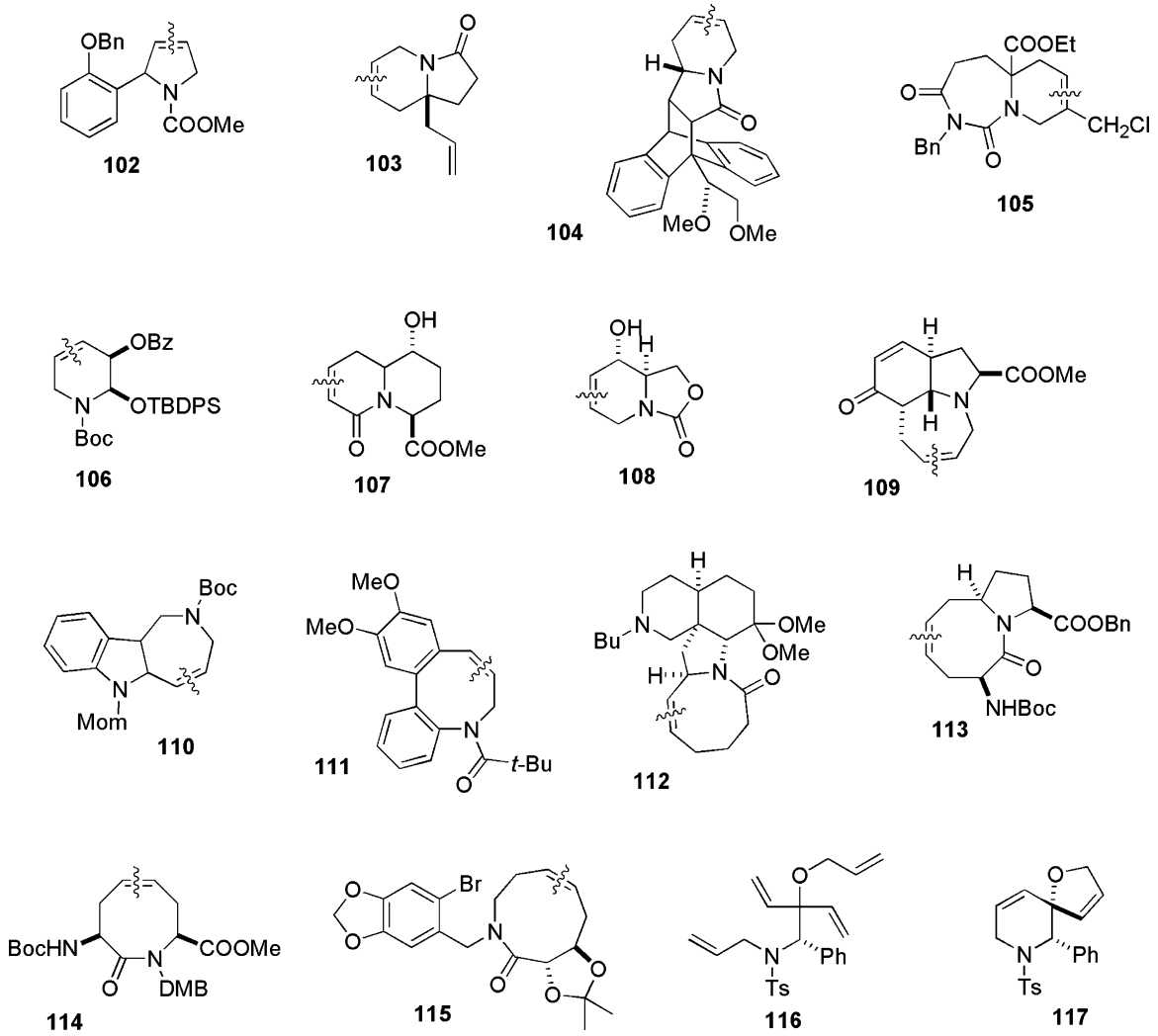


Fig. 8. Representative N-heterocycles produced through an RCM reaction (bond constructed through RCM indicated) (includes N,O heterocycles).

2005, including: (1) formation of dihydropyrrole derivatives [370–374]; (2) formation of dihydropyrroles for total synthesis of pentabromopseudilin (*e.g.* **102**) [375], nicotine [376], and trachelanthamidine [377]; (3) asymmetric synthesis of cyclic amides (*e.g.* **103**) from precursors featuring enantiotopic alkene groups using a chiral molybdenum carbene complex as a catalyst [378]; (4) formation of an α,β-unsaturated γ-lactam for total synthesis of dideoxy iminotalitol [379]; (5) formation of five- to seven-membered ring N-heterocycles fused to a pyrrolidinone ring (*e.g.* **104**) [380]; (6) formation of six-membered ring tetrahydropyridines where the alkene is conjugated to an ester [381]; (7) formation of quinolones [382]; (8) formation of six-membered ring amines spiro fused to a glucofuranose ring [383]; (9) formation of six-membered ring cyclic amide/allylic chlorides (*e.g.* **105**) [384]; (10) formation of a six-membered ring carbamate-protected amine (*e.g.* **106**) for total synthesis of 1-deoxygulonojirimycin total synthesis [385]; (11) formation of fused six-membered ring lactams for total synthesis of epiquinamide (*e.g.* **107**) [386], lentiginosine [387,388], and swainsonine and deoxymannojirimycin (*e.g.* **108**) [389]; (12) synthesis of cyclic amino acid derivatives [390]; (13) formation of a six-membered ring for antascomicin B total synthesis [391]; (14) formation of carbamate-protected six-membered ring cyclic amines for synthesis of the sparteine core [392]; (15) tetrahydropyridines (and seven-membered ring analogs) fused to carbohydrate rings [393]; (16) formation of a six-membered ring fused to a tetrahydropyridone ring for deoxynupharidine total synthesis [394]; (17) formation of a six-membered ring amine-ketone via RCM of employing a silyl enol ether followed by hydrolysis for alkaloid 205B total synthesis [395]; (18) formation of six- to eight-membered rings fused to imidazoles [396]; (19) formation of six-membered ring β,γ-unsaturated lactams for CP 99994 and L 733061 total syntheses [397]; (20) simultaneous formation of two six-membered ring cyclic compounds for total synthesis of isosparteine [398]; (21) formation of six-membered spirocyclic carbamate-protected amine derivatives [399]; (22) formation of seven-membered ring cyclic amines [400]; (23) formation of seven-membered ring amines fused to a menthol template [401]; (24) formation of seven-membered ring amines fused to a lactone and a lactam [402]; (25) formation of seven-membered ring cyclic amines for total synthesis of tuberostemonine (*e.g.* **109**) [403]; (26) formation of seven-membered ring amide derivatives fused to carbohydrate ring systems [404]; (27) formation of seven-membered ring amides [405]; (28) formation of carbamate protected seven-membered ring amines fused to indole rings (*e.g.* **110**) [406]; (29) formation of seven-membered rings tosylamines for synthesis of cysteine protease inhibitors [407]; (30) formation of eight-membered ring amides within a biphenyl framework (*e.g.* **111**) [408]; (31) formation of eight-membered ring cyclic amides (*e.g.* **112**) for synthesis of manzomanine A segments [409]; (32) formation of seven- to nine-membered rings fused to a proline derivative (*e.g.* **113**) [410]; (33) formation of eight-membered ring cyclic amino acids [411]; (34) formation of eight- to ten-membered ring lactams (*e.g.* **114**) [412,413]; (35) preparation of nine-membered ring lactams (*e.g.* **115** for total synthesis of cripowellins [414,415]; (36) synthesis of peptides bridged by nine-membered rings [416]; and (37) formation of ten-membered ring bridged peptides [417]. Diastereoselective double RCM of tetraene **116** led to the spirocyclic compound **117** [418]. Patents were awarded for the formation of cyclic amines [419].

Many examples of oxygen heterocycle synthesis using the RCM reaction were reported in 2005 (Fig. 9), including: (1) formation of a dihydrofuran for furylglycine synthesis [420]; (2) formation of furanones [421]; (3) synthesis of furanones for partial synthesis of stemoamide [422], the Geissman–Waiss lactone [423], and umbelactone [424]; (4) formation of bridged dihydrofurans (*e.g.* **118**) for synthesis of eleutherobin analogs [425]; (5) formation of benzofurans [426]; (6) formation of five- to seven-membered ring lactones (*e.g.* **120**) in competition with formation of macrocyclic bis(lactones) (*e.g.* **121**) in the treatment of **119** with Grubbs catalyst II [427]; (7) formation of bifuryls (*e.g.* **123**) and bipyrolyls via double RCM reaction of tetraene-acetal derivatives (*e.g.* **122**) followed by acid [428]; (8) formation of six-membered ring ethers [429,430]; (9) formation of six-membered ring α,β-unsaturated lactones for total synthesis of fostriecin (*e.g.* **124**) [431,432], discodermolide analogs [433], anamarine [434,435], centrolobine [436], borolide [437], and tarchonanthuslactone [438,439]; (10) formation of six-membered ring β,γ-unsaturated lactones [440,441]; (11) formation of glycals [442]; (12) formation of six-membered ring oxygen heterocycles fused to a tetrahydrofuran ring (*e.g.* **125**) for malayamycin A total synthesis [443]; (13) formation of chromenes [444]; (14) formation of six-membered ring spiroketals (*e.g.* **126**) [445]; (15) formation of tricyclic lactones (*e.g.* **127**) [446]; (16) formation of the six- to nine-membered cyclic ethers present in brevitoxin and related marine toxins (*e.g.* **128**, **129**) [447–454]; (17) formation of seven-membered ring cyclic ether **130** as part of a total synthesis of isoprelaurefucin [455]; (18) failure to form a seven-membered ring ether in a failed synthetic route to zoapatanol [456]; (19) formation of seven-membered ring cyclic ethers fused to quinolone rings [457]; (20) formation of a seven-membered ring α,β-unsaturated lactone fused to an aromatic ring for total synthesis of floresolide B [458]; (21) diastereoselective formation of eight-membered ring cyclic ethers (*e.g.* **131**) through kinetic resolution [459]; (22) formation of eight-membered ring ether **132** for laurencin total synthesis [460]; (23) formation of a benzo-fused eight-membered ring ether for heliannuol G and H synthesis [461]; (24) formation of an eight-membered ring-fused diether fused to a ribonucleoside derivative [462]; (25) formation of nine-membered ring cyclic ether **133** for total synthesis of an asbestinin derivative [463]; (26) formation of nine-membered ring ether eleutherobin analogs [464]; (27) formation of 10-membered ring lactones for total synthesis of SCH 642305 [465], dictyostatins (*e.g.* **134**) [466], microcarpolide (*e.g.* **135**) [467–469], epi SCH 642305 [470], cladospolide B [471], and cladospolide C [472]. A patent was awarded for the preparation of six-membered ring cyclic ethers [473].

Heterocyclic compounds involving elements other than N and O were also constructed via the RCM reaction (Fig. 10). Examples include: (1) formation of cyclic aminoboranes (*e.g.* **136**) [474]; (2) synthesis of cyclic siloxanes (*e.g.* **137**) for

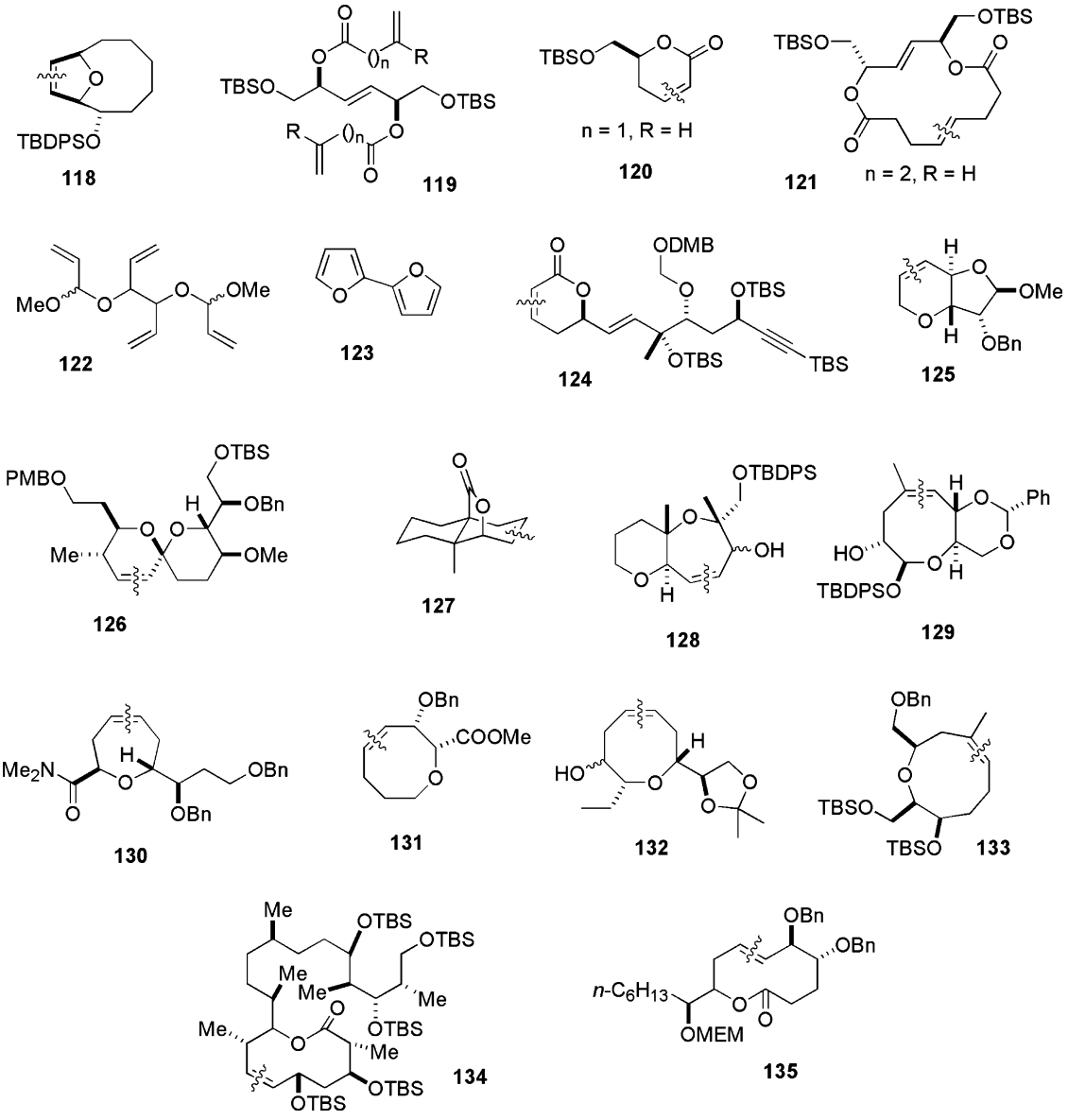


Fig. 9. Representative oxygen-heterocycles produced through an RCM reaction (bond constructed through RCM indicated).

total synthesis of pterocarpans [475]; (3) preparation of seven-membered ring cyclic siloxanes (*e.g.* **138**) [476]; (4) synthesis of nine-membered ring cyclic siloxanes (*e.g.* **139**) for synthesis of epothilone segments [477]; (5) dendrimeric silacyclopentenes [478,479]; (6) formation of cyclic phosphonates [480,481]; (7) formation of cyclic phosphates fused to nucleosides (*e.g.* **140**) [482]; (8) diastereoselective formation of cyclic phosphonates (*e.g.* **142**) from trienes featuring enantiotopic vinyl groups (*e.g.* **141**) [483]; (9) formation of bicyclic phosphate esters (*e.g.* **143**) [484]; (10) formation of cyclic sulfones [485]; (11) formation cyclic sulfonate ester **144** for mycothiazole total synthesis [486]; (12) cyclic sulfamoyl derivatives [487]; (13) cyclic sulfoximines [488].

Numerous examples of successful macrocyclic ring closure (formation of rings with ≥11 atoms) using the RCM reaction were reported in 2005 (Fig. 11), including: (1) formation of macrocyclic ether **145** for total synthesis of kendamycin [489]; (2) formation of a macrocyclic keto-ether **146** for coleopheremone total synthesis [490]; (3) formation of a macrocyclic lactone for preparation of the tetracyclic core of tetrapetalones [491]; (4) formation of a macrocyclic lactone-ether for total synthesis of SCH 351448 [492]; (5) formation of a macrocyclic lactone for total synthesis of jimenezin [493]; (6) formation of the macrocyclic lactones for synthesis of salicylhalamide derivatives (*e.g.* **147**) [494,495]; (7) formation of macrocyclic lactone-diaryl ether **148** for total synthesis of aspercyclide [496]; (8) formation of macrocyclic keto-lactones (*e.g.* **149**) for radicicol total synthesis [497,498] and pochonin A total synthesis [499]; (9) preparation of macrocyclic lactone-fused carbohydrates [500]; (10) formation of a polyene lactone for dactylide total synthesis (an early step of the same synthesis employs an RCM reaction) [501]; (11) formation of a macrocyclic lactam-ether [502]; (12) synthesis of macrocyclic peptide derivatives [503–512]; (13) formation of a macrocyclic amine for dihy-

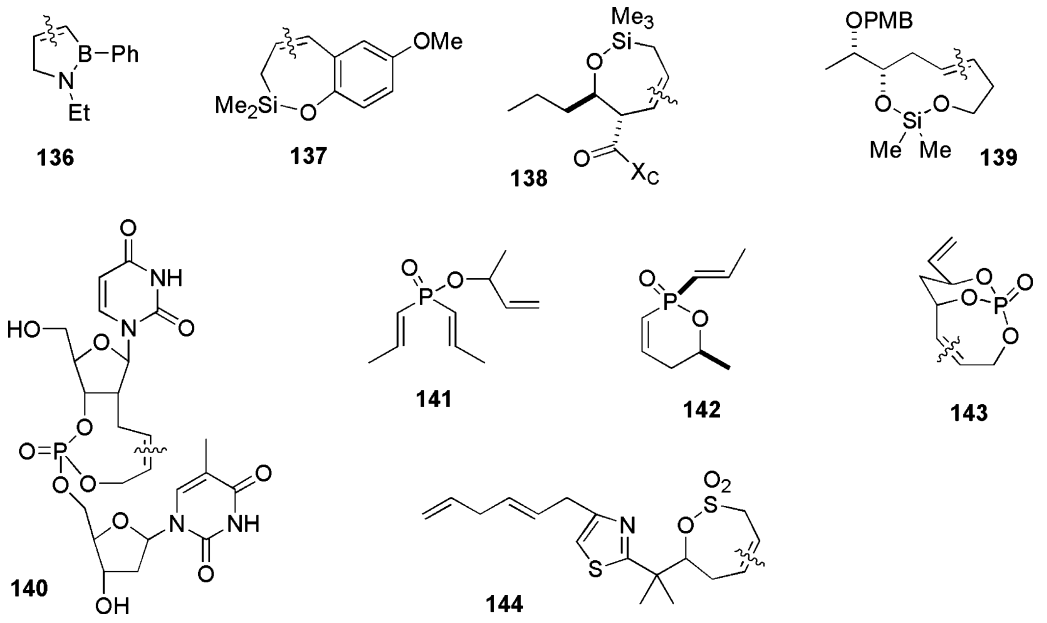


Fig. 10. Representative examples of other heterocycles prepared via the RCM reaction (bond constructed through RCM indicated).

dromotuporamine total synthesis [513]; (14) formation of a macrocyclic tris(amide) [514]; (15) macrocycle-bridged carbohydrates [515]; (16) formation of a furan-bridged macrocycle [516]; (17) formation of furan-bridged macrocyclic bis(lactone) **150** for total synthesis of the reported structure of feigrisolide C [517]; (18) formation of a dihydropyran-bridged macrocycle [518]; (19) formation of a macrocycle-bridged bipyridyl derivative [519,520]; (20) synthesis of macrocyclic peptidourethanes (*e.g.* **151**) [521]; (21) macrocycle-bridged imidazolium salts [522]; (22) formation of a macrocycle-bridged *p*-cyclophane derivative for preparation of geldamycin analogs [523]; (23) preparation of meta benzene-bridged *p*-cyclophanes (*e.g.* **152**) [524]; (24) preparation of *p*-cyclophanes and cyclic allenes [525]; (25) synthesis of macrocyclic bis(lactone)-bridged *p*-cyclophane **153** for total synthesis of 10-hydoxyasimicin [526]; (26) formation of macrocycle-bridged pyrone derivatives [527]; (27) preparation of a bicyclic macrocycle [528]; (28) synthesis of catenanes [529–531]; (29) preparation of bridged calixarenes [532,533]; (30) formation of pseudorotaxanes [534]; (31) synthesis of triple-stranded helicates [535]; (32) preparation of macrocyclebridged ferrocene derivatives (*e.g.* **154**) [536]: (33) formation of macrocycle-bridged platinum-pincer pyridine complexes [537]; (34) preparation of macrocycle-bridged bis(ruthenium) tripyridine complexes [538]; (35) macrocycle-bridged tetrakis(zinc-porphyrin) derivatives [539]; (36) synthesis of macrocycle-bridged tetrakis(zinc-porphyrin) where the porphyrin rings are linked through conjugated acetylene and arene units [540]; (37) formation of macrocycle-linked porphyrin derivatives from pre-associated porphyrin derivatives with alkene appendages [541,542]; (38) cyclization of dendrimers that contain alkene appendages [543]; (39) preparation of macrocycle-bridged polymer-bound bis(copper) tripyridine complexes [544]; (40) a failed attempt to for a polyether-bridged *p*-cyclophane [545]. A computational study of macrocyclic RCM was reported [546]. It was noted that the *cis*/*trans* selectivity in the formation of **156** was highly dependent on which alkene of **155** reacts initially with the carbene complex. Patents were awarded for the preparation of macrocyclic peptides [547,548].

Several examples of ring rearrangement metathesis (RRM) were reported in 2005 (see Scheme 9). These examples include: (1) conversion of an aminocyclopentene derivative (**157**) to a tetrahydropyridine (**158**) for total synthesis of castanospermine [549]; (2) conversion of aminocyclohexene **159** to tetrahydropyridine **160** for *trans*-195A total synthesis [550]; (3) conversion of oxanorbornene **161** to cyclopentenone **162** for kumausyne total synthesis [551]; (4) conversion of triene **163** to tricyclic compound **164** for total synthesis of cyanthiwigin [552]; (5) conversion of oxanorbornene **165** to the seven-membered ring lactam **166** [553]. A tandem RRM-CM sequence led to the tricyclic allylsilane derivative **168** from norbornene derivative **167** [554].

1.1.2.6. 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 2005; representative examples are depicted in Scheme 10. Intermolecular examples of enyne metathesis include: (1) alknylboronates (*e.g.* **170**) and monosubstituted alkenes (*e.g.* **171**) to afford dienes (*e.g.* **172**) as nearly exclusively the *Z* stereoisomer and a single regioisomer [555]; (2) tandem enyne metathesis intramolecular Diels–Alder reaction (*e.g.* metathesis of **173** and **174** to provide **175** and subsequently **176**) [556]; (3) metathesis of alkynylazulenes (*e.g.* **177**) and various monosubstituted alkenes [557]; (4) metathesis of alkynyl ketone derivatives and ethylene for synthesis of Vitamin D analogs [558]; (5) porphyrin-substituted terminal alkynes with ethylene [559]; (6) propargylic esters and enol ethers [560]. Examples of intramolecular enyne metathe-

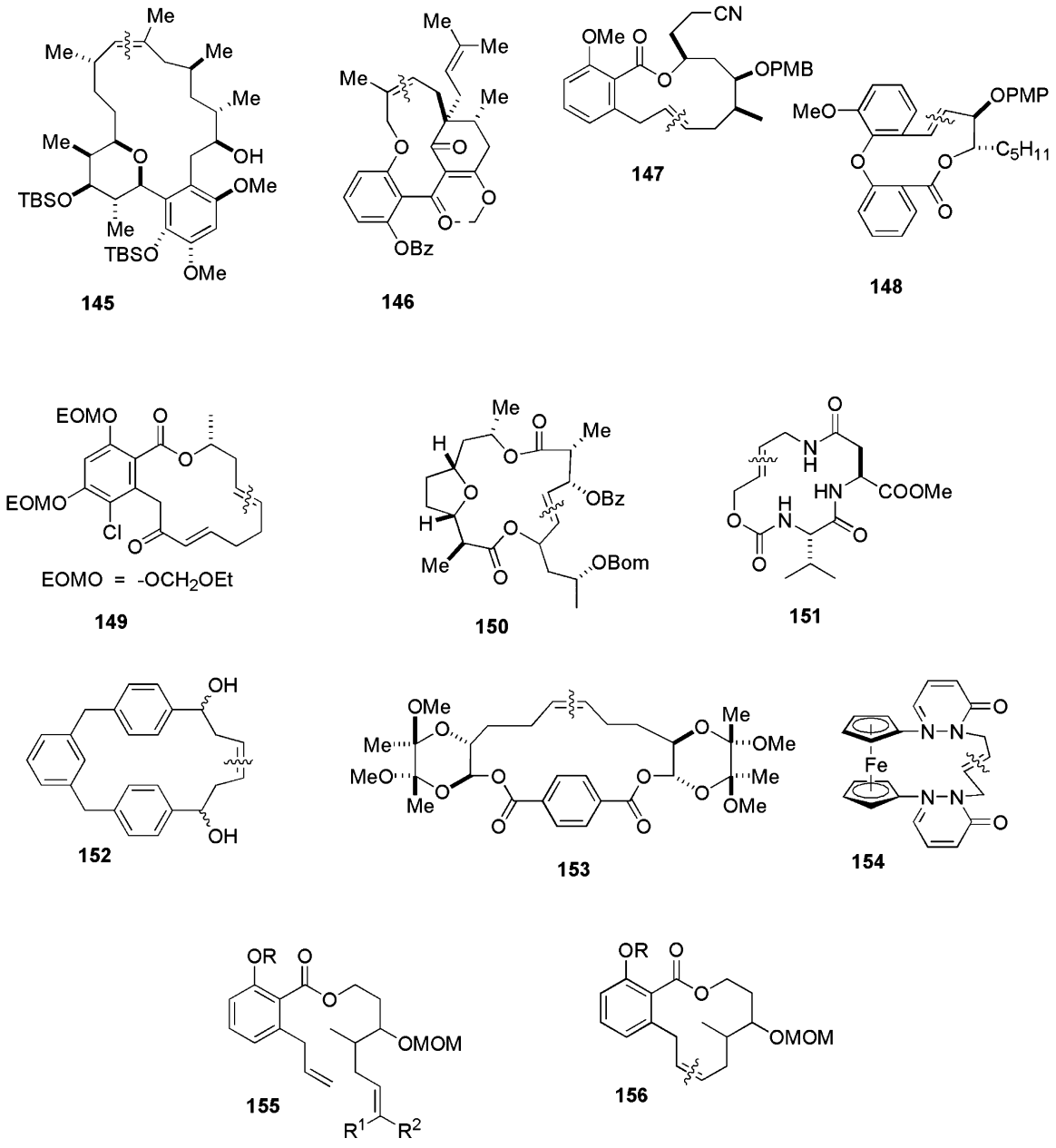
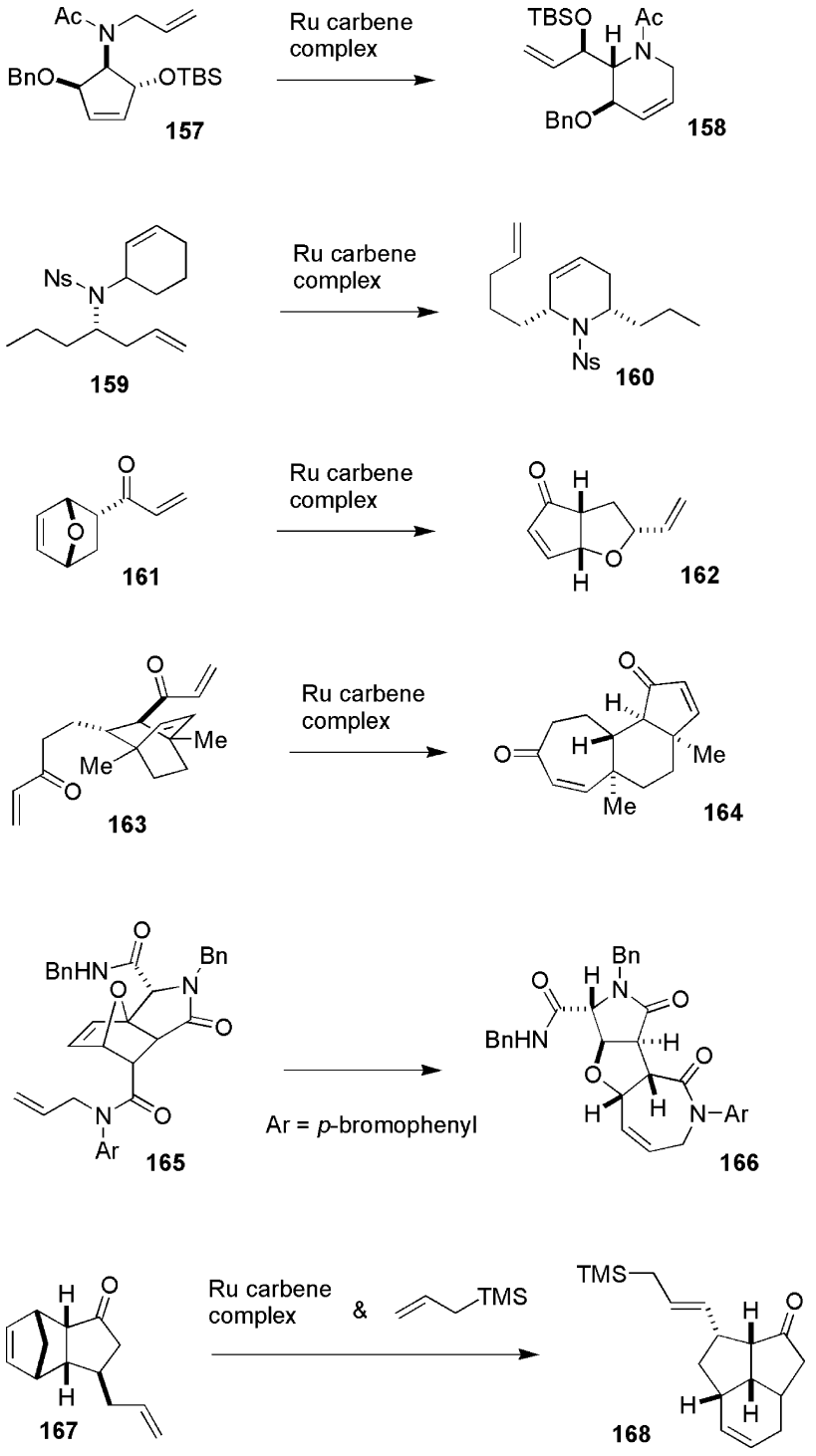


Fig. 11. Representative macrocycles (ring size >10) Prepared using the RCM reaction (bond constructed through RCM indicated).

sis include: (1) formation of cyclic boronates (*e.g.* **180**) [561]; (2) formation of cyclopentenes (*e.g.* **182**) and evidence for an "alkyne-first" mechanism based on substrate limitations [562]; (3) formation of six-membered carbocyclic rings [563]; (4) formation of vinyl dihydronaphthalenes [564]; (5) formation of six-membered ring amine derivatives [565]; (7) synthesis of seven-membered ring dienes **184** for total synthesis of dihydroxyxanthatin [566]; (8) enyne-RCM using allenynes (*e.g.* **185**), which proceeds through an "alkene first" mechanism [567]; (9) formation of six-membered rings fused to indoles [568]; (10) formation of seven-membered rings fused to imidazoles [569]; (11) enyne RCM using *O*-propargylic, *N*-allylic hydroxylamine analogs [570]; (12) intramolecular enyne metathesis concomitant with ring expansion using alkyne-cyclobutene **187** [571].

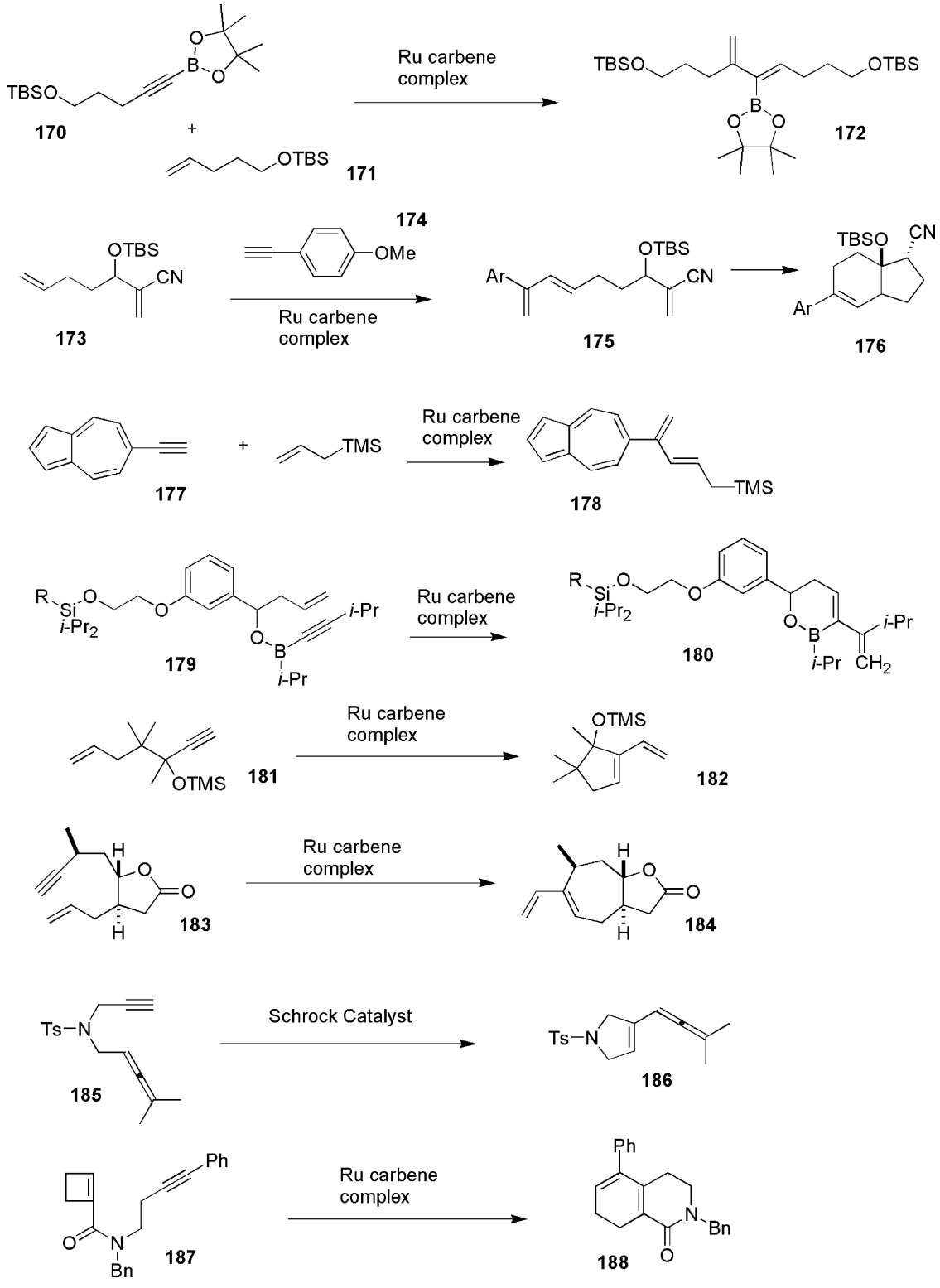
Examples of tandem enyne metathesis-alkene metathesis are depicted in Scheme 11. Tandem intramolecular enyne metathesis and cross metathesis (*e.g.* conversion of **189** and *cis* 2-butene to **190**) was employed for the synthesis of cyclic siloxanes [572]. A similar tandem enyne metathesis-cross metathesis sequence (conversion of **191** and methyl vinyl ketone to **192**) was employed for eight-epi-xanthin total synthesis [573]. Examples of tandem enyne metathesis-RCM are depicted in Scheme 12. Tandem enyne metathesis–RCM was employed for cyclic siloxane synthesis (*e.g.* conversion of **193** to **195**) [574] and for the synthesis of carbocyclic 5,7-fused ring compounds [575]. A net cycloaddition involving tandem intermolecular enyne metathesis-RCM that employs 1,5-hexadiene and simple alkynes was reported [576]. The cycloaddition product (*e.g.* **197**)



Scheme 9.

was formed from the *Z* triene (*e.g.* **196**). The *E* triene intermediate **196** can undergo subsequent CM with methyl acrylate. The head-to-tail double enyne metathesis product **200** was obtained from treatment of enyne **199** with Grubbs catalyst I [577]. Enyne metathesis reactions involving polyynes are depicted in Scheme 13. The intramolecular metathesis of conjugated diynes (*e.g.* **201**) and alkenes was reported [578]. In some cases the intermediate alkynylcarbene complex (**202**) undergoes a 1,3-shift to afford rearranged metathesis products (*e.g.* **205**). The alkyne substituent had a big influence on the course of the reaction. The same reaction was applied to more complex systems featuring multiple conjugated diene groups (*e.g.* **206**) [579].

The kinetics of intermolecular enyne metatheses (1-hexene or ethylene plus various monosubstituted alkynes) using Grubbs catalyst II were probed [580]. The focus of this investigation was determining the effect of propargyl substitution (alkyl groups as

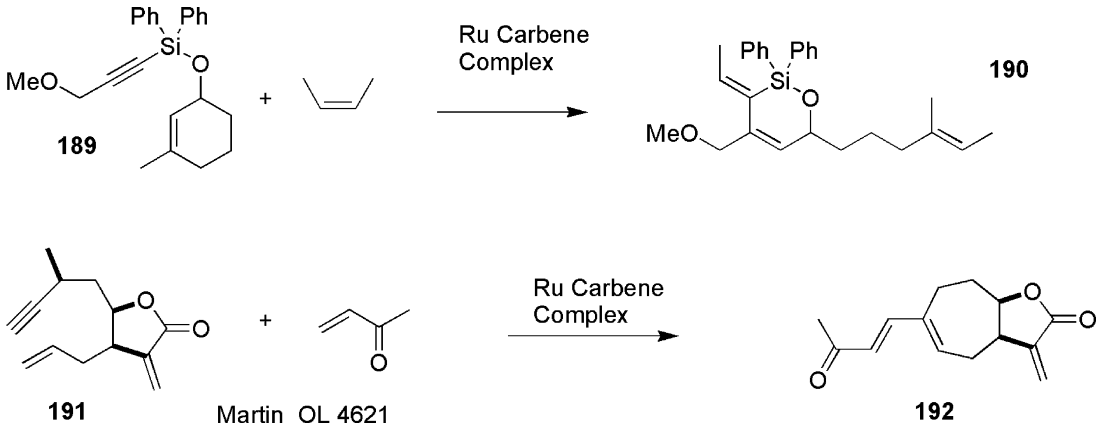


Scheme 10.

well as potential chelating groups) on the overall rate of the reaction.

A mechanistic study of enyne metathesis using various labeling schemes was reported [581]. Deuterium labeling studies were supportive of the "ene-first" pathway.

1.1.2.7. Non-metathesis reaction processes involving the Grubbs and related catalysts. Several publications in 2005 report on processes unrelated to metathesis that are initiated by ruthenium carbene complex catalysts **1**–**4** and structurally-related carbene complexes.

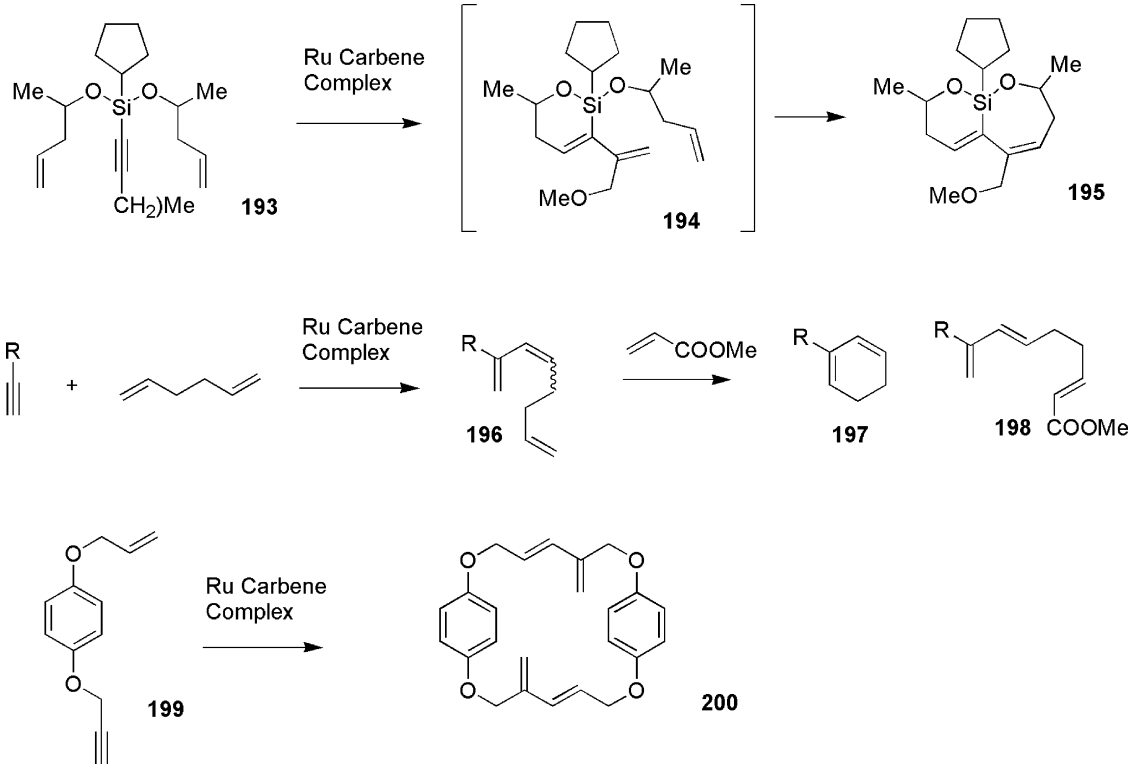


Scheme 11.

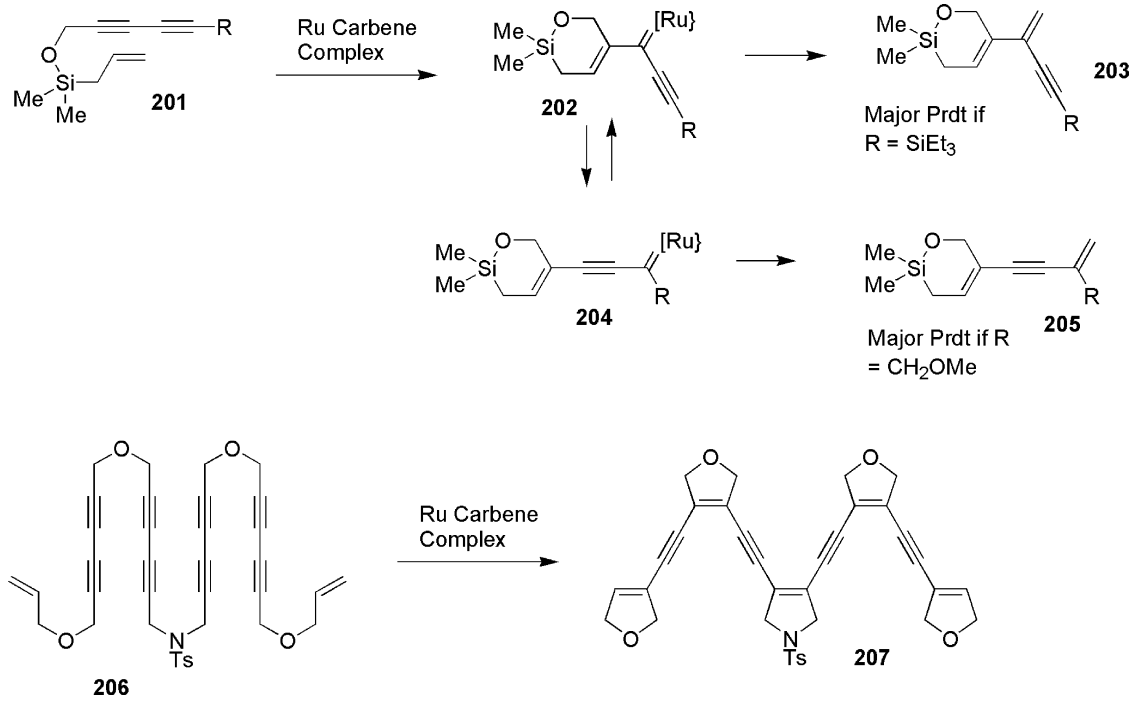
Use of Grubbs catalyst I for intramolecular alkyne trimerization of tris(alkyne) **210** (Scheme 14) was reported [582]. Use of the Hoveyda–Grubbs catalyst for alkyne polymerization was also reported [583].

Several examples employing ruthenium–carbene complexes to initiate free-radical reactions were reported in 2005 (Scheme 15). A tandem RCM–double Kharasch reaction was demonstrated for compound **212** and styrene using Grubbs catalyst I [584]. This process ultimately affords lactam **215** via RCM product **213** and intramolecular Kharasch product **214**, which then undergoes the intermolecular Kharasch reaction with styrene to afford **215**. Tandem RCM–Kharasch reaction was also employed for the synthesis of five-membered ring lactones fused to six-membered rings [585]. A study to determine optimal conditions for RCM reactions in competition with Kharasch reactions using substrates **216** and **217** was reported [586]. The RCM reaction leading to **218** was preferred at room temperature. The Kharasch reaction initiates at temperatures above 70 °C. Treatment of a 1:1 mixture of **216** and **217** with Grubbs catalyst I above 70 °C led only to **218** and **219**. If the Kharasch reaction is performed on substrate **217** and then **216** was added, compound **220** was produced. Apparently Grubbs catalyst I decomposes thermally to afford the Kharasch catalyst. Deuterium-labeled compound **221** led to complete scrambling of the deuterium label in the product **222** during a tandem Kharasch-elimination reaction [587].

Use of Grubbs-catalysts II for the generation of carbenoids from diazo compounds was reported (Scheme 16) [588]. Reac-



Scheme 12.



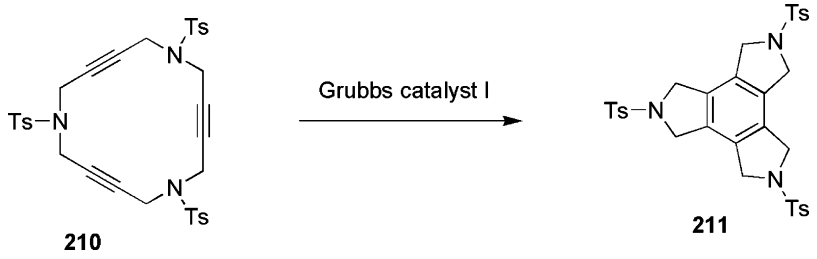
Scheme 13.

tion of Grubbs catalyst II (**2**) with ethyl diazoacetate (**223**) led to diethyl maleate (**224**). Exposure of styrene to the crude reaction mixture from the preparation of **224** led to the metathesis product, *trans* stilbene (**225**), indicating that a metathesis active species was present after the formation of **224**. The proposed mechanism involves phosphine dissociation and formation of tris(carbene) complex **226**, followed by addition of ethyl diazoacetate to the acylated carbene carbon to afford intermediate diazonium salt **227**, followed by elimination of unsaturated carbene complex **228** and formation of diethyl maleate. Reaction of pentenyl diazoacetate (**229**) with catalyst **2** led to the carbene-dimerization-RCM product **230**.

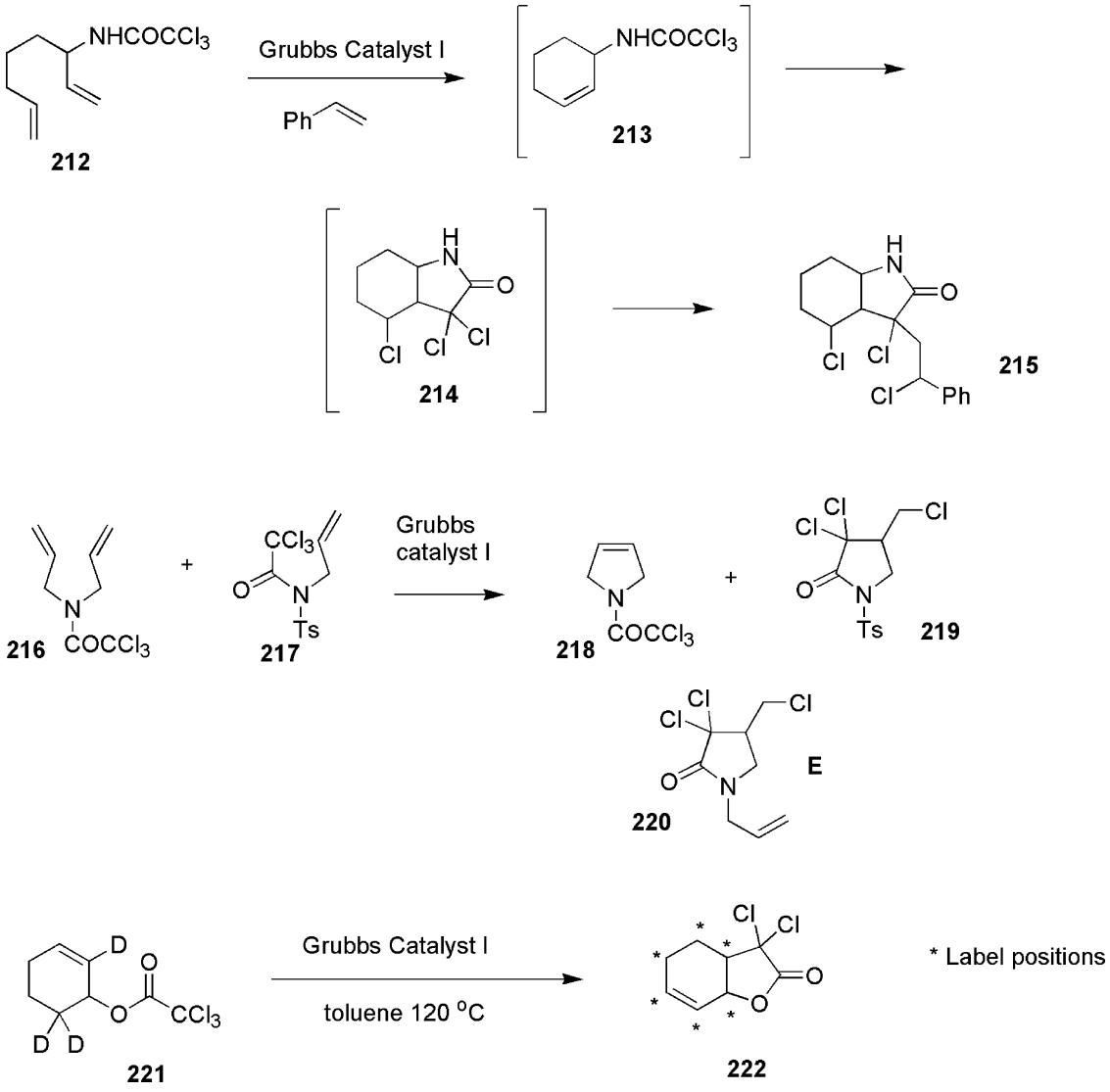
A frequent side reaction during metathesis is alkene isomerization; examples are depicted in Scheme 17. This side reaction has been attributed to the formation of metal hydride complexes under the conditions necessary for metathesis. The RCM of diene **231** followed by addition of hydride reagents led to alkeneisomerized product **232** [589]. RCM of diene **234** in the presence of ruthenium hydride additives (*e.g.* **235**) led to the preferential formation of seven-membered rings (**236**) in a sequence involving alkene migration to diene **237** prior to RCM [590]. Isomerization of *N*-allylureas (*e.g.* **238**) to the corresponding enamines (**240**) and subsequent hydrolysis products (**241**) in competition with CM was reported [591]. In this case the isomerization process was actually inhibited by the addition of phosphoric acid derivatives. Maximum yields of metathesis dimerization products (**239**) were obtained using Grubbs catalyst II in the presence of the phosphoric acid additive. Maximum alkene isomerization was obtained using Grubbs catalyst II with no additives present. Deallylation of amines through carbene complex-induced isomerization followed by enamine hydrolysis was also reported [592].

The ability to stop metathesis reactions using carbon monoxide was further explored [593]. Treatment of Grubbs catalyst II with CO led to the ring-expanded complex **242** (Scheme 18). The analogous methylidene complex also underwent this transformation. The ring expansion process could also be induced by isocyanides. The phenylcycloheptatriene complex **242** was the predominant ruthenium-containing species isolated from treatment of a metathesis in progress with CO.

Use of Grubbs catalysts I and II as catalysts for the hydrosilylation of alkynes (*e.g.* **243**, Scheme 19) was reported [594–596]. Failure of Grubbs catalysts I or II as catalysts for alkene hydrosilylation was reported [597].



Scheme 14.



Scheme 15.

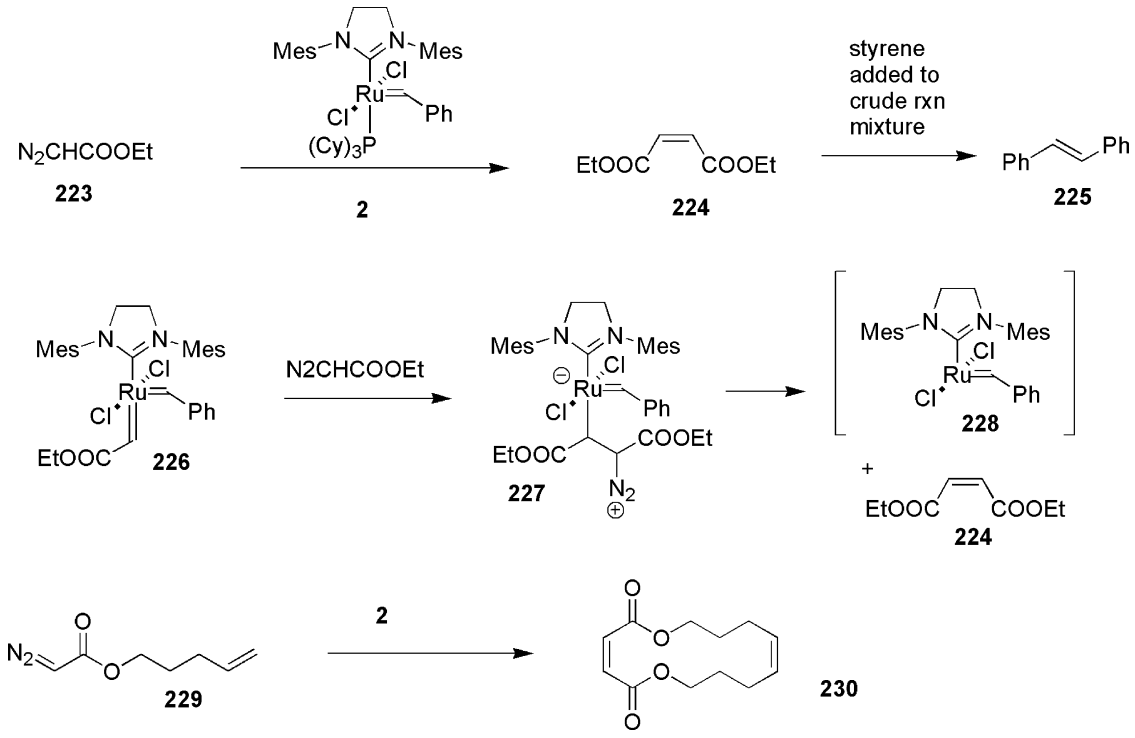
Unusual processes occurred if methylenecyclopropanes were reacted with carbene complex metathesis catalysts (Scheme 20). Coupling of methylenecyclopropane-containing enyne **247** with ruthenium carbene complexes led to either the trimethylenemethane cycloaddition product **248** or the enyne metathesis product **249** or **250** [598]. The reaction fate can be controlled by the choice of catalysts. Reaction with Grubbs catalyst I led to the cycloaddition product **248**. Reaction with Grubbs catalyst II or the Hoveyda–Grubbs catalyst led to mixtures of the regioisomeric enyne metathesis products **249** and **250**.

The ruthenium carbide complex **252** (Scheme 21) was prepared through the coupling of Grubbs catalyst I with vinyl acetate [599]. The reaction proceeds through the acetoxycarbene complex **251**, which can be observed in the crude NMR spectrum. Reaction of carbide complex **252** with sulfur leads to the thiocarbonyl complex **254**. Reaction with dimethyldioxirane leads to the carbonyl complex **255**. The thiocarbonyl complex can be converted back into the carbide complex by treatment with molybdenum complex **253**.

1.1.3. Individual carbene or alkylidene complexes classified according to metal

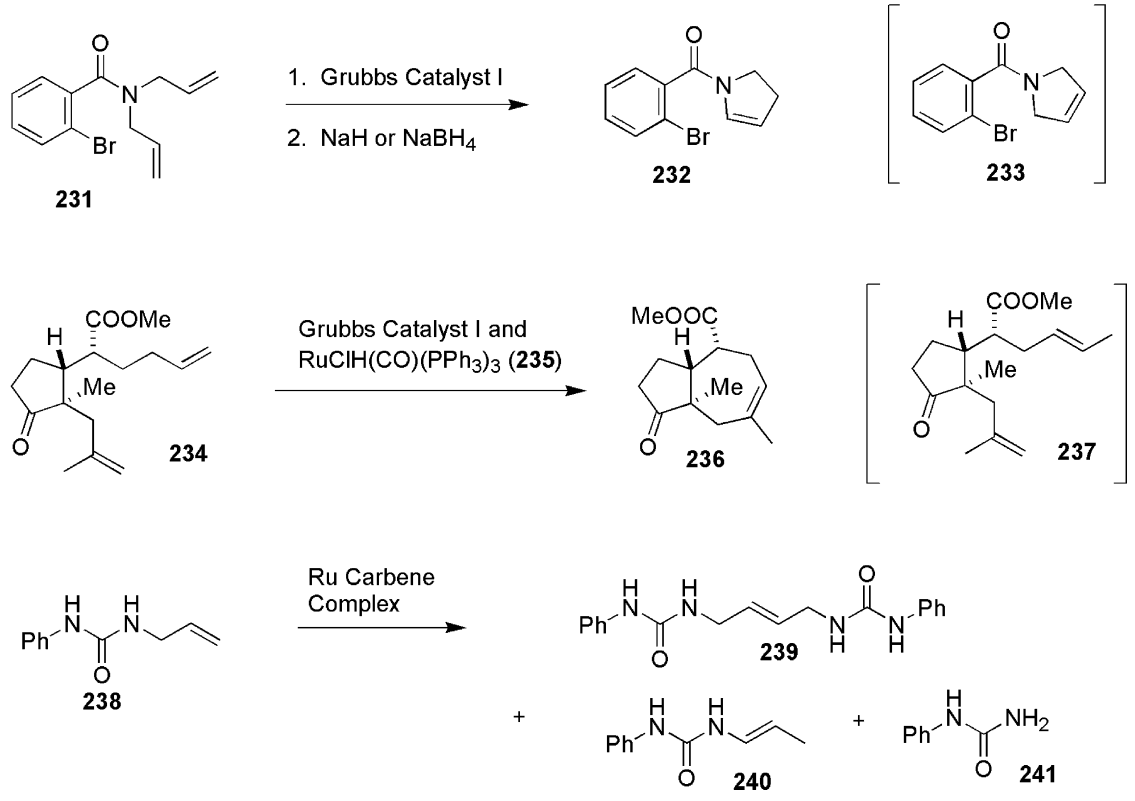
1.1.3.1. Group 4 metal–carbene complexes. Both isolable titanium–carbene complexes and reactions that involve titanium alkylidene complexes are covered in this section.

Exchange of alkyl ligands of titanium carbene complex **260** (Scheme 22) through C–H activation reactions of the solvent was reported [600]. The proposed reaction mechanism involves the generation of titanium carbyne complexes (*e.g.* **261**) through thermolysis of titanium carbene complex **260**. Once generated, the carbyne complex afforded C–H oxidative addition products upon treatment with benzene. The mechanism was supported by deuterium labeling and computational studies. Analogous carbene complexes featuring tridentate PNP ligands (*e.g.* **264**) were prepared through oxidation of titanium(III) alkyl complex **263** [601]. Treatment of carbene complex **264** with amides or phosphides led to the imido (or phosphido) complex analogs (**265**). Related studies were reported for imidoacetoacetate-ligated complexes **267** [602]. Titanium carbene complex **267** was

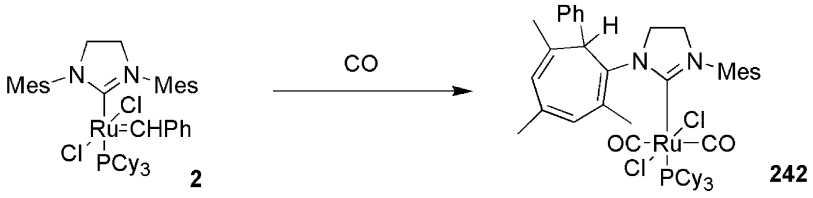


Scheme 16.

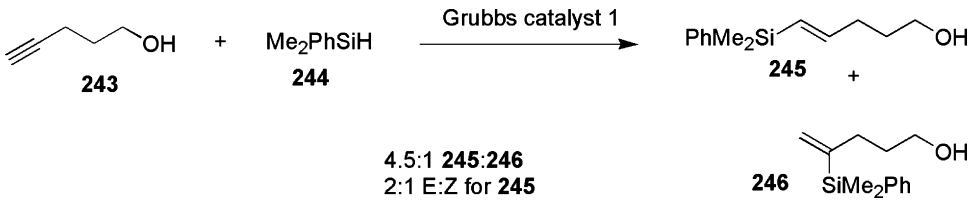
obtained through oxidation of titanium(III) bis(alkyl) complex **266**. Cycloaddition reactions and carbonyl olefination reactions were reported for carbene complex **267**. Thermolysis of **267** led to complex **271** and intramolecular metathesis product **272**. Alkylation reactions were also reported for carbene complex **267** [603]. Thermolysis of the trimethylsilylmethyl(carbene) complex **273** led to complex **274** and the dimeric complex **275**, which afforded the intramolecular metathesis product **276** upon treat-



Scheme 17.



Scheme 18.

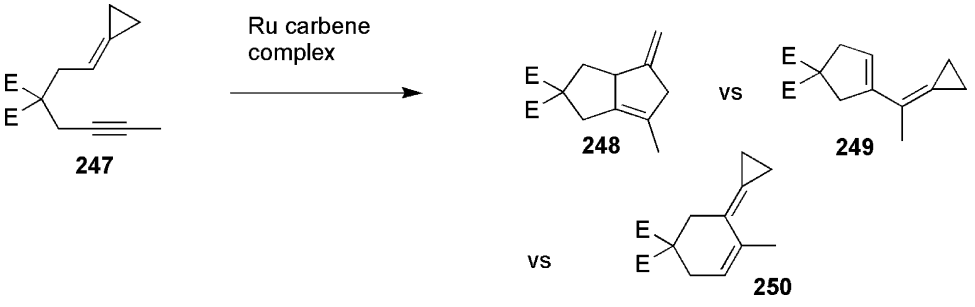


Scheme 19.

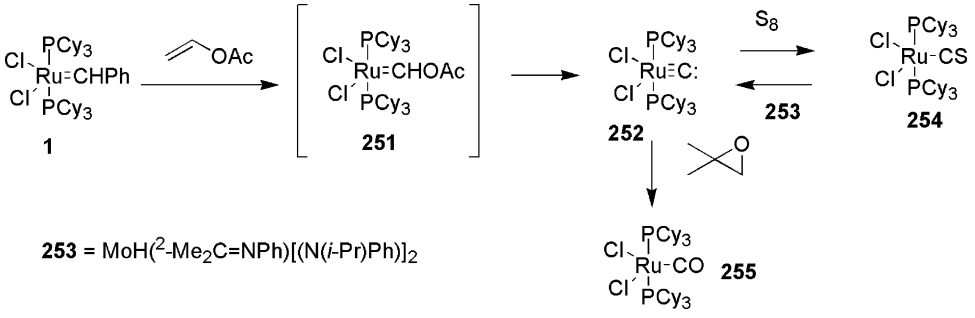
ment with THF. Reduction led to the C–H activation product **277**.

Titanium carbenoids (*e.g.* **281**, Scheme 23, the bonding is a 3-center-8-electron bond between titanium and the two adjacent carbons) and alkynyltitanium dimers (*e.g.* **280**) were produced in the cocyclization of titanium(II)-alkyne complexes (**278**) and bis(alkynyl)silanes (*e.g.* **279**) [604]. The course of the reaction was highly dependent on the steric bulk of the Cp ligands. Only the compounds where the Cp ligand contains at least three methyl groups (or Cp^* analogs) lead to complex **281**. Two mechanisms, an insertion mechanism and a divalent mechanism were proposed to account for the formation of the titanacycles.

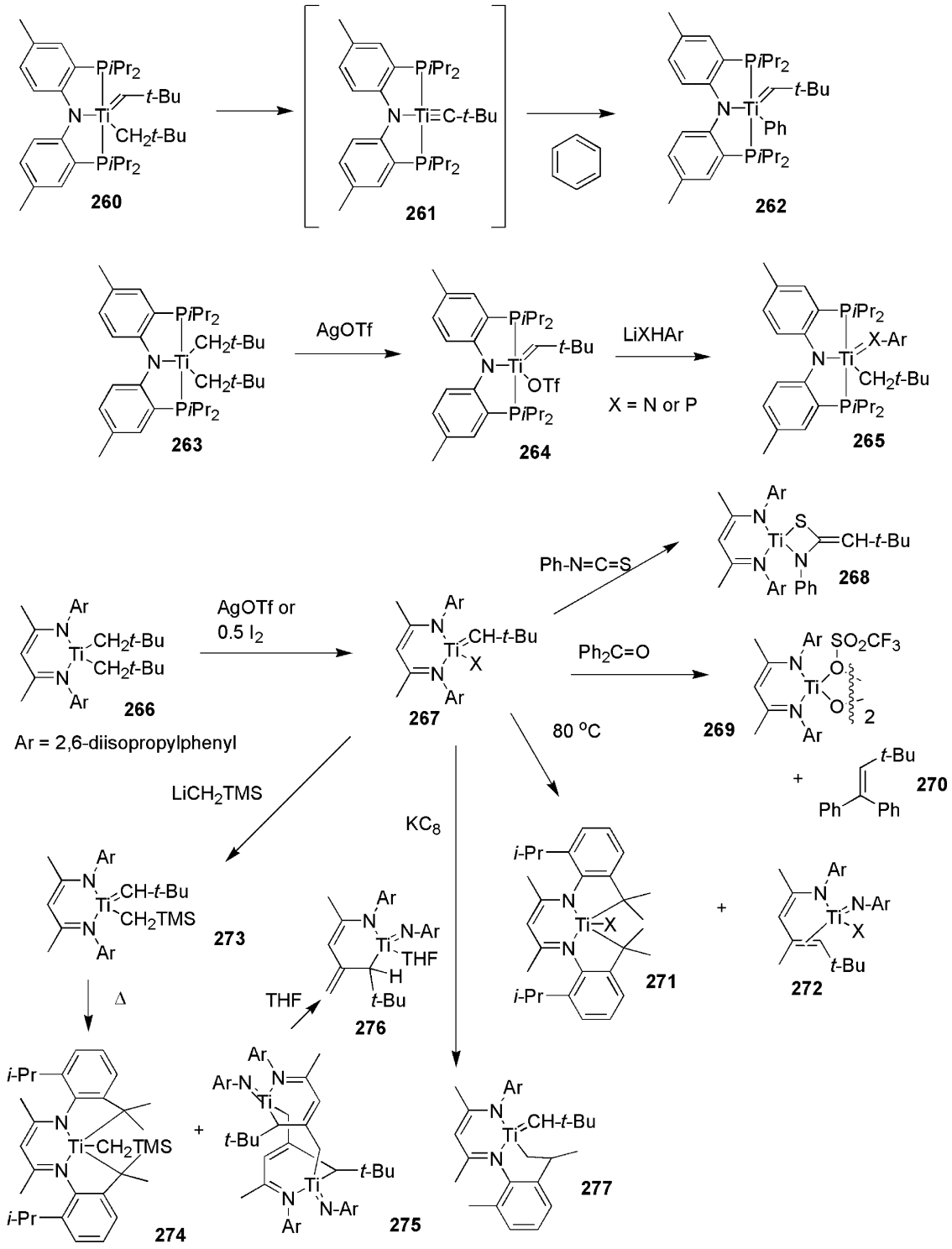
Several examples employing *in situ*-generated titanium–carbene complexes in synthetic organic chemistry were demonstrated in 2005; representative examples are depicted in Scheme 24. Tandem carbonyl olefination and RCM were observed upon treatment of compound **282** with the titanium ethylidene reagent generated from 1,2-dibromoethane/low valent titanium for gambeirol total synthesis [605]. A similar reaction was initiated using a titanium methylene reagent [606]. Tandem carbonyl-olefination and RCM was observed in the reaction of alkene-amides (*e.g.* **285**) with the Petassis reagent (**286**) [607]. Methylenation of carbonyl compounds (*e.g.* **289**) using the Petassis and/or Tebbe reagents was reported [608–610]. A partial total synthesis of the natural product vinigrol employs both a Petassis olefination and a failed RCM reaction [611]. Generation of titanium carbene complexes from alkynyldithiane derivatives (*e.g.* **292**, Scheme 25) and titanium(II) species **293** was reported [612]. The reaction afforded insertion and olefination products arising from the



Scheme 20.

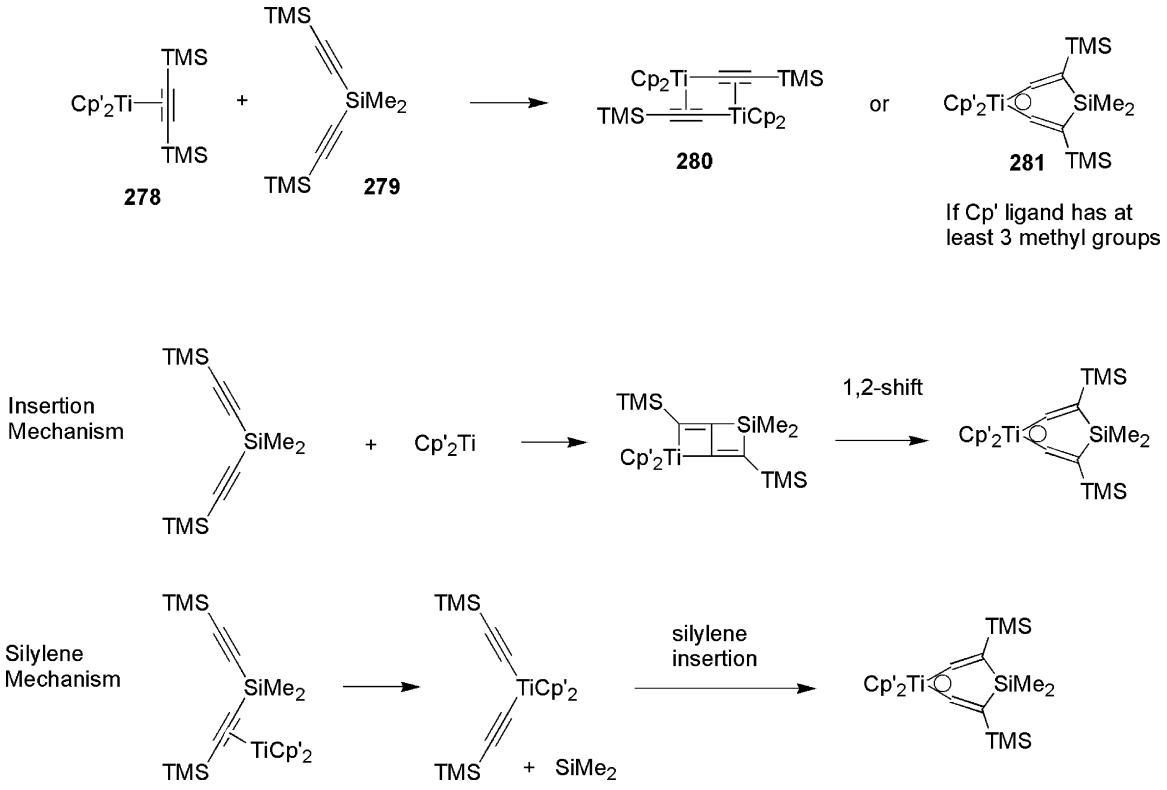


Scheme 21.



Scheme 22.

1,3-rearranged carbene complex **295**. Related reactions with heteroatom-functionalized alkenes (*e.g.* **300**) were also reported [613]. This reaction leads to cyclopropanes (*e.g.* **301**) in addition to open-chain products (*e.g.* **302** and **303**). The cyclopropane **301** and vinyl compound **302** were obtained from the metallacyclobutane **304** through either reductive elimination or metathesis processes. The involvement of the cyclopropyltitanium complex was supported through deuterium labeling studies. The allyl compound **303** was proposed to arise from the regioisomeric metallacyclobutane **307**. Intramolecular carbonyl olefination of amides using thioacetal-generated titanium carbene complexes was also reported [614]. Formation of allenes (*e.g.* **311**) from 1,1-dihaloalkenes, titanium complex **293**, and ketones (*e.g.* **310**) was reported [615]. Formation of a titanium vinylidene followed



Scheme 23.

by olefination was proposed. Group 4 metal methylene complexes (*e.g.* **312**, Scheme 26) were generated from the coupling of two equivalents of methyllithium and Group 4 tetrahalides, and employed for carbonyl olefination, ROMP catalysis, and alkyne addition reactions [616].

Laser-ablated zirconium atoms generated in the presence in methane afforded a carbene complex, $H_2C{=}ZrH_2$, that could be observed by IR spectroscopy [617,618]. The hypothetical carbene complex was studied by DFT and the calculated IR spectrum compared with the observed IR spectrum. Laser-ablated hafnium atoms generated in the presence in methane afforded a carbene complex, $H_2C{=}HfH_2$, that could be observed by IR spectroscopy [619]. The hypothetical carbene complex was studied by DFT and the calculated IR spectrum compared with the observed IR spectrum. The carbene complex features an agostic interaction that is weaker than the analogous interaction in titanium and zirconium analogs. Similar studies were reported for titanium [620].

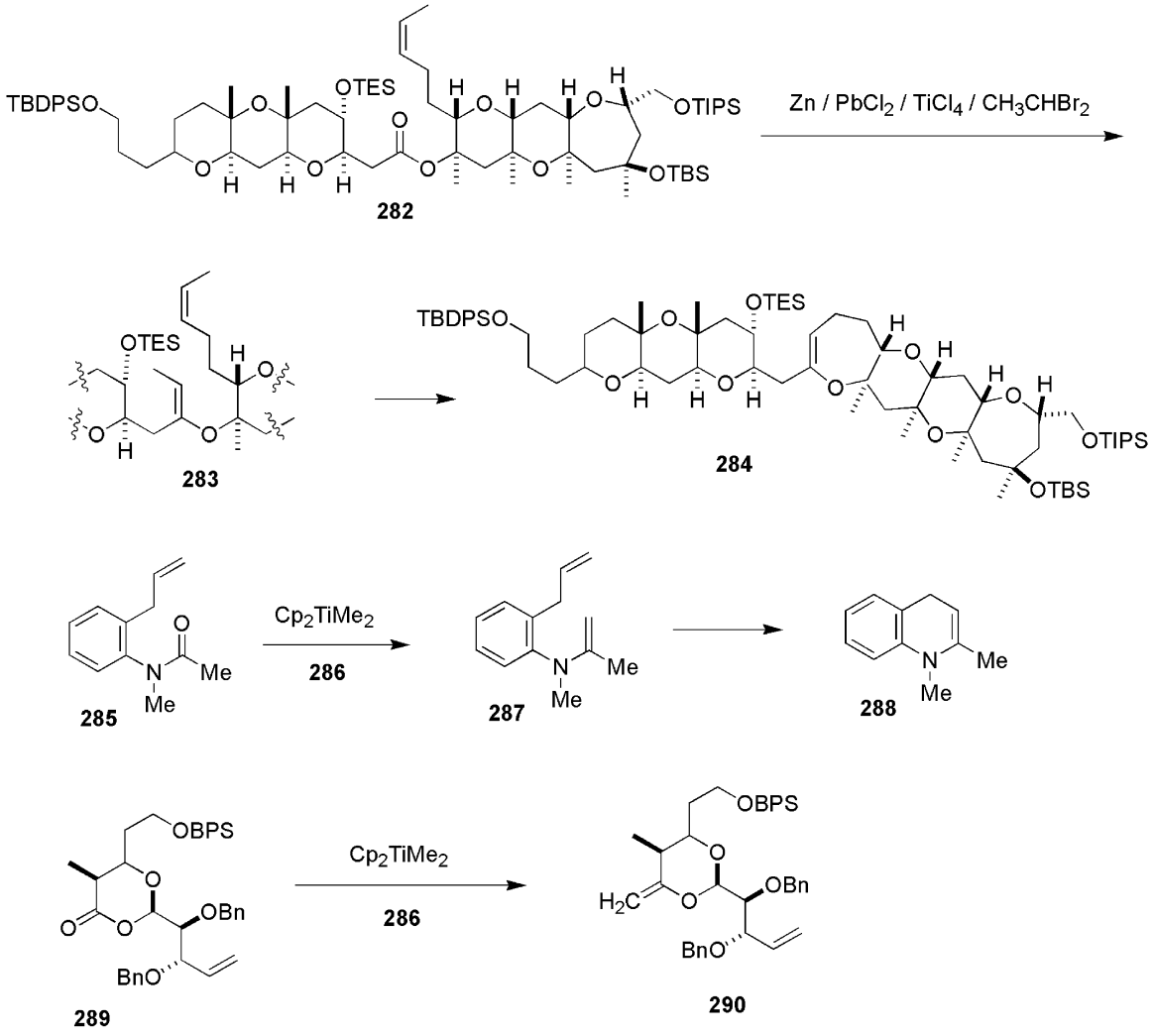
1.1.3.2. Group 5 metal–carbene complexes. Tantalum and niobium carbene complexes (*e.g.* **317**, Scheme 27) were generated in the thermolysis of tris(tri-*t*-butylsilyl)niobium (or tantalum) alkene complexes (*e.g.* **315**) [621]. The reaction proceeds via intramolecular C–H oxidative addition and alkene insertion to provide the observable (in the tantalum case) oxametallacycle **316**, followed by α-hydride elimination and reductive elimination to afford the carbene complexes. The reaction occurs with a very high energy of activation, however the carbene species is usually favored at equilibrium. These processes were also studied computationally. Tantalum carbene complexes (*e.g.* **320**) were generated in the reaction of allyltrisilane derivative **318** with tantalum pentachloride followed by reaction with TMEDA [622]. The coupling of hydrogen-bridged bis(tantalum) complexes (*e.g.* **321**) and alkynes was reported [623]. Reaction with terminal alkynes led to the bis(carbene) complexes **322**. Extended storage under vacuum led to loss of hydrogen and formation of the bis(carbene)-bridged ditantalum complexes **323**. Analogous reaction with internal alkynes led to formation of an alkyne complex at a single tantalum group.

The coupling of tantalum carbene complex **324** (Scheme 28) with (tris)phenolate ligands (*e.g.* **325**) was reported [624]. The reaction with ligand **325** led to the carbene addition product **326**. Reaction of ligand **325** with pentabenzyltantalum led to the stable complex **328**. Thermolysis of **328** led to the dimeric carbene complex **329**, possibly through a mononuclear carbene complex, as a single diastereomer.

Tantalum carbene complexes were proposed as intermediates in the metathesis of propane using tantalum catalysts [625]. Group 5 metal carbene complexes were proposed as intermediates in metal-catalyzed alkane hydrogenolysis and alkane metathesis [626]. A vanadium–carbene alkene metathesis catalyst (**19**, Fig. 2) was noted in the metathesis section [157].

1.1.3.3. Group 6 metal–carbene complexes (further classified according to structure and reaction type).

1.1.3.3.1. Schrock-type carbene complexes. A significant portion of this subject material has already been presented in the alkene metathesis section; the Schrock catalyst (**5**) belongs to this class of compounds.



Scheme 24.

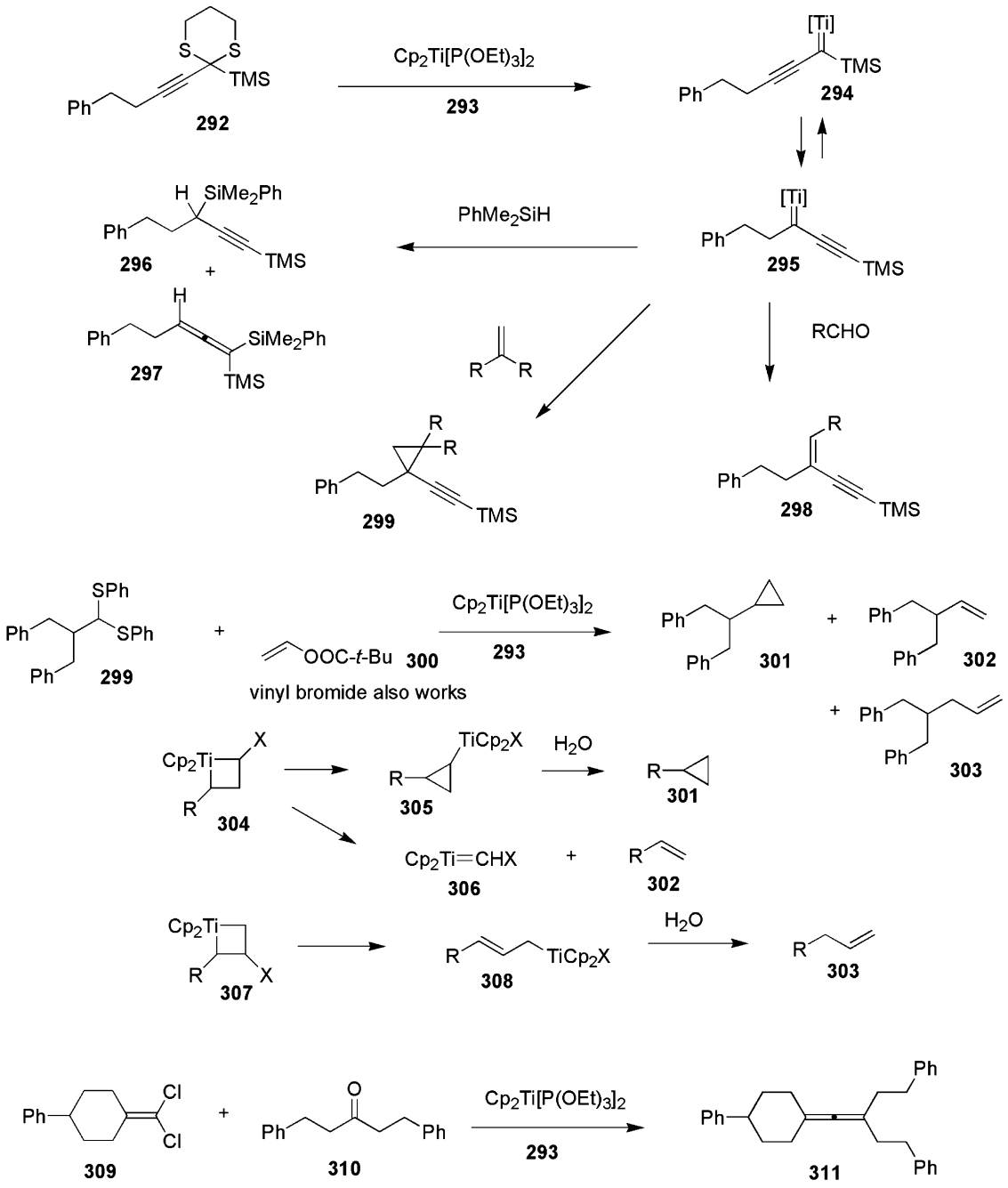
The reaction of tungsten–carbene complex **333** (Scheme 29) with phosphaalkynes (*e.g.* **334**) was reported [627]. The reaction affords a mixture of carbene complex **335** and diphosphine–tungsten complex **336**. Complex **335** was obtained through [2 + 2]-cycloaddition (affording phosphametallacyclobutene **338**) followed by migration of an alkoxide group to phosphorous. The other product was obtained from alternate regioisomer **338**, followed by ring opening and insertion of a second mole of phosphaalkyne.

The synthesis of germylcarbene complexes (*e.g.* **343**, Scheme 30) through stoichiometric metathesis of vinylgermanes (*e.g.* **341**) and derivatives of the Schrock carbene complex (*e.g.* **342**) were reported [628]. Related compounds featuring other Group 14 metal-substituted molybdenum and tungsten–carbene complexes were also reported [629,630].

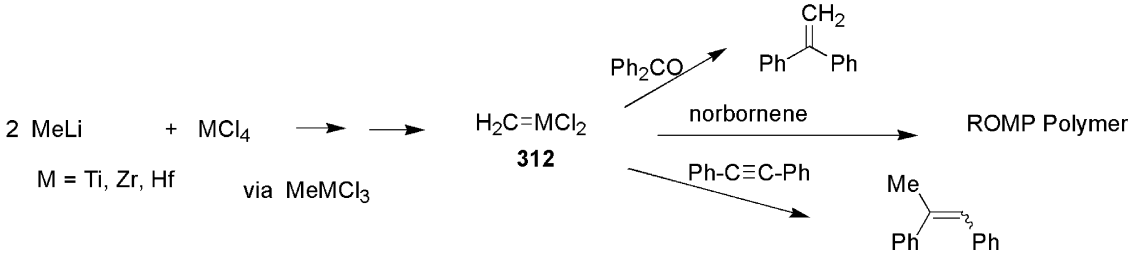
Group 6 metal carbene complexes were generated in the reaction of laser-ablated Group 6 metal atoms with fluoromethane [631]. Initially CH_3–M–F was formed, which transforms to CH_2=M(H)F, and then CH≡$M(H)_2$F. Chromium afforded only the alkyl complex, molybdenum formed all three, and tungsten formed the carbene and carbyne complexes. The infrared spectra were acquired and compared with calculated spectra.

Other studies of carbene complexes in this class include: (1) molybdenum-catalyzed cyclopolymerization of dialkynes in supercritical CO_2 (ligation to carbon dioxide to molybdenum carbene complex intermediates was discussed) [632]; (2) a computational study focusing on the structure and aromaticity of tungstacyclobutadiene complexes [633]; (3) a proposal that chromium(III) carbene complexes are intermediates in the carbonyl olefination of aldehydes using 2-alkoxy-1,1,1-trichloro derivatives and chromium(II) chloride [634]; (4) discussion of carbene character η^2-thioacyl–tungsten complexes based on the X-ray structure [635].

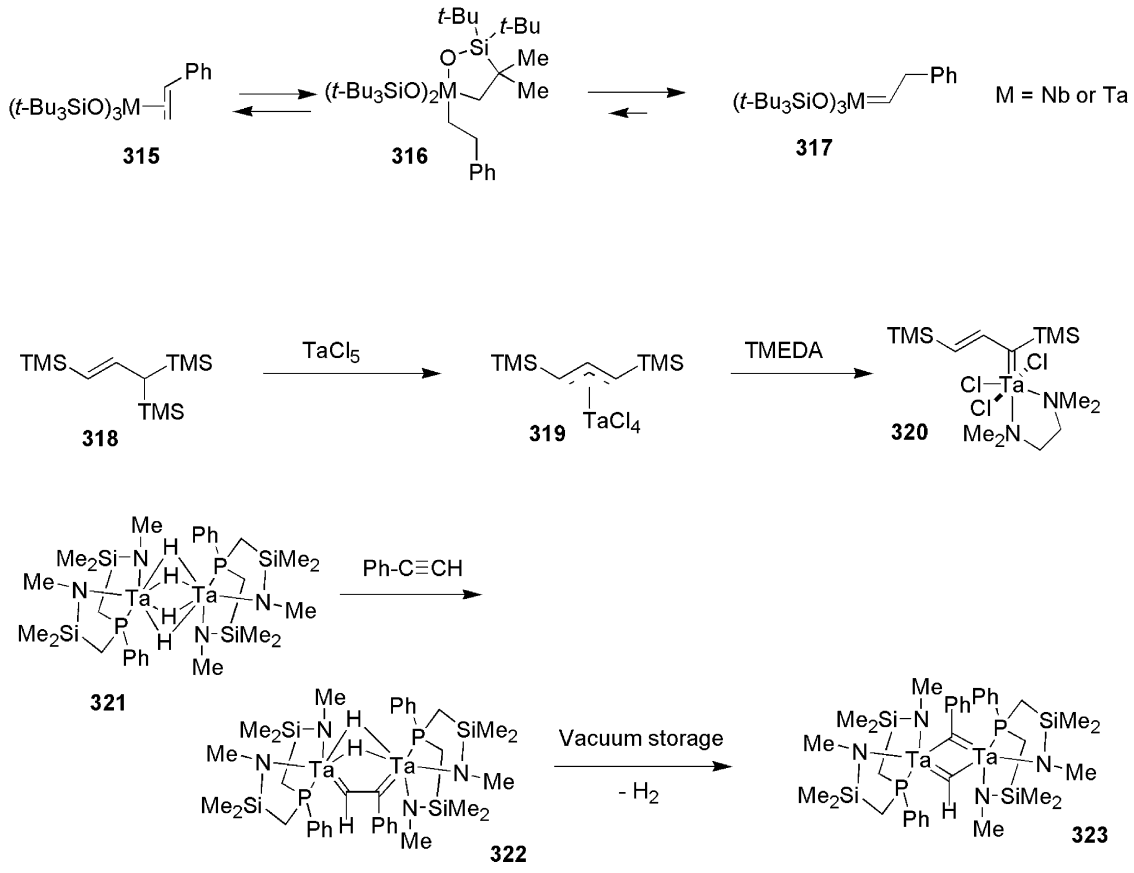
1.1.3.3.2. Publications focusing on synthesis, formation, or physical properties of Fischer carbene complexes of Group 6 metals. The most common procedure used for the synthesis of Group 6 metal–carbene complexes is the Fischer synthesis, which involves coupling of an organolithium reagent with a Group 6 metal carbonyl derivative, followed by alkylation of the resulting acylate. Both traditional synthetic routes and newer synthetic routes are included in this section.



Scheme 25.

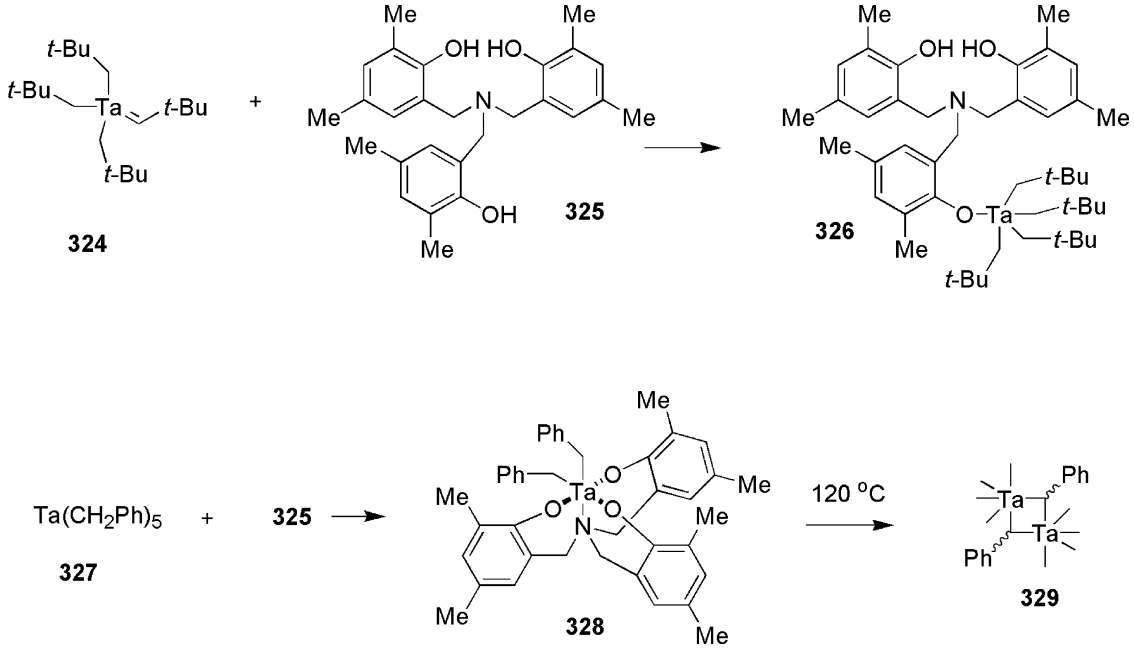


Scheme 26.

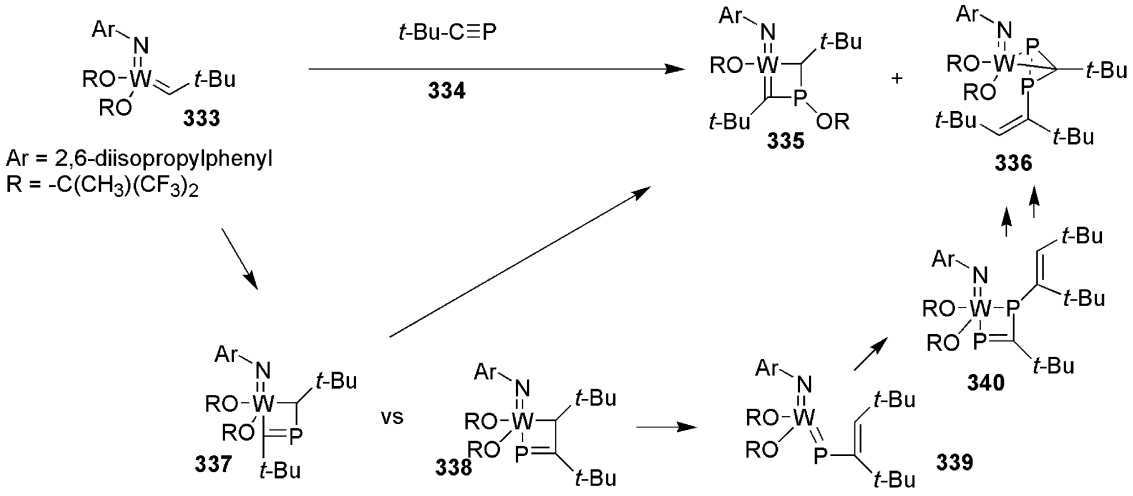


Scheme 27.

Synthesis of chelated ferrocenylcarbene complexes (*e.g.* **346**, **349**, Scheme 31) was reported [636]. Initial synthesis of the alkoxycarbene complex **344** using the Fischer synthesis, followed by subsequent transformation to the aminocarbene complexes through aminolysis and further alkylation of the aminocarbene complexes was also reported. Conversion of the allylamino complexes to the alkene-coordinated complexes occurs upon thermolysis. Chelating allenyl complexes (*e.g.* **349**)



Scheme 28.



Scheme 29.

were obtained through thermolysis of the allylaminocarbene complex analog **348** [637]. Related $(Cp)Fe(CO)_2R$-substituted carbene complexes (*e.g.* **351**, **354**) were also reported [638]. These complexes were prepared through the Fischer route (**351**) or through an aldol condensation route (**354**). Aminolysis reactions were also reported for these complexes [639]. A modified Fischer synthesis was also employed for the synthesis of heterocyclic bis(carbene) complexes (*e.g.* **357**) [640]. Monobenzannulation reactions were reported for the bis(chromium) and mixed chromium/tungsten complexes. Palladium-catalyzed dimerization was also reported.

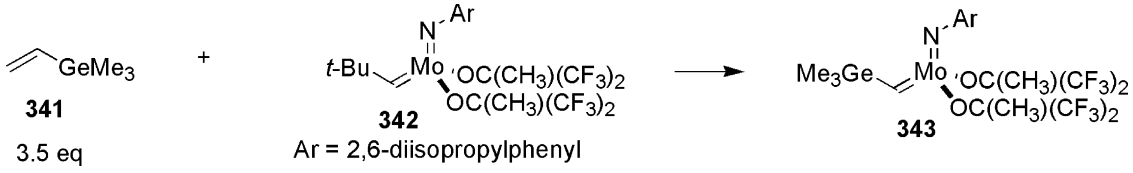
Bis(bridging carbene)–dimolybdenum complexes (*e.g.* **359**, **361**, Scheme 32) were prepared through alkylation or protonation of the bridging acyl(carbene)–dimolybdenum complexes (*e.g.* **358**) [641]. The bis(methoxycarbene) complex **359** was a fluxional molecule in equilibrium with bridging alkyne complex **360**. The bridging hydroxycarbene complex **361** was generated at low temperature and underwent CO dissociation upon warming to room temperature. Contribution of a carbene resonance contribution to bridging iminyldimolybdenum complexes was discussed [642].

The tungsten–phosphaalkene complex **368** (Scheme 33) was prepared through coupling of tungsten complex **363** with the N-heterocyclic silylene derivative **364** [643]. Initial formation of *N*-ylide **365**, followed by ring opening and intramolecular attack by nitrogen on a CO ligand, followed by coupling with a second mole of the silylene was proposed.

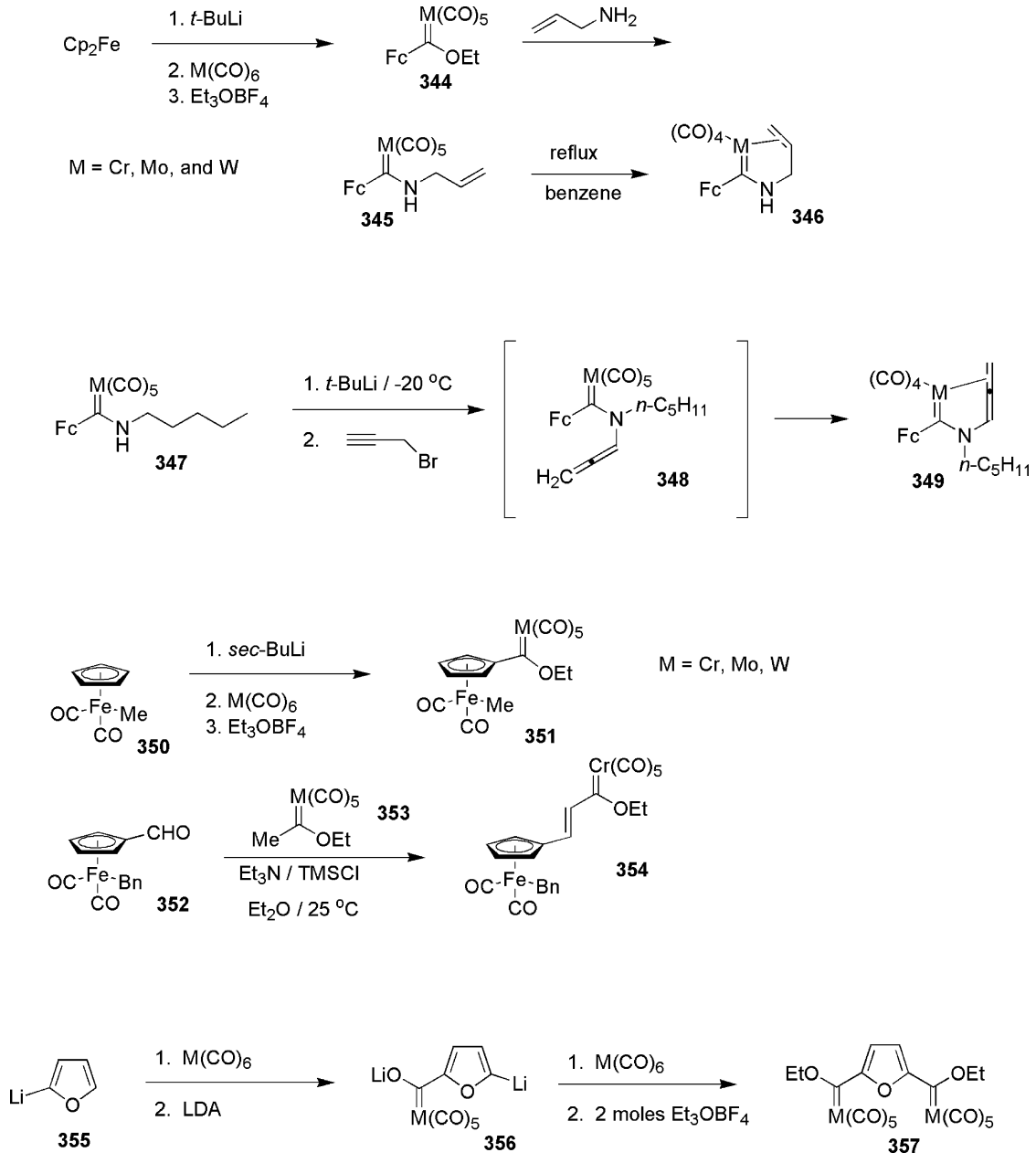
1.1.3.3.3. Reaction of Group 6 metal–carbene complexes with alkenes and dienes. This section focuses on reactions of Group 6 metal–carbene complexes involving coupling with alkenes at the carbene carbon. Other examples of the coupling of carbene complexes with alkenes where the reactive site is elsewhere can be found ahead under the heading: cycloaddition reactions occurring at the C–C π-bond of α,β-unsaturated metal–carbene complexes (Section 1.1.3.3.7).

Examples of the coupling of carbene complexes with alkenes are depicted in Scheme 34. Solid-phase reaction of carbene complexes with alkenes was reported [644]. Carbene complexes bound to the solid support via an isocyanide ligand (*e.g.* **369**) were prepared through reaction of the polymer-bound isocyanide with chromium hexacarbonyl followed by the Fischer synthesis. Reaction with methyl acrylate afforded cyclopropanation and alkene addition products **370–372**. The reaction of carbene complexes (*e.g.* **373**) with alkylidenecyclopropanes (*e.g.* **374**) was reported [645]. The reaction leads to cyclopentenones (*e.g.* **375**). A mechanism involving [2 + 2]-cycloaddition to afford **376** followed cyclopropylcarbinyl metal ring expansion to afford metallacyclopentane **377**, followed by CO insertion and reductive elimination was proposed.

1.1.3.3.4. Reaction of Group 6 metal–carbene complexes with alkynes—benzannulation. Many examples of benzannulation using α,β-unsaturated chromium–carbene complexes and alkynes (commonly known as the Dötz reaction) were reported in 2005. Examples are depicted in Scheme 35 and include: (1) formation of naphthalene–$Cr(CO)_3$ complexes (*e.g.* **380**) and subsequent studies of haptotropic rearrangements [646,647], and analogous studies with phenanthrene–$Cr(CO)_3$ complexes [648]; (2) formation of a complex phenol derivative (**383**) for synthesis of kendamycin segments [649]; (3) synthesis of curcuquinone (**386**) [650]; (4) benzannulation of an aryloxycarbene complex (**388**) for synthesis of iodotyrosine [651]; (5) coupling of α,β-unsaturated carbene complexes (*e.g.* **390**) and propargyl



Scheme 30.

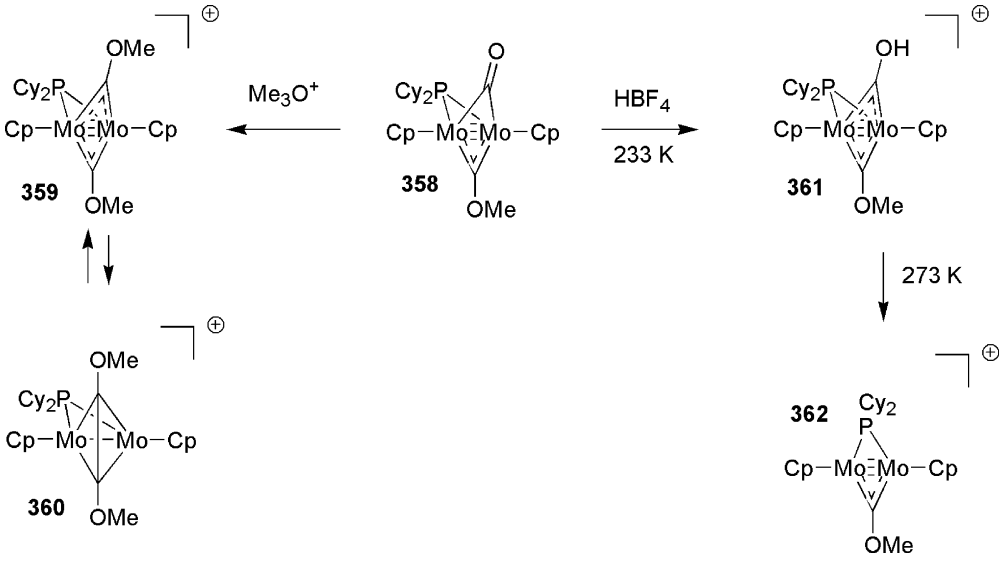


Scheme 31.

amide derivatives (*e.g.* **391**) under ultrasound conditions [652]; (6) formation of helicene-type compounds (*e.g.* **394**) [653,654]; (7) benzannulation using arylcarbene complexes fused to a ferrocene ring (*e.g.* **396**) [655]; (8) binding of arylcarbene complexes to a solid support followed by subsequent solid-phase benzannulation [656].

1.1.3.3.5. Nonbenzannulation reactions of Group 6 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 2005.

Several cycloaddition reactions involving the coupling of alkynes with β-aminoalkenylcarbene complexes (*e.g.* **401**, **404**, **409**, and **414**, Scheme 36) were reported [657]. Reaction of β-aminoalkenylcarbene complexes (*e.g.* **401**) with simple alkynes led to aminocyclopentadienes (*e.g.* **403**) through a mechanism involving alkyne insertion followed by cyclization of the intermediate dienylcarbene complex **402**. In several examples reactive organic groups were incorporated for the deployment of tandem multiple ring forming reactions. Reaction with bis(alkenyl)acetylenes (*e.g.* **405**) led to indanone derivatives (*e.g.* **408**) in a complex tandem process involving formation of the bis(alkenyl)aminocyclopentadiene **406**, followed by electrocyclic ring closure to form cyclohexadiene derivative **407**, followed by elimination of amine, aromatization, and enol ether hydrolysis [658]. Coupling of β-aminoalkenylcarbene complexes with 2 equiv. of a terminal alkyne led to the cyclic fulvene derivatives (*e.g.* **410**) [659]. The proposed mechanism involves



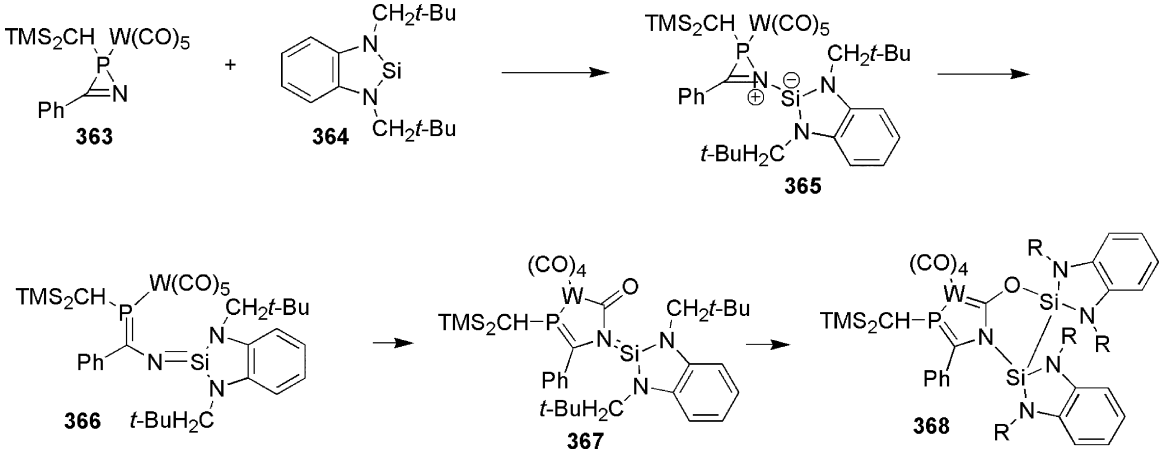
Scheme 32.

insertion of two moles of alkyne to afford trienylcarbene complex **411** and CO insertion to afford ketene intermediate **412**. Intramolecular hetero Diels–Alder reaction followed by elimination of amine led to the observed product. Reaction employing the ketal-functionalized carbene complex **414** and alkynes led to aminocyclopentadienes **415**, which undergo an aldol cyclization to triquinanes (**416**) upon treatment with acid [660].

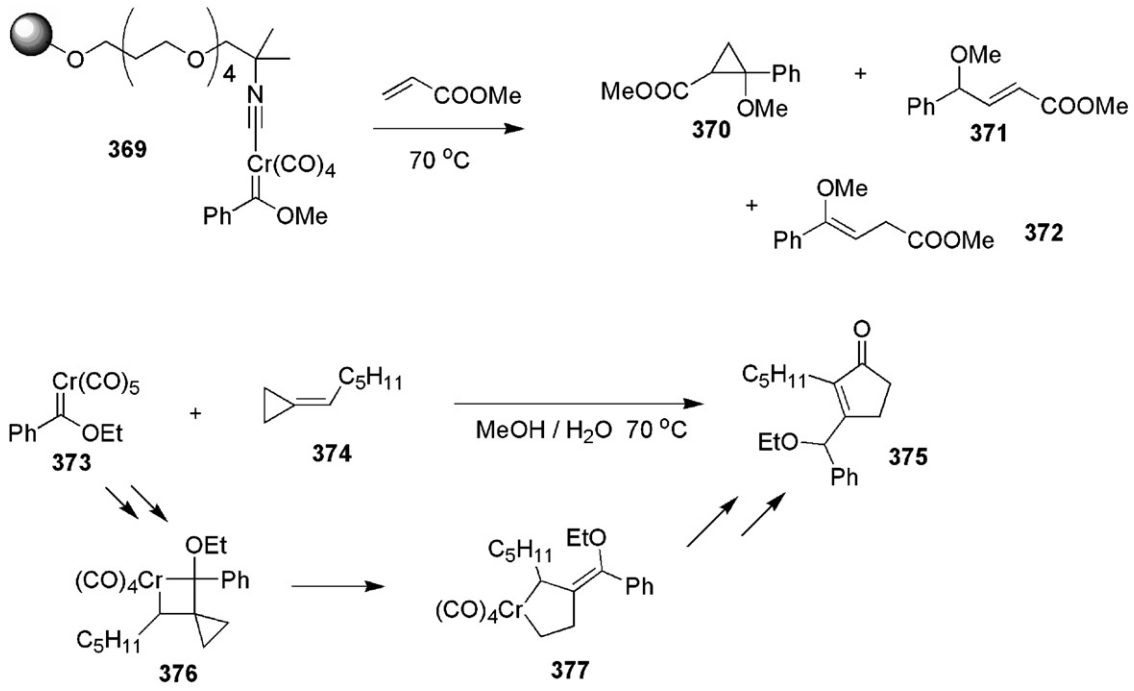
Designed annulation processes employing the coupling of carbene complexes with highly conjugated acetylene derivatives are depicted in Scheme 37. The coupling of dienyne-aldehydes (*e.g.* **417**) with simple carbene complex **418** was reported [661]. The reaction proceeded through alkyne–carbene complex coupling followed by formation of isobenzofuran intermediate **419**, which then undergoes intramolecular Diels–Alder reaction, followed by opening of the oxygen bridge. The coupling of 2-alkynylbenzoyl compounds (*e.g.* **422**) with γ,δ-unsaturated carbene complexes (*e.g.* **423**) was reported [662]. The reaction proceeded by formation of a similar isobenzofuran intermediate (**424**) followed by intramolecular Diels–Alder reaction and ring opening, and ultimately afforded hydrophenanthrenone derivatives (*e.g.* **426**). In many cases the yields were enhanced in an aqueous solvent system. Coupling of carbene complexes with conjugated dienynes where the middle ring is part of a heterocyclic ring (*e.g.* **427**) led to the benzofurans (*e.g.* **429**) [663]. Coupling of simple enyne aldehydes (*e.g.* **430**) with alkenylcarbene complexes (*e.g.* **431**) leads to dienylfurans, which undergo [8 + 2]-cycloaddition upon treatment with dimethyl acetylenedicarboxylate [664].

Synthesis of bulgaramine using an intramolecular carbene–alkyne coupling as the key step was reported (Scheme 38) [665]. Thermolysis of aminocarbene complex **434** led to the pentacyclic compound **436**. The proposed mechanism involves intramolecular alkyne insertion to afford intermediate carbene complex **435** followed by cyclization to form **436**.

The coupling of iminocarbene complex **437** (Scheme 39) with alkynes was reported [666]. The reaction with internal alkynes leads to 2-imino-substituted diene derivatives (*e.g.* **439**). A mechanism involving formation of a metallacyclobutene (**438**) followed by β-hydride elimination and reductive elimination was proposed. The mechanism was supported by DFT calcu-



Scheme 33.



Scheme 34.

lations. The reaction employing the complex **440** can lead to four different reaction types of reaction products (**441**–**444**) depending upon the structure of the R^1 group and the alkyne substituents. The mechanism for formation of each of these products was explored and evaluated computationally.

1.1.3.3.6. Generation of ketenes from Group 6 metal–carbene complexes. Iron-induced conversion of dienylcarbene–chromium complexes (*e.g.* **445**, Scheme 40) to phenols (*e.g.* **447**) was reported [667]. Initially the cyclohexadienone–iron complexes (*e.g.* **446**) were formed, which convert to phenols upon demetallation. The cyclization proceeded with a high degree of stereoselectivity in formation of the cyclohexadienone complex. No definitive mechanism was proposed, however the authors suggested that there is either formation of a diene–iron complex followed by formation of a ketene and cyclization, or transfer of the carbene ligand from chromium to iron followed by formation of a ketene and cyclization.

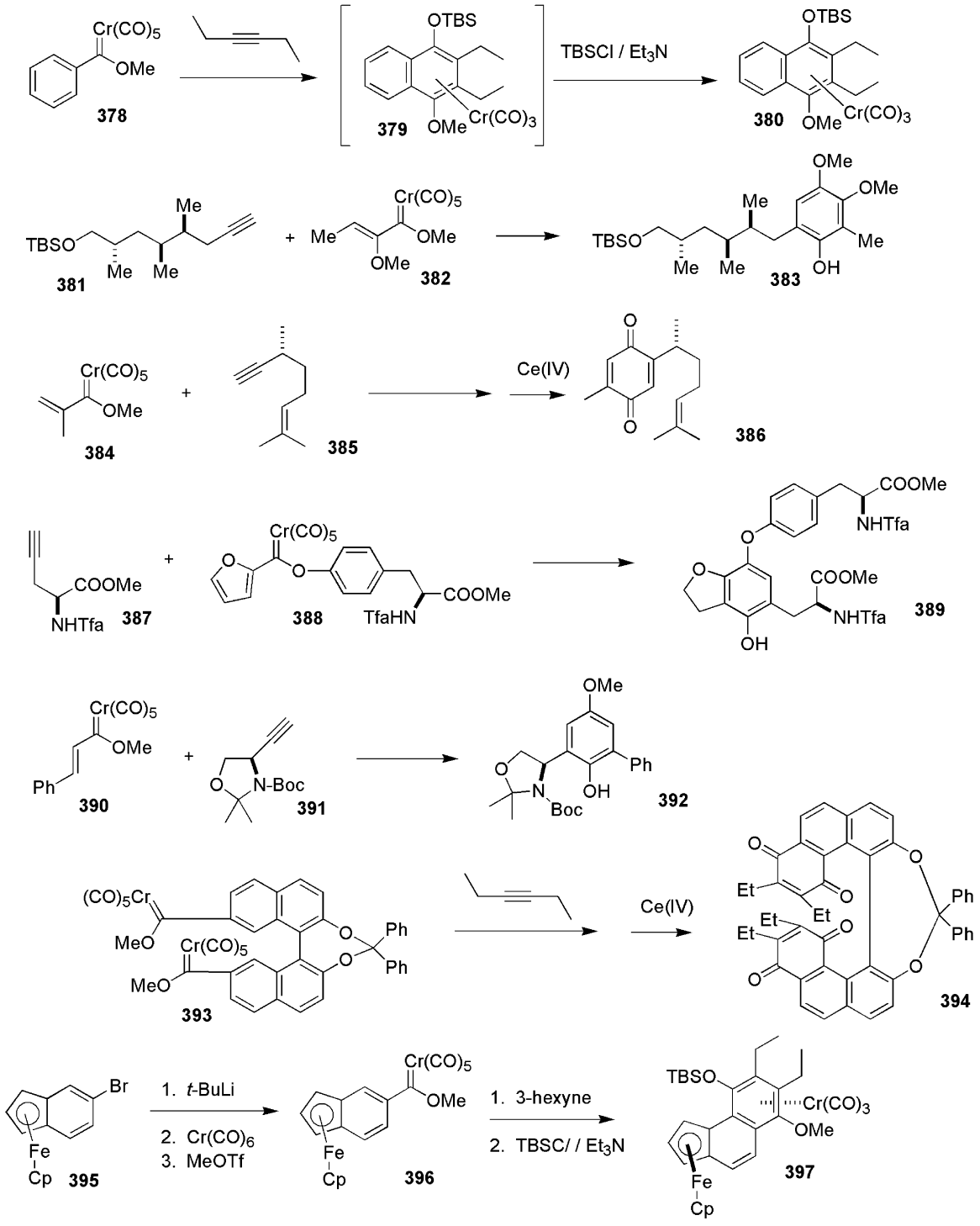
A computational study of photocarbonylation of Fischer carbene complexes was reported [668]. Photoirradiation of a carbene complex to afford the lowest energy singlet excited state followed by intersystem crossover leads to the triplet leads to the triplet ketene complex, which then converts to the singlet state upon interaction with the solvent. Subsequent reaction with the ketenophile then leads to the ketene derived products. Initial formation of the triplet ketene from the carbene complex is an endothermic and highly reversible process.

1.1.3.3.7. Reactions occurring at the conjugated C–C π-bond of α,β-unsaturated Group 6 metal–carbene complexes. Numerous reaction processes were reported in 2005 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").

Diels–Alder reactions were reported for pentamethylcyclopentadiene and alkynylcarbene complexes (*e.g.* **448**, Scheme 41) [669]. A secondary benzannulation reaction was observed when the reaction was conducted at 50 °C. The initially expected product **451** could be detected in the crude reaction mixture however the primary isolated product was rearranged compounds **452** and **453**. A tandem imino Diels–Alder reaction—[2 + 2]-cycloaddition process leading to tricyclic compounds (*e.g.* **456**) was observed in the reaction of two equivalents of an alkynylcarbene complex (*e.g.* **448**) with azadiene **454** [670].

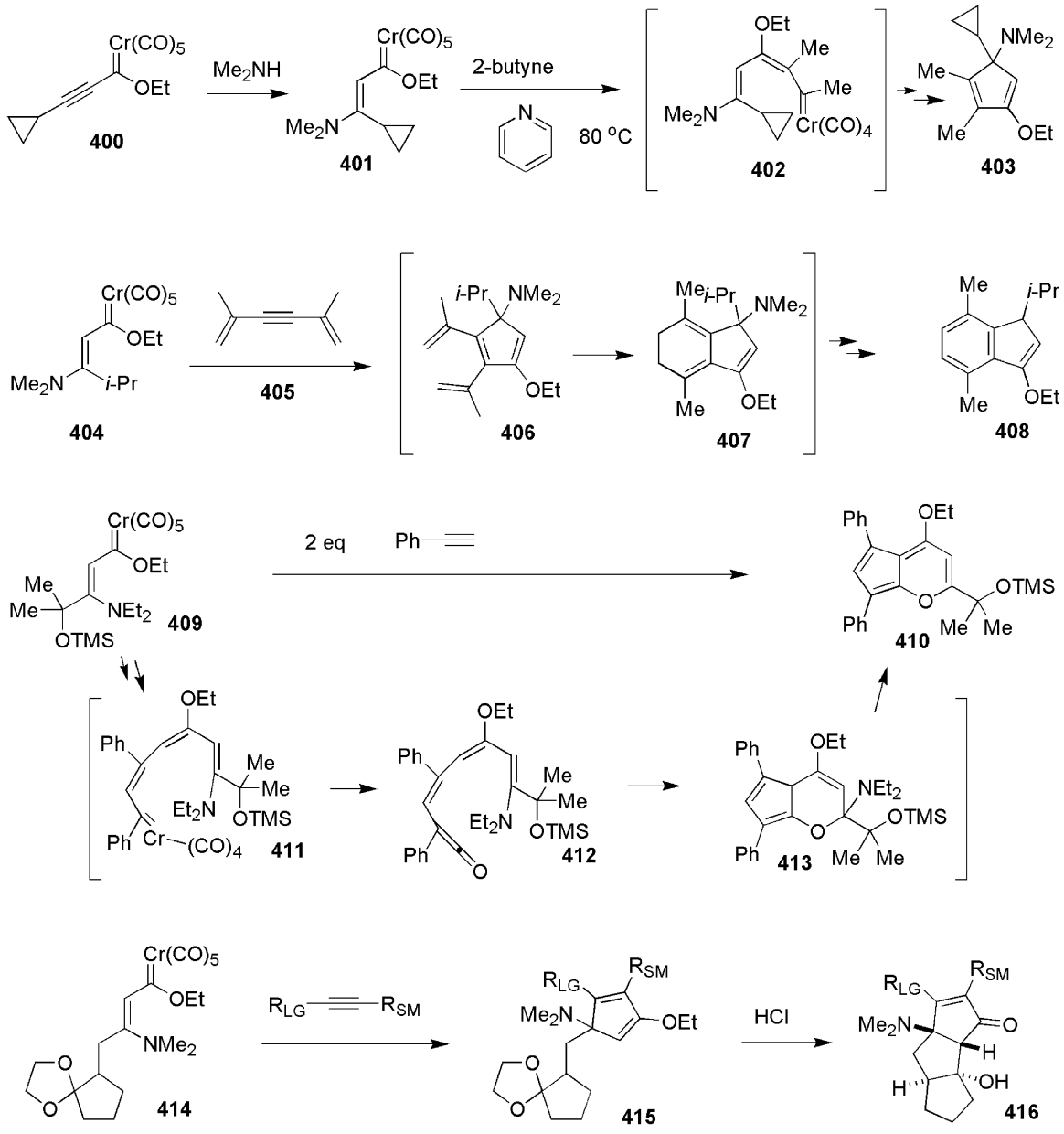
A net [4 + 2]-cycloaddition reaction was observed in the coupling of *o*-lithiated stilbene oxides (*e.g.* **459**, Scheme 42) with α,β-unsaturated carbene complexes (*e.g.* **458**) [671]. A mechanism involving Michael addition to form intermediate **460**, followed by intramolecular S_N2 reaction at the epoxide in a 6-endo fashion was proposed. The reaction proceeded with a very high degree of stereoselectivity. A new synthesis of cyclopropylcarbene–chromium complexes (*e.g.* **465**) from α,β-unsaturated chromium carbene complexes (*e.g.* **462**) and lithiated aryloxiranes (*e.g.* **463**) was reported [672]. A mechanism involving Michael addition to form intermediate **464** followed by intramolecular nucleophilic displacement of the epoxide was proposed. The reaction proceeded with a very high degree of diastereoselectivity. The Michael addition reaction of alkynylcarbene–tungsten complexes (*e.g.* **466**) with pyrazoles (**467**) was reported [673].

1.1.3.3.8. Physical organic chemistry of Group 6 Fischer carbene complexes. The kinetic parameters for the aminolysis of Group 6 metal–thiocarbene complexes (*e.g.* **469**, Scheme 43) were reported [674]. General base catalysis was confirmed for the reaction. The tetrahedral intermediates of the reaction (*e.g.* **470** and **471**) were undetectable. The tungsten complexes were



Scheme 35.

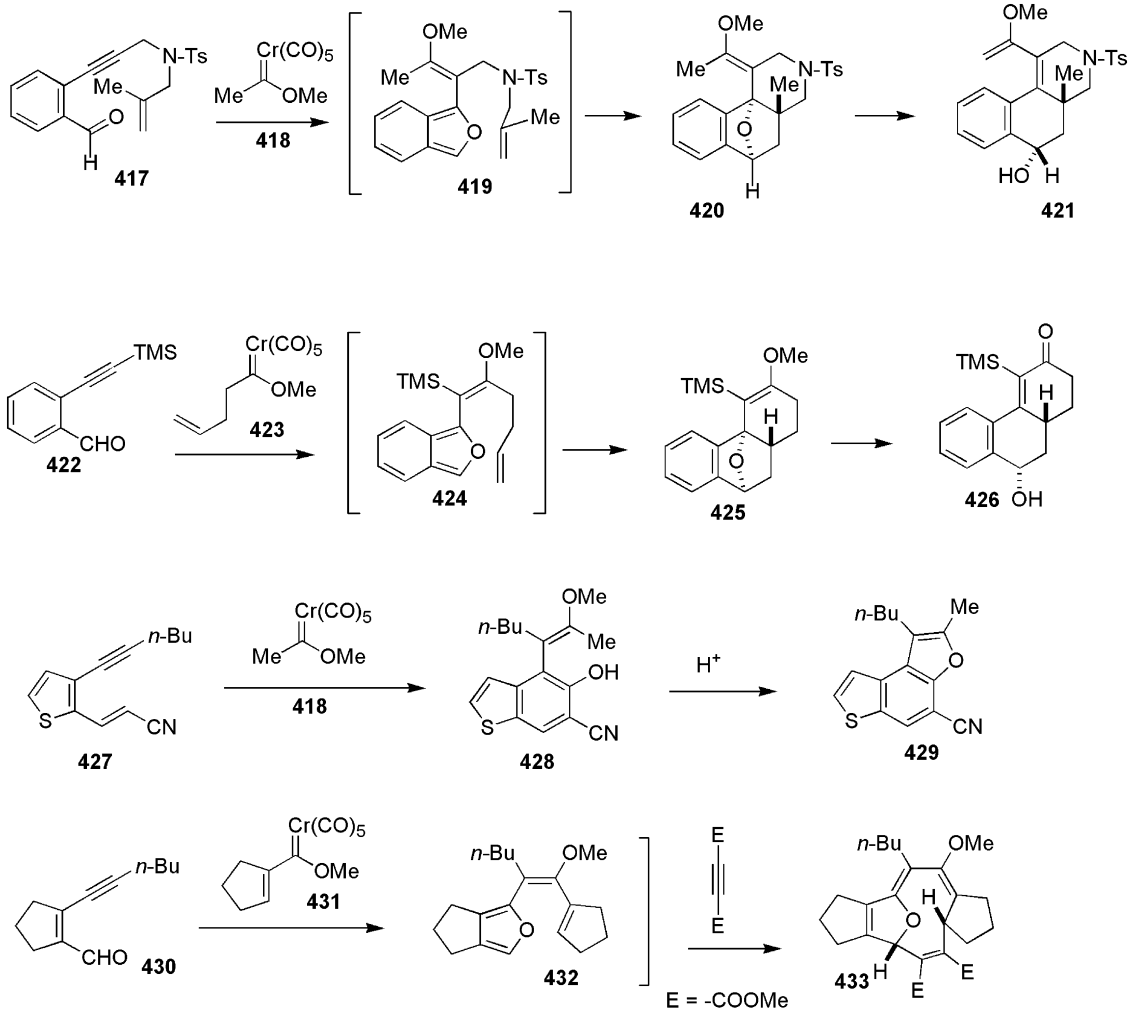
more reactive than the chromium complexes. The rate constants for the reaction of Fischer phenyl(alkylthio)carbene complexes PhC[=M(CO)$_5$]SR with nitrile- and nitro group-stabilized carbanions was reported [675]. The substitution reaction follows second order kinetics. The relative reactivity observed was $CH(CN)_2^- > p\text{-}O_2NC_6H_4CHCN^- > PHCOCHNO_2^-$. The tungsten–carbene complexes were more reactive than the chromium carbene complexes. The attachment of DABCO to alkoxycarbene and thiocarbene complexes was reported [676]. Methoxycarbene complexes were found to be more reactive than the analogous thiocarbene complexes. This was attributed to the greater π-bonding of the alkoxy group in the starting complex. Alkaline hydrolysis of *p*-substituted styrylcarbene-chromium complexes *p*-PhCH=CHC[=M(CO)$_5$]OR to cinnamaldehyde derivatives *p*-PhCH=CHCHO was reported [677]. Electron-withdrawing substituents increase the rate. The rate-determining step was addition of hydroxide ion to the carbene carbon to form a tetrahedral intermediate.



Scheme 36.

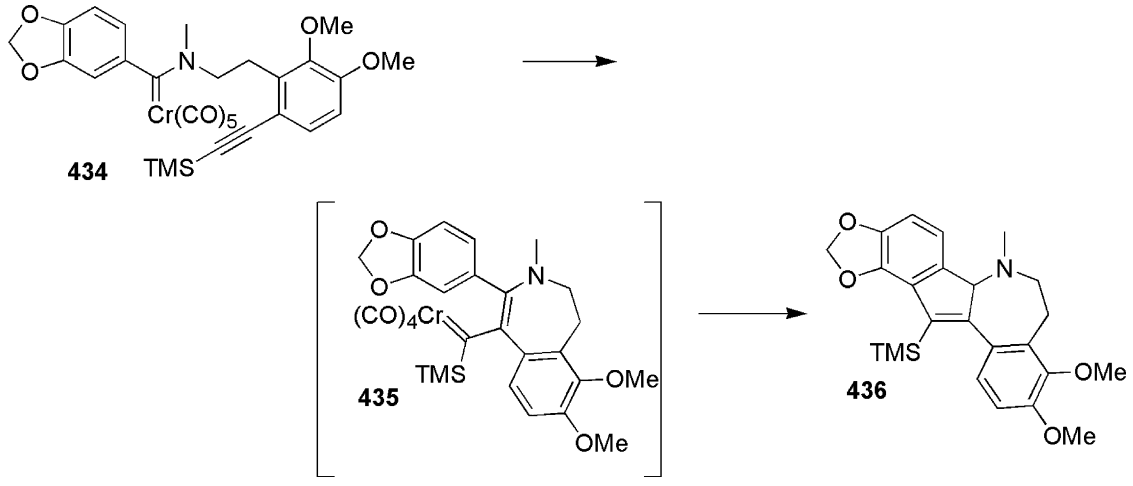
1.1.3.3.9. Synthesis and reactivity of Group 6 metal–vinylidene complexes, and reactions that involve vinylidene–metal complexes as intermediates; also includes other process that involve the formation of a carbene complex from an alkyne and a noncarbene metal complex. The reaction of vinylidene–tungsten complexes (*e.g.* **475**, Scheme 44) with enamines was reported [678]. The reaction of vinylidene complex **475** with cyclopentenyl-enamine **476** led to the α,β-unsaturated carbene complex **480**. A mechanism involving deprotonation of the vinylidene followed by nucleophilic addition of the resulting alkynyltungsten species **477** to the iminium salt **478** was proposed. A rearrangement of the resulting vinylidene complex **479** then leads to the observed product and imine **481**. An additional type of product, aminocarbene complex **484** was observed in the coupling of vinylidene complex **475** with acyclic enamine **482**. Formation of aminocarbene complex **484** was attributed to condensation of the α,β-unsaturated carbene complex **483** with byproduct cyclic imine **481**. The reaction of phosphinoalkynyltungsten complex **485** (Ar=Ph or Mes) with HCl was reported [679]. The reaction initially affords a neutral vinylidene complex (**486**), which dimerizes to afford complex **487**. More hindered variants of **486** (Ar=Mes) have longer lifetimes and could be reacted with other vinylidene complexes to afford unsymmetrical dimers (*e.g.* **488**).

The synthesis and reactivity of pentacarbonyl Group 6 metal–vinylidene complexes (*e.g.* **490**, Scheme 45) was reported [680]. Photolysis led to dimerization product **492** via dimerization of the CO insertion product **491**. Pentacarbonyl Group 6 metal–allenylidene complexes (*e.g.* **495**, **499**) were also reported [681]. The complexes were pre-

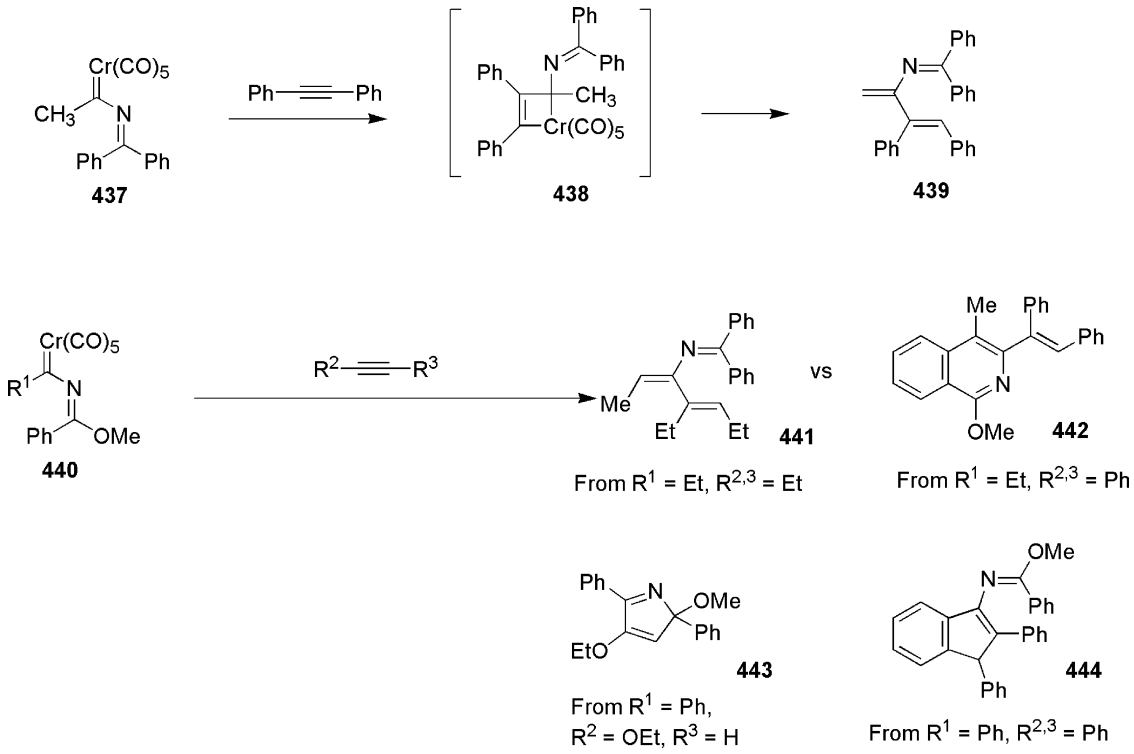


Scheme 37.

pared through reaction of lithioacetylene **494** and chromium pentacarbonyl sources followed by *O*-alkylation. Aminolysis led to the diaminoallenylidene complex **496**. Significant resonance interaction between the amine and carbene complex functionalities was noted in the X-ray structures. Diamines (*e.g.* **497**) led to cyclic aminocarbene complexes (*e.g.* **498**). Reaction of chromium diaminoallenylidene complexes (*e.g.* **499**) with amidine derivatives (*e.g.* **500**) led to heterocyclic carbene complexes (*e.g.* **502**) via nucleophilic substitution followed by acid-catalyzed cyclization [682]. A similar reaction



Scheme 38.



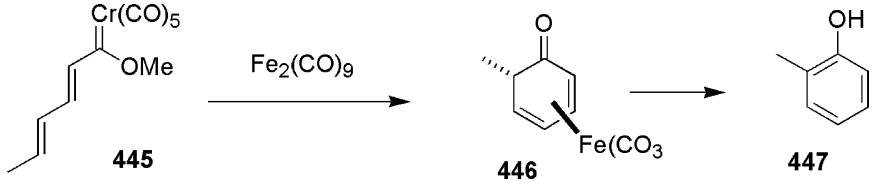
Scheme 39.

was reported using aminopyrazole derivatives. Reaction of monoaminoallenylidene complexes with secondary amines led to β-amino-α,β-unsaturated aminocarbene complexes [683]. Reaction with large excesses of ammonia or primary amines resulted in amine-exchanged aminoallenylidene complexes.

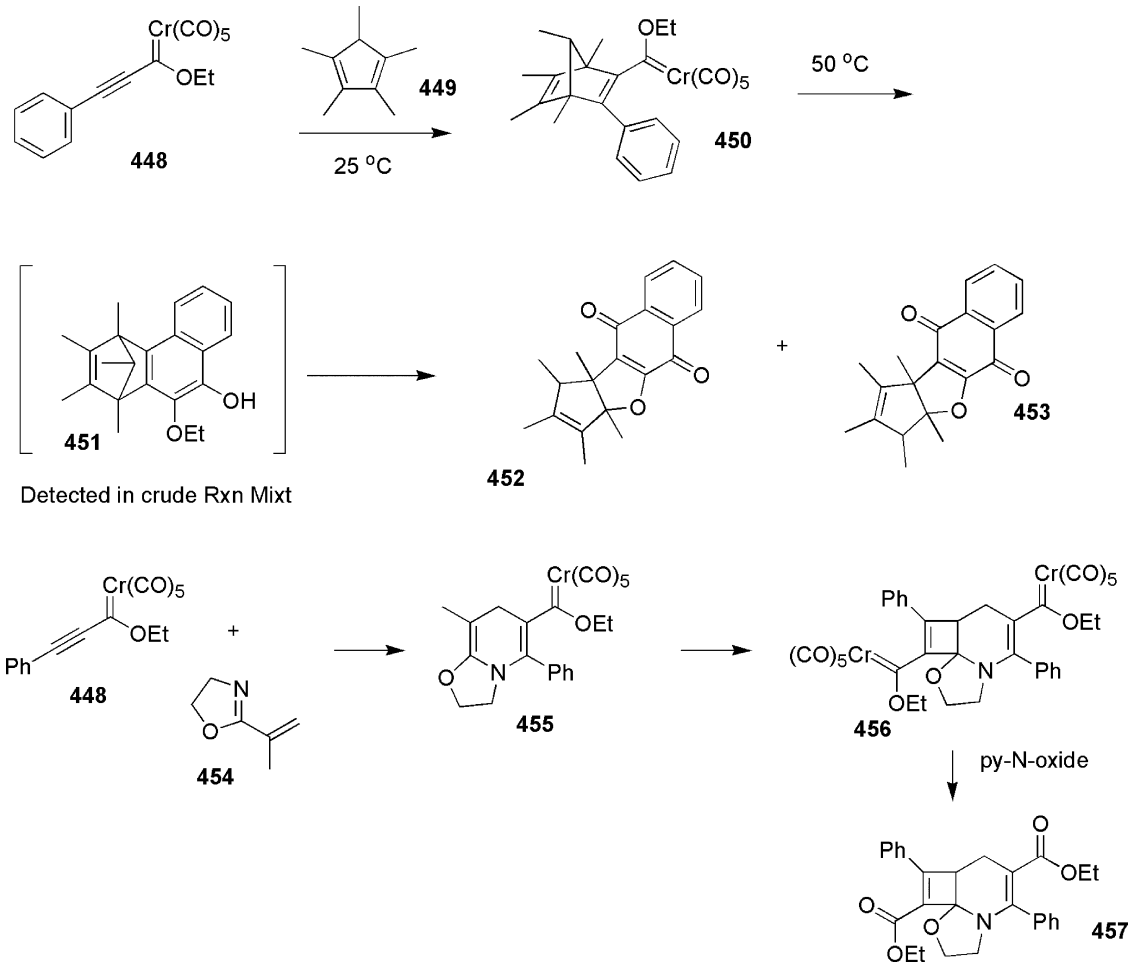
The synthesis of eight-membered rings (*e.g.* **507**, Scheme 46) from enynols (*e.g.* **503**) and tungsten pentacarbonyl sources was reported [684]. The mechanism for this process involves formation of a vinylidene complex (*e.g.* **504**) followed by formation of the cyclic carbene complex (*e.g.* **505**), followed by an intramolecular cyclopropanation to afford a tricyclic compound (*e.g.* **506**). Acid-induced opening of the cyclopropane ring of **506** affords the eight-membered ring compound. If the reaction was performed at elevated temperature the enol ether derivative **508** was obtained, presumably through base-induced decomposition of carbene complex intermediate **505**. Similar reaction pathways were observed in the coupling of dien-yne-ols (*e.g.* **509**) and tungsten pentacarbonyl sources [685]. The reaction can produce either the analogous cyclopropane ethers (*e.g.* **512**) through the vinylidene pathway or methylenetetrahydrofurans (*e.g.* **515**) through the π-alkyne complex. The direction of the reaction was highly dependent on the substituents at the homopropargyl position and the choice of tungsten pentacarbonyl source. The reaction pathways were evaluated computationally.

The formation of tricyclic compounds (*e.g.* **520**, Scheme 47) through coupling of enyne-ketones (*e.g.* **516**) with ketene acetals (*e.g.* **517**) in the presence of tungsten pentacarbonyl sources was reported [686]. A mechanism involving formation of a π-alkyne complex and nucleophilic attack by the carbonyl oxygen to afford the pyrilium cation derivative **518**, followed by 1,3-dipolar addition with the electron-deficient alkene to afford bicyclic carbene complex **519**, followed by intramolecular C–H insertion was proposed. A similar intermediate carbene complex (**522**) could also be trapped by intermolecular H–Si insertion, affording silane **523**.

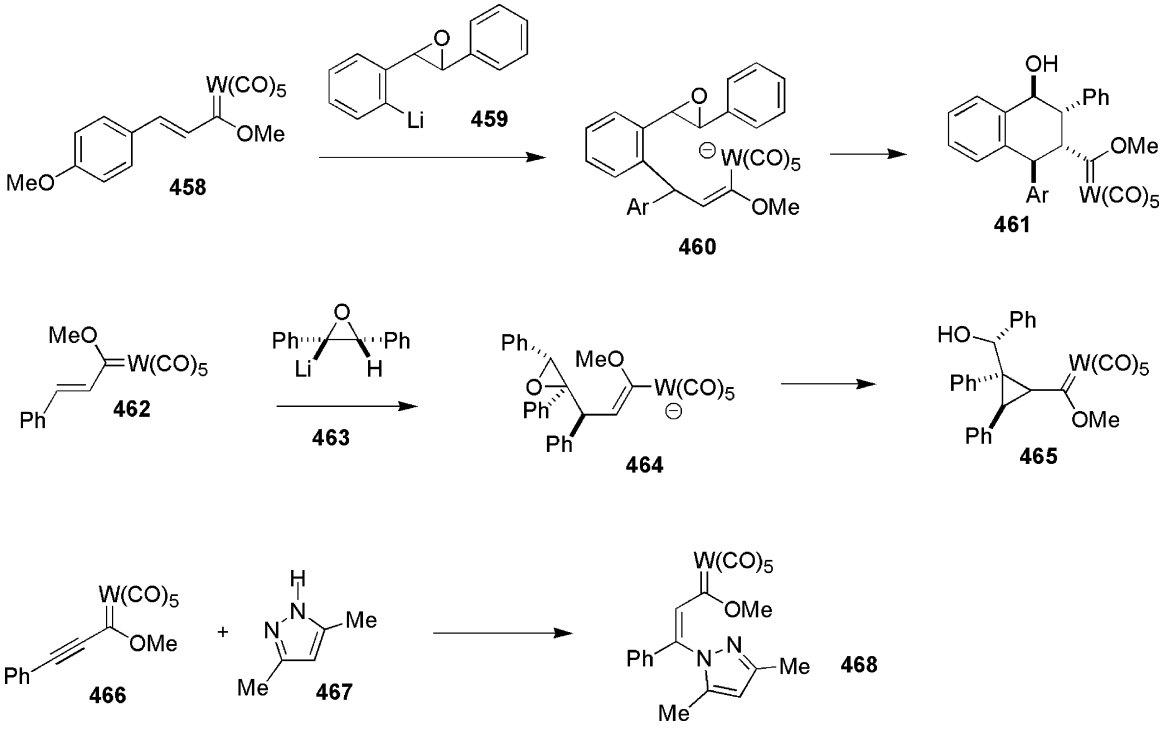
Several examples of the reaction of alkynols with tungsten pentacarbonyl sources were reported in 2005; examples are depicted in Scheme 48. Reaction of carbamate alkynol **524** with tungsten pentacarbonyl sources and base led to the glycal derivative **527** through intermediate tungsten–vinylidene complex **525** and cyclic Fischer carbene complex **526** [687]. This event was a key step in the total synthesis of daunosamine. A similar glycal synthesis (conversion of **528**–**529**) was employed as a key step in the total synthesis of altromycin C [688]. A related cyclization afforded a glycal (**531**) accompanied by a protected dienol



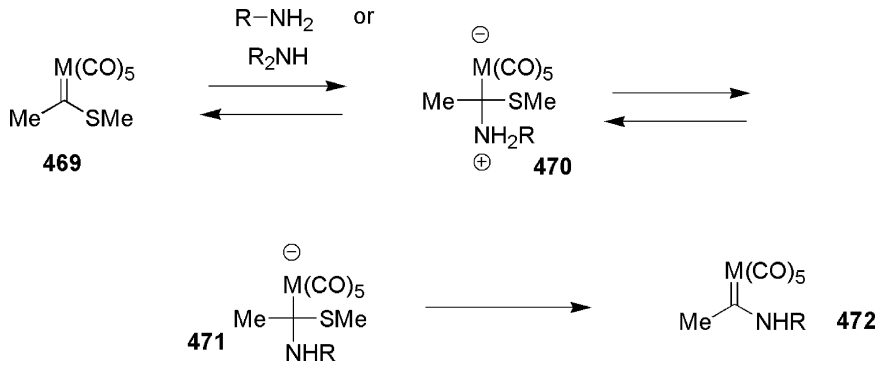
Scheme 40.



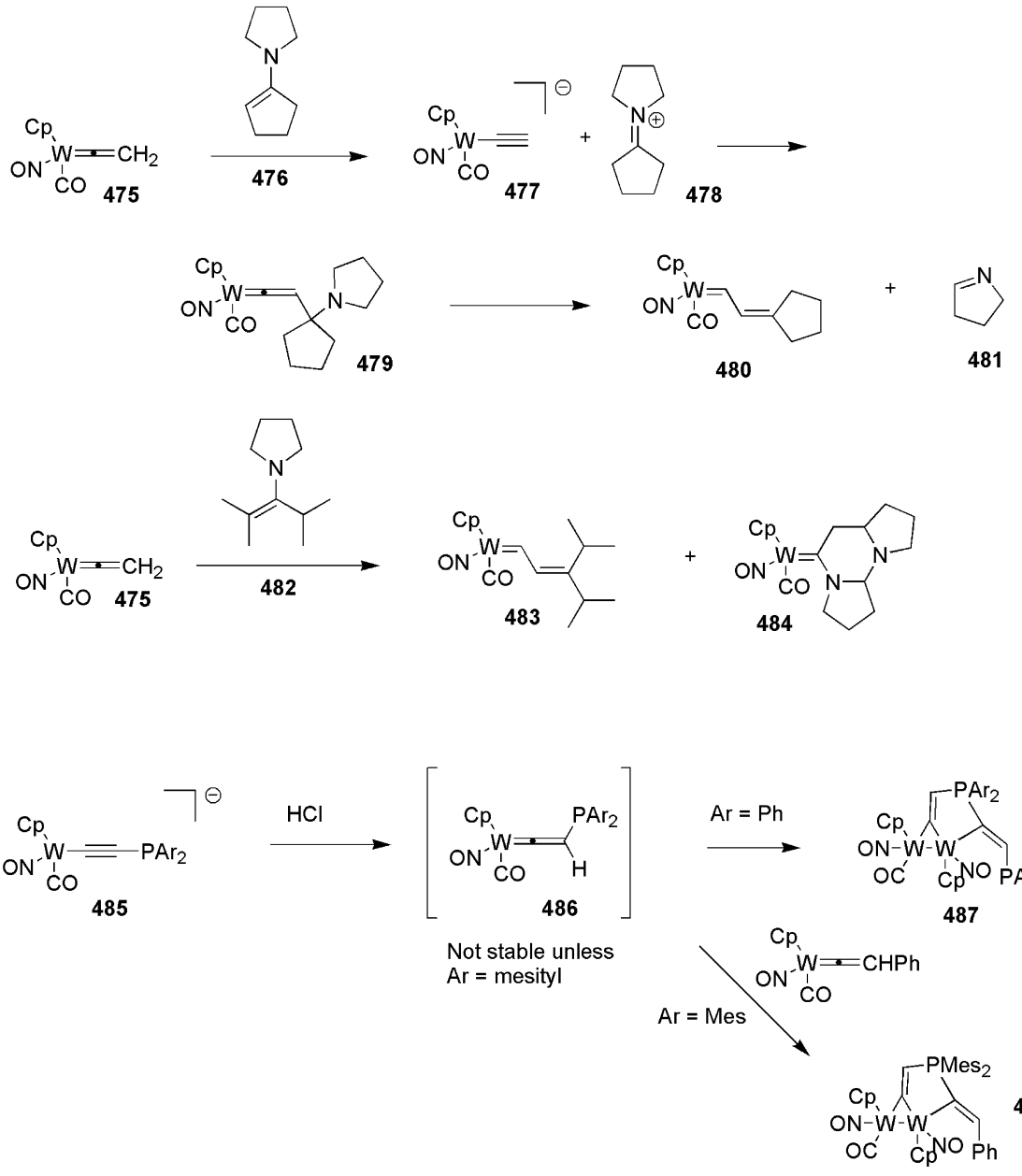
Scheme 41.



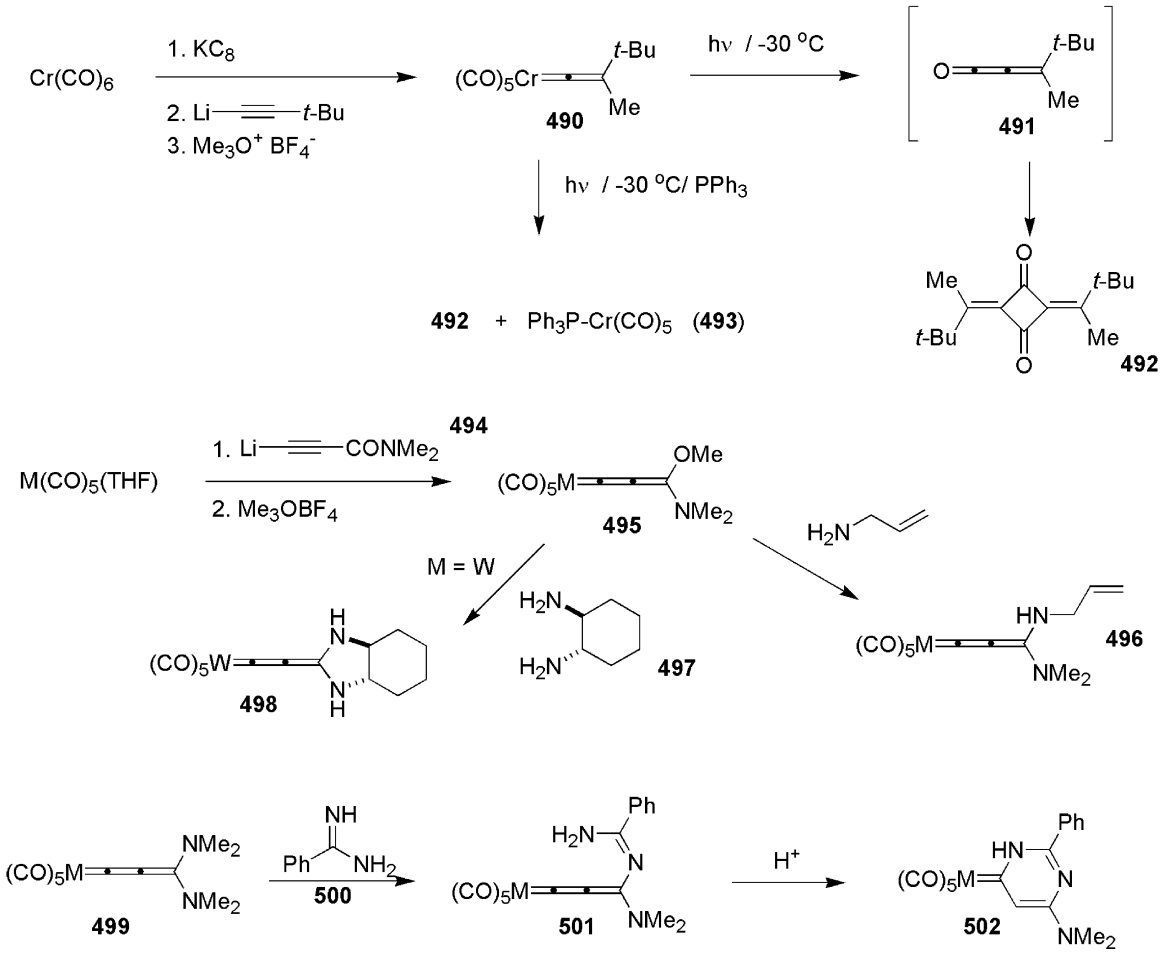
Scheme 42.



Scheme 43.



Scheme 44.



Scheme 45.

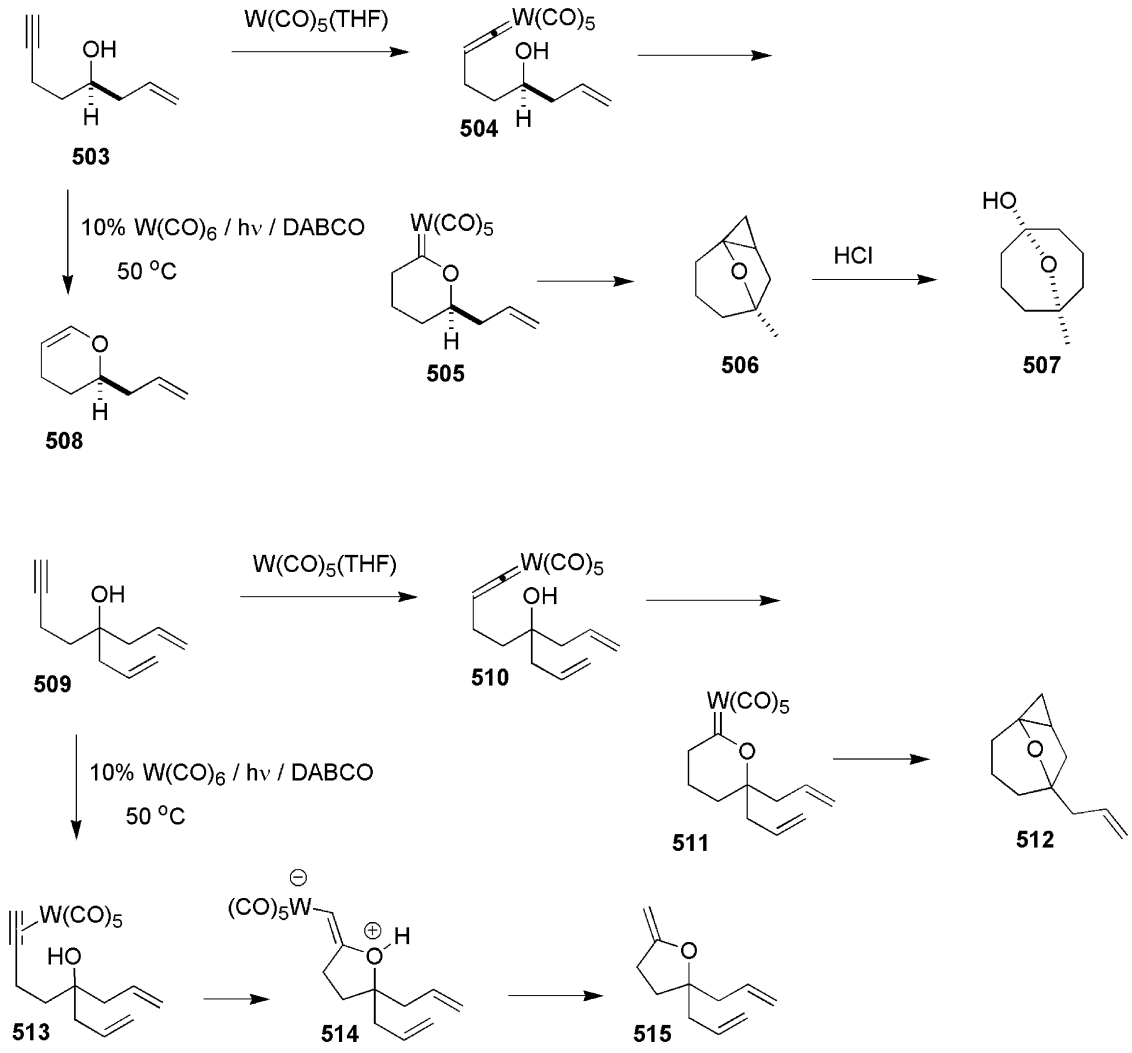
side product (**532**) [689]. The side product was proposed to arise through elimination in the cyclic carbene complex to afford the α,β-unsaturated carbene complex **534** followed by isomerization to the β,γ-unsaturated carbene complex **535**, followed by retro hetero Diels–Alder reaction with expulsion of tungsten hexacarbonyl.

A theoretical study of tungsten-catalyzed alkynol cycloisomerization was reported [690]. Similar studies were reported for molybdenum catalyzed cycloisomerizations [691]. Observation of π-alkyne complexes and not vinylidene complexes was reported in laser flash photolysis of alkynes in the presence of Group 6 metal hexacarbonyls (the conversion of the π-alkyne complexes to the vinylidene was calculated to be endothermic) [692].

1.1.3.3.10. Reactions involving carbanions derived from deprotonation of Group 6 metal–carbene complexes. Deprotonation of Fischer carbene complexes (*e.g.* **538**, Scheme 49) followed by treatment with electrophilic heteroatom reagents was reported [693]. Reaction of the intermediate carbanion with Ph_2PCl led to the expected phosphorylation product **539** in the case of tungsten. The analogous chromium compound was not stable and led to mixtures of the chelating carbene complex **540** and in the case of chromium the phosphine-chelated complex **541**. Reaction of the intermediate anion from the chromium complex with sulfur led to the thioamide complex **542**. A mixture of thiolated carbene complex **544** and doubly thiolated complex **545** was obtained upon treatment of the carbanion with $[Me_2(MeS)S][BF_4]$. The coupling of carbene complex acylates (or nitrogen analogs) (*e.g.* **546**, **550**) with gold(I) salts (*e.g.* **547**) was also reported [694]. The acylate complex led to the acyl transfer product **548**. The lithium salt provided a more complex aggregate of acylgold, ether, lithium and the tungsten pentacarbonyl halide complex. A related iminylgold complex **551** was obtained from the nitrogen analog **550**.

The three-component coupling of Fischer carbene complexes (*e.g.* **552**, Scheme 50), aldehydes, and silyloxyfuran **553** was reported [695]. The reaction proceeds by initial aldol-type condensation to afford the α,β-unsaturated carbene complex (*e.g.* **555**), which is then attacked by the nucleophilic furan derivative to afford isolatable carbene complex **556**, which could be oxidized to form esters (*e.g.* **557**) or methylenated with diazomethane to afford enol ethers (*e.g.* **558**). Thermolysis in acetonitrile led to the intramolecular cyclopropanation product **559**.

Additional studies of carbene complex-derived anions are depicted in Scheme 51 and include: (1) binding of Fischer carbene complexes to polyethylene glycol scaffolds (*e.g.* **562**, **565**) through either alkylation and metathesis and subsequent use as labeling agents for proteins [696]; (2) coupling of carbene com-



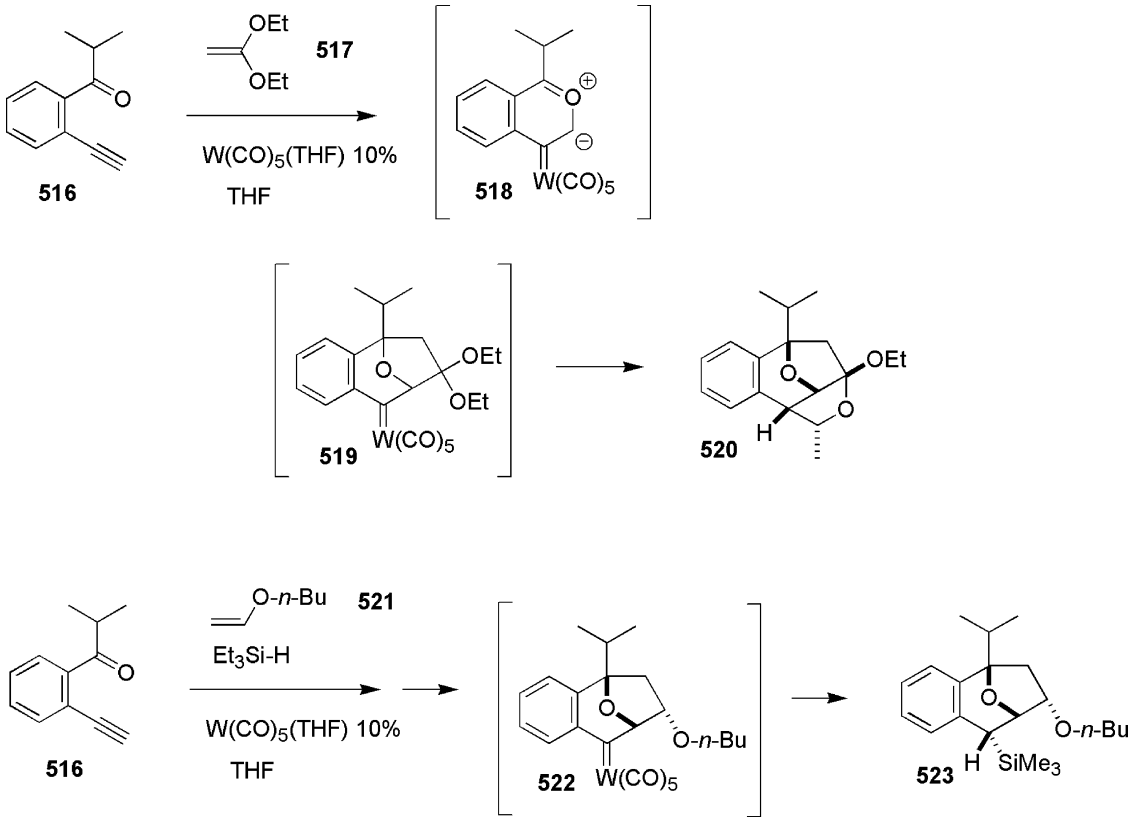
Scheme 46.

plexderived anions (*e.g.* **566**) with pyrilium cations (and other chalcogen analogs) (*e.g.* **567**) or pyrilium-containing aldehydes (*e.g.* **569**) to form highly polarized carbene complexes (*e.g.* **568**, **570**) and subsequent studies on UV–vis and NLO properties [697].

1.1.3.3.11. Reactions involving the addition of nucleophiles to the carbene carbon. The coupling of alkynylphenylcarbene–chromium complexes (*e.g.* **571**, Scheme 52) with dihydropyridine derivatives and with carbon nucleophiles (*e.g.* MeLi) was reported [698]. The reaction led to indane-fused furanone derivatives (*e.g.* **574**) through a process involving nucleophilic addition to the carbene carbon, followed by CO insertion and alkyne insertion. The process uses three of the CO ligands in the original chromium hexacarbonyl starting material. Related nucleophilic additions to γ,δ-unsaturated carbene complexes (*e.g.* **575**) led to cyclopentenones (*e.g.* **576**) through a related mechanistic process involving CO insertion and alkene insertion after the initial addition of carbanion to the carbene carbon.

The reaction of sulfoxide-stabilized carbanions (*e.g.* **578**, Scheme 53) with carbene complexes (*e.g.* **577**) was reported [699]. Reaction with DMSO anion led to the allylic sulfoxide (*e.g.* **579**) via a mechanism involving nucleophilic acyl substitution to afford the unstabilized carbene complex **581**, followed by addition of another mole of DMSO anion and elimination to afford the product. Use of the more hindered sulfoxide-stabilized carbanion **583** led to the enol ether **585**. Elimination occurred directly from the initially-formed tetrahedral intermediate **584** in this case.

Reaction of ketene acetals (*e.g.* **587**, Scheme 54) with carbene complexes (*e.g.* **586**) was reported [700]. The identity of the reaction product was dependent on the R group of the alkoxycarbene complex. Carbene complexes featuring hindered R groups led to the cyclopropanone acetals (*e.g.* **588**). The methoxy complex led to γ-lactones (*e.g.* **589**). A mechanism involving nucleophilic addition to the carbene carbon to form zwitterionic intermediate **590**, followed by formation of a metallacyclobutane (**591**) and reductive elimination was proposed for formation of the cyclopropanes. In the case where R = methoxy, zwitterionic intermediate **590** converts to oxonium ion **592**, which then affords the lactone **589** in a sequence involving formation of unstabilized carbene complex **593**, C–H activation,



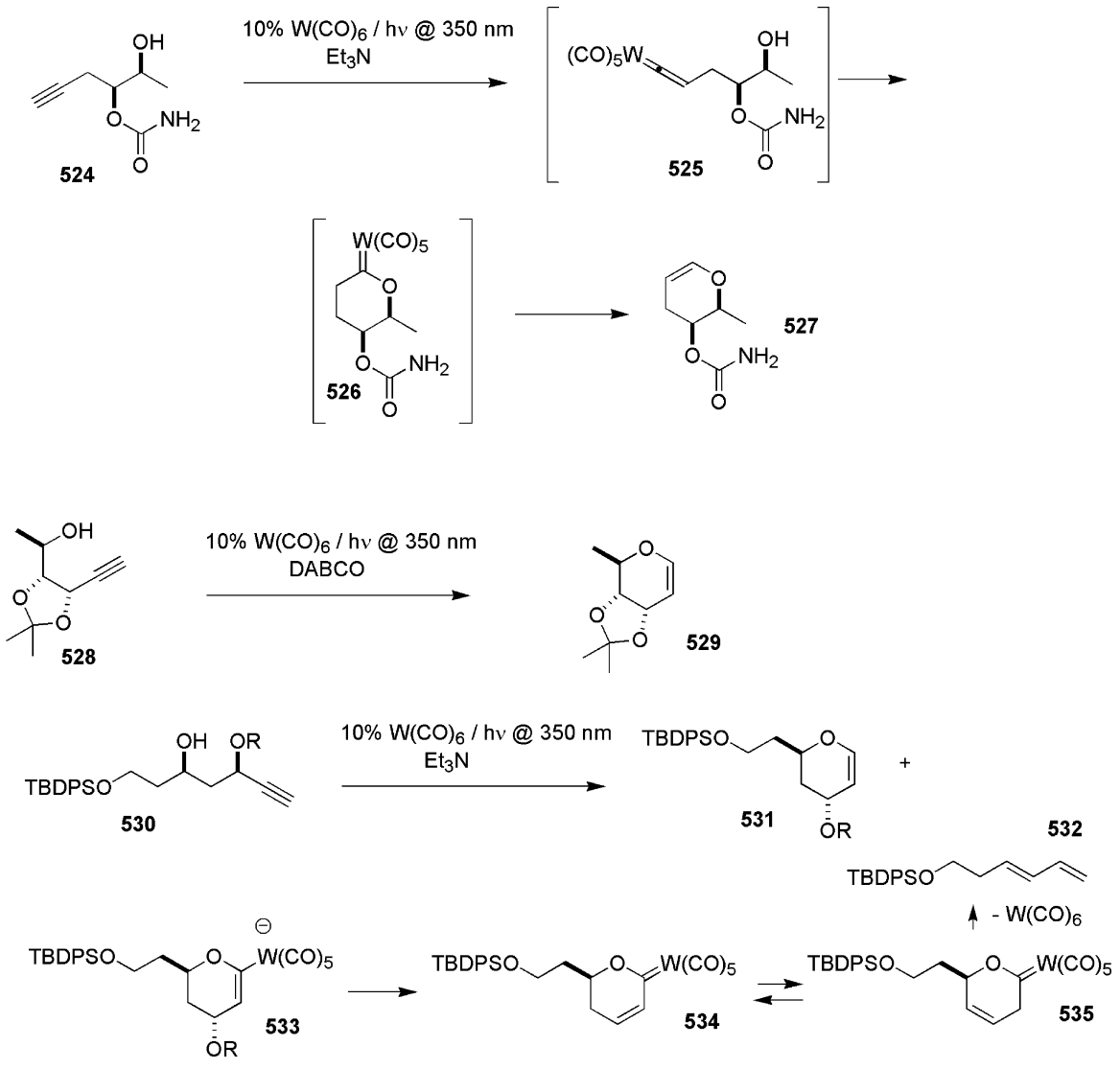
Scheme 47.

alkyl shift, reductive elimination, and ortho ester hydrolysis. Additional reaction pathways were observed in some cases. Formation of cyclic anhydrides (*e.g.* **596**) through the addition of ketene acetals to Fischer carbene complex **594** in the presence of base was reported [701]. A mechanism involving nucleophilic addition of the *in situ*-generated carboxylate dianion to form tetrahedral intermediate **597**, followed by CO insertion and displacement of ethoxide to afford the ketene complex, followed by cyclization and protonation was proposed.

Synthesis of uracil-like carbene complexes (*e.g.* **602**, **603**, Scheme 55) was reported [702]. Addition of urea derivatives (*e.g.* **601**) to alkynylcarbene complexes (*e.g.* **600**) affords the uracil complexes through nucleophilic addition to the carbene carbon and alkynyl carbons. Tetrakis(carbene complexes) (*e.g.* **605**) were also prepared. Reaction of the monouracil-alkynylcarbene complex **602** with ethylenediamine led to the complex **605**.

A net [6 + 3]-cycloaddition process (Scheme 56) was observed in the coupling of α,β-unsaturated chromium carbene complexes (*e.g.* **606**) with aminofulvenes (*e.g.* **607**) [703]. In this reaction, a mechanism involving nucleophilic attack of the 2-carbon of the fulvene at the carbene to afford zwitterionic compound **610**, followed by simultaneous 1,2-shift of chromium and nucleophilic attack at the exocyclic carbon of the delocalized cation to form iminium salt **611**, followed by proton transfer was proposed.

New diastereoselective five- and seven-membered ring forming cycloaddition reactions that utilize the coupling of alkenylcarbene complexes (*e.g.* **462**, Scheme 57) and enolates (*e.g.* **612**, **616**, **619**) was reported [704]. The ultimate course of the reaction was highly dependent on the structure of the enolate. All of the products form via initial nucleophilic addition of the enolate to the carbene carbon to form a tetrahedral intermediate (**613**, **617**, **620**). Formation of five-membered rings (*e.g.* **615**) occurs through addition of a second mole of the enolate to the ketone to provide a pentanoyl–tungsten complex (**614**), which affords the five-membered ring through addition of the carbanion-like chromium-containing carbon to the carbonyl group. Formation of seven-membered rings (*e.g.* **618**) occurs through a similar series of steps, however the final ring forming step occurs with allylic rearrangement. An additional type of seven-membered ring (*e.g.* **621**) forms from coupling of an alkenylcarbene complex and a conjugated enolate (*e.g.* **619**). In this case the tetrahedral intermediate (**620**) undergoes intramolecular Michael addition with allylic rearrangement. A novel ring expansive cycloaddition of benzocyclobutenols (*e.g.* **622**) and alkynylcarbene complexes (*e.g.* **623**) resulting in seven-membered rings (*e.g.* **624**, **625**) was reported [705]. A mechanism involving opening to the anionic *o*-quinonedimethane **626**, followed by nucleophilic addition to the carbene complex to afford aldehydealkynyl–tungsten complex **627**, followed by 1,2-shift of tungsten and attack at the aldehyde was proposed. The cyclized intermediate **628** either undergoes a hydride shift to produce **624** or attack of the alkoxide at the oxonium ion to afford **625**.



Scheme 48.

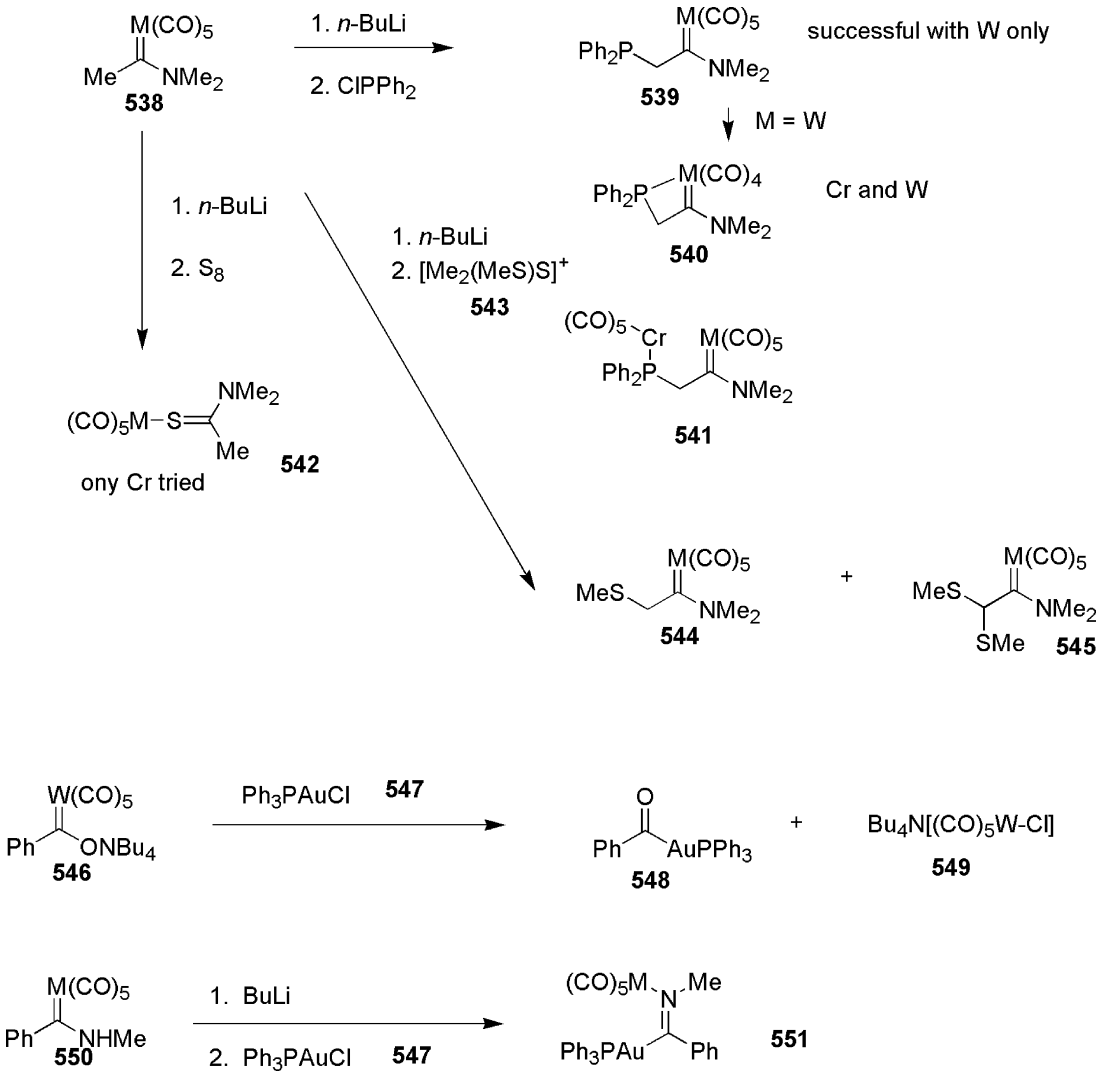
A new synthetic route to alkynylcarbene complexes (*e.g.* **633**, Scheme 58) was reported [706]. Reaction of carbene complexes (*e.g.* **629**) with alkoxyacetylide anions (*e.g.* **630**) afforded alkynyl alkoxycarbene complexes (*e.g.* **633**) through a mechanism involving nucleophilic addition to the carbene carbon, followed by loss of methoxide and 1,3-rearrangement.

The reaction of tungsten–carbene complex **480** (Scheme 59) with enamines (*e.g.* **476**) was reported [707]. Coupling affords the acyl(allyl)tungsten chelate complex **634**. A mechanism involving addition to the carbene carbon to afford zwitterionic intermediate **635**, followed by attack of the anionic tungsten at the resulting iminium salt to afford metallacyclobutane **636**, followed by CO insertion and conversion to the π-allyl complex was proposed. A similar reaction process was reported for vinylidene complex **475**, which affords the analogous complex accompanied by the η^2-diene complex **639**. Hydrogen transfer and reductive elimination from the 1,2-addition product **638** led to the diene complex.

Mass spectral detection of Fischer carbene complex cyanide ion adducts was reported [708]. Predominant fragmentation of carbohydrate-substituted carbene complexes was through retro-aldol processes.

1.1.3.3.12. Reactions that involve transfer of a Fischer carbene ligand to another metal. The reaction of tungsten–carbene complexes with various palladium salts was reported (Scheme 60) [709]. Reaction of the aminocarbene complex **645** with palladium complex **646** led to dimeric palladium carbene complex **647**. Extended time at room temperature led to the conversion of this complex to the iminium salt **650**. Conversion to monomeric complexes (*e.g.* **648**, **649**) upon treatment with ligand additive was also observed. Analogous reaction of alkoxy arylcarbene (**577**) or alkenylcarbene complexes (**462**) led to π-allyl complexes (**651**, **652**). Reaction with the methylcarbene complex **552** led to the enol ether **653**. All of the reactions involving alkoxycarbene complexes were proposed to arise through palladium–carbene complex (*e.g.* **654**).

The coupling of alkenylcarbene complexes (*e.g.* **655**, Scheme 61) with alkynes in the presence of $Ni(COD)_2$ was reported [710]. This reaction afforded chromium complexed cycloheptatriene derivatives (*e.g.* **657**) with a high degree of

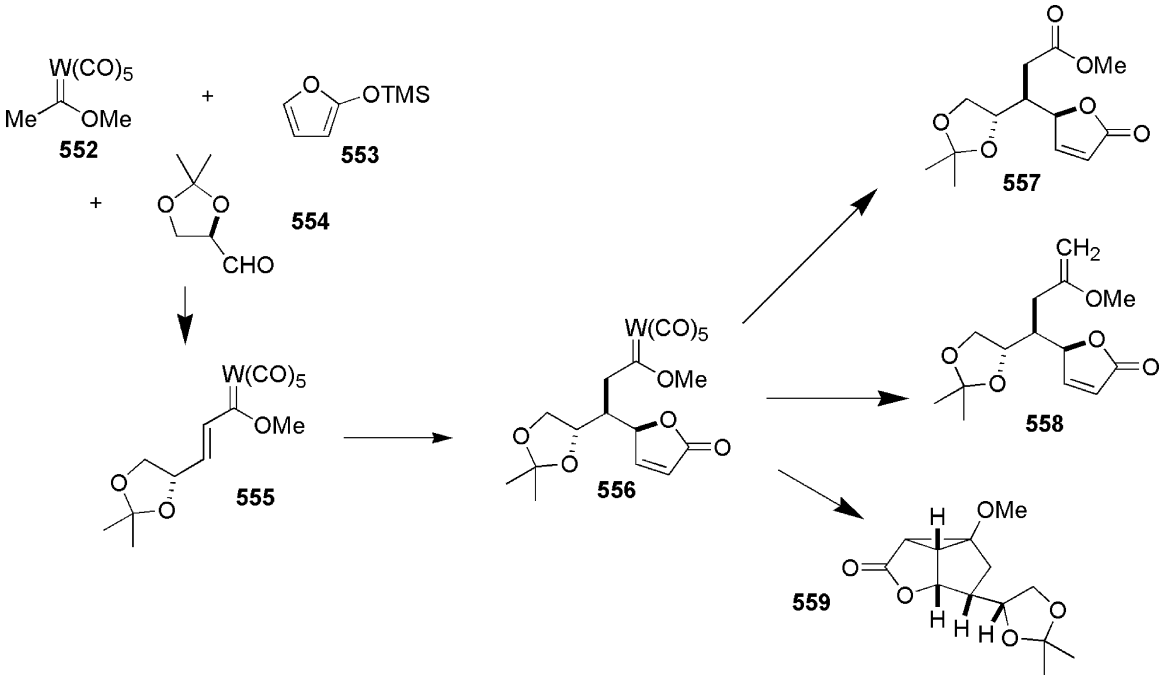


Scheme 49.

diastereoselectivity. A mechanism involving transmetallation of the carbene ligand to nickel to form a nickel carbene complex (*e.g.* **656**) followed by double alkyne insertion and cyclization was proposed. The coupling of alkenylcarbene–chromium complexes (*e.g.* **658**) with allenes (*e.g.* **659**) in the presence of rhodium catalysts (*e.g.* **660**) was reported [711]. The reaction affords indenones that result from incorporation of two moles of allene (*e.g.* **665**). A mechanism involving transfer of the carbene ligand to rhodium to afford rhodium carbene complex **661**, followed by [2 + 2]-cycloaddition, followed by insertion of another allene, oxidative addition into the ortho C–H bond, CO insertion and reductive elimination was proposed.

1.1.3.3.13. Other reactions of Group 6 metal–carbene complexes. The reaction of cyclopropylcarbene complexes (*e.g.* **666**, Scheme 62) with halogens and pseudohalogens was reported [712]. The reaction affords ring opened diiodides (*e.g.* **668**) with a high degree of stereoselectivity for the alkene isomer depicted. A mechanism involving activation of the carbene complex (formation of **667**) followed by nucleophilic attack of iodide at the cyclopropane carbon and ring opening was proposed. Cyclopropyl thiocarbene complexes that feature carbocation stabilizing groups were difficult to prepare due to ring opening of the acetoxy carbene complex intermediate. For example, attempted formation of a thiocarbene complex from acylate salt **669** resulted in ring-opened product **670**.

Photoinduced reactions of phosphine-chelated aminocarbene complexes (*e.g.* **671**, Scheme 63) were reported [713]. The reaction affords either the imine-coordinated compound **672** or the carbene excision product **673**, depending on the substitution at nitrogen. Various mechanistic pathways were evaluated computationally. A free radical mechanism was determined to be the most energetically reasonable reaction pathway. The imine complexes arise through rearrangement of the initially-generated diradical **674** to the free carbene **675** followed by β N–H insertion. The carbene excision product arises through cleavage of the C–N bond to form diradical **676** followed by reduction of the diradical to form intermediate **677** which then loses the carbene ligand to afford **673**. Numerous other carbene complexes that do not engage in photochemical ketene generation were also examined.



Scheme 50.

Electrospray ionization mass spectrometry (negative ions) was reported for Fischer carbene complexes [714]. Ionization of various alkenylcarbene and alkynylcarbene complexes occurs only in the presence of hydroquinone or tetrathiafulvalene additives. Ionization was proposed to occur through electron transfer from hydroquinone radical anions to the carbene complex. The observed fragmentation pathways were verified/supported through deuterium labeling studies and DFT calculations.

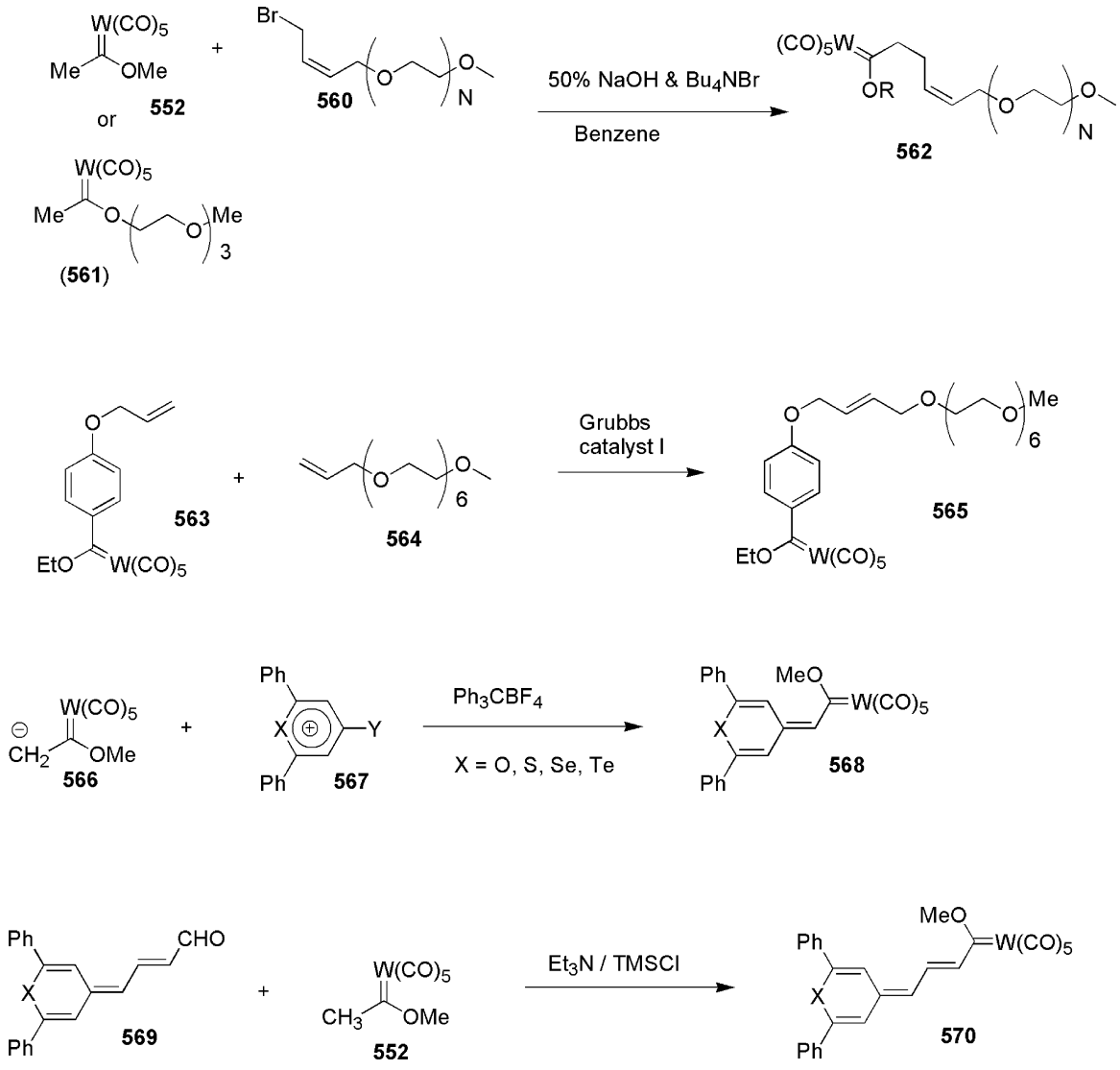
Gas-phase formation of carbene complexes in the reaction of chromium atoms with fluoroacetone was reported (Scheme 64) [715]. The species $[CrC_3H_4O]^+$ proposed to be an equilibrium mixture of species **678–680**. Various collision-induced dissociation reactions consistent with carbene complex contributor **680** were reported. Carbene complexes [H_2C=MoHF] and carbyne complexes [HC≡MoH_2F] were generated through laser ablation of molybdenum complexes in the presence of fluoromethane and observed by IR spectroscopy [716]. The structure of these complexes was evaluated computationally and compared with the IR spectrum.

Other experimental studies of Group 6 metal–carbene complexes are depicted in Scheme 65 and include: (1) formation of germacyclic Fischer carbene complexes (*e.g.* **682**) from the coupling of chromium hexacarbonyl with germacyclopropabenzenes (*e.g.* **681**) [717]; (2) comparison of the electrochemical properties of a variety of alkoxycarbene- and aminocarbene–chromium and tungsten–carbene complexes [718]; (3) generation of chromium nanoparticles through thermal decomposition of simple Fischer carbene complex **418** [$CH_3C(OCH_3)$=$Cr(CO)_5$] in the presence of trioctylphosphine [719]; (4) a proposal that tungsten–carbene complexes (*e.g.* **684**) are intermediates in the dimerization of norbornene catalyzed by ditungsten complex **683** [720]; (5) formation of N-heterocyclic carbene–tungsten complexes (*e.g.* **687**) through treatment of azidoisocyanide–tungsten complexes (*e.g.* **686**) with triphenylphosphine [721]; (6) examination of the electrochemistry of aminocarbene–chromium complexes [722]; (7) contribution of the carbene resonance form to various molybdenum isocyanide complexes [723].

1.1.3.4. Group 7 metal–carbene complexes. The synthesis of a variety of manganese and rhenium Fischer carbene complexes (*e.g.* **691**, Scheme 66) was reported [724]. The bimetallic complex **691** was successfully obtained through the Fischer synthesis using the dimetal decacarbonyl as the starting material. Treatment with iodine or bromine led to the monometallic complexes (*e.g.* **692**) through cleavage of the metal–metal bond. Aminolysis reactions were demonstrated for the bimetallic carbene complexes.

The synthesis and reactivity of alkynylcarbene–manganese complexes (*e.g.* **695**, Scheme 67) with phosphine derivatives was reported [725]. Treatment of the Fischer carbene complex **693** with BCl_3 afforded the carbyne complex (**694**), which was transformed to the alkynylcarbene complex (**695**) by reaction with alkynyllithium reagents. Reaction of alkynylcarbene complex **695** with triphenylphosphine led to the nucleophilic addition product, allenylmanganese complex **696**. Reaction of the alkynylcarbene complex with trimethylphosphine led to observable 1,2-addition product **697** in hexane, which transformed to the allenyl complex **698** and subsequently the phosphacyclopentene complex **699** at room temperature in dichloromethane. Reaction with diphenylphosphine led to the allene complex **700** and the regioisomeric ketene complexes **701** and **702**.

Cationic rhenium carbene complexes (*e.g.* **706**, **707**, Scheme 68) were formed in the reaction of cationic η^2-benzene–rhenium complexes (*e.g.* **703**) with 2-methoxyfuran [726]. The carbene complex was a fluxional complex consisting



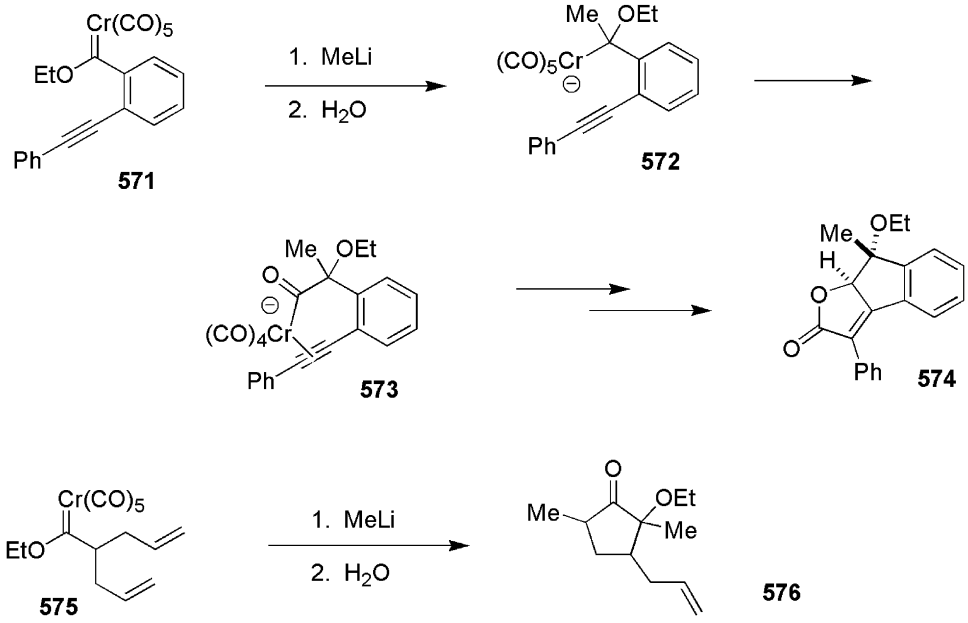
Scheme 51.

of an equilibrating cis/trans mixture. A mechanism involving ligand substitution followed by furan ring opening was proposed. In the same manuscript, η^2-alkenylrhenium complexes (*e.g.* **710**) were suggested as intermediates in the formation of acetylcyclopentene–rhenium complexes (*e.g.* **711**) from η^2-furanrhenium complexes (*e.g.* **708**) and α,β-unsaturated carbonyl compounds in the presence of Lewis acids. Similar complexes were proposed as intermediates in the stereoisomerization of the product acetylcyclopentenerhenium complexes.

Rhenium carbene complexes (*e.g.* **718**, Scheme 69) were suggested as intermediates in a novel rheniumcatalyzed cycloisomerization of dienynes (*e.g.* **712**) [727]. Reaction of dienyne **712** with $ReCl(CO)_5$ led to a diastereomeric mixture of cycloisomerization products (**714**, **715**). A mechanism involving alkyne complexation, followed by nucleophilic addition of the enol ether to the alkyne complex, followed by intramolecular nucleophilic addition to afford rhenium carbene complex **718** was proposed. The carbene complex then undergoes a reduction to afford the products. A mechanistically related but nonreductive cycloisomerization occurs using tungsten pentacarbonyl sources.

Reaction of manganafurans (*e.g.* **719/720**, Scheme 70) with alkynes was reported [728]. Mixtures of the pyrilium complexes (*e.g.* **721**) and cycloheptadienyl complexes (*e.g.* **722**) were obtained. The proposed mechanism for formation of complex **722** involves alkyne insertion to form dienylmanganese complex **723** followed by formation of a cyclopropane (**724**) and ring opening. This mechanism was supported through deuterium labeling studies. Alkyne insertion reactions involving aromatic fused analogs were also reported [729].

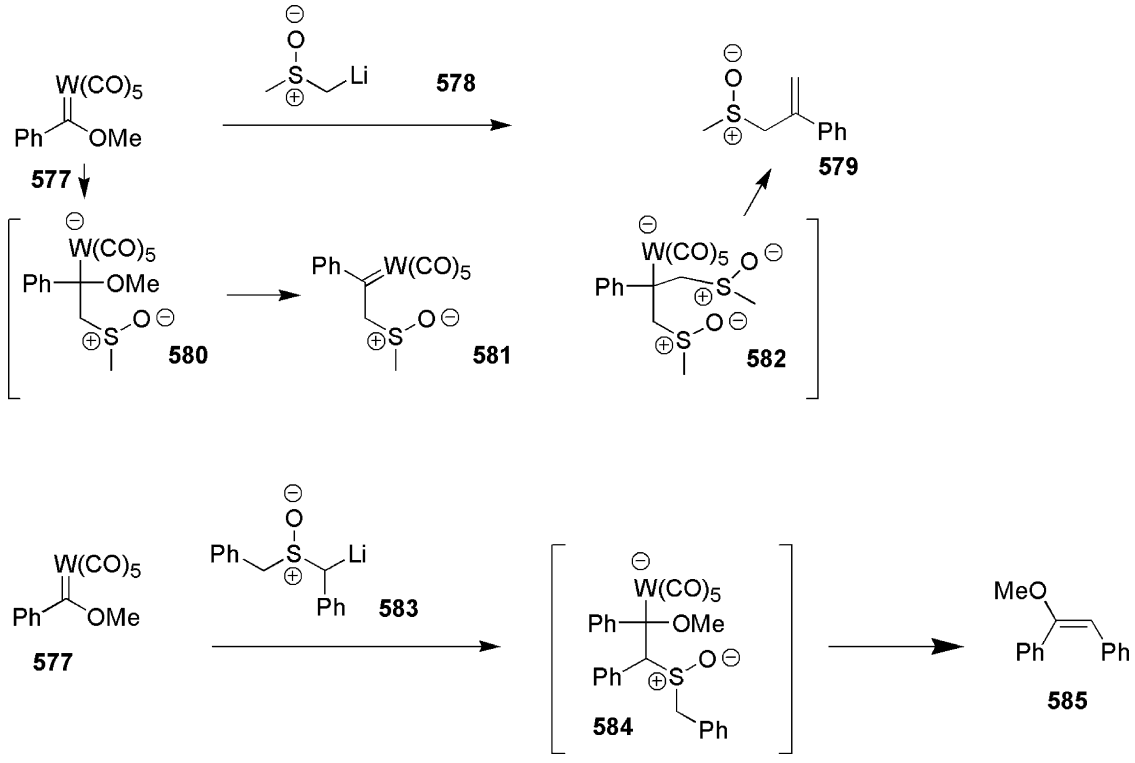
Additional studies of Group 7 metal–carbene complexes that are not cumulenes are depicted in Scheme 71. These studies include: (1) formation of rhenium carbene complex **726** from the coupling of rhenium complex **725** with dimethyl acetylenedicarboxylate [730]; (2) formation of manganese N-heterocyclic carbene complexes through addition of propargylamines to manganese isocyanide complexes followed by intramolecular triple bond hydroamination [731]; (3) a proposal that rhenium carbene



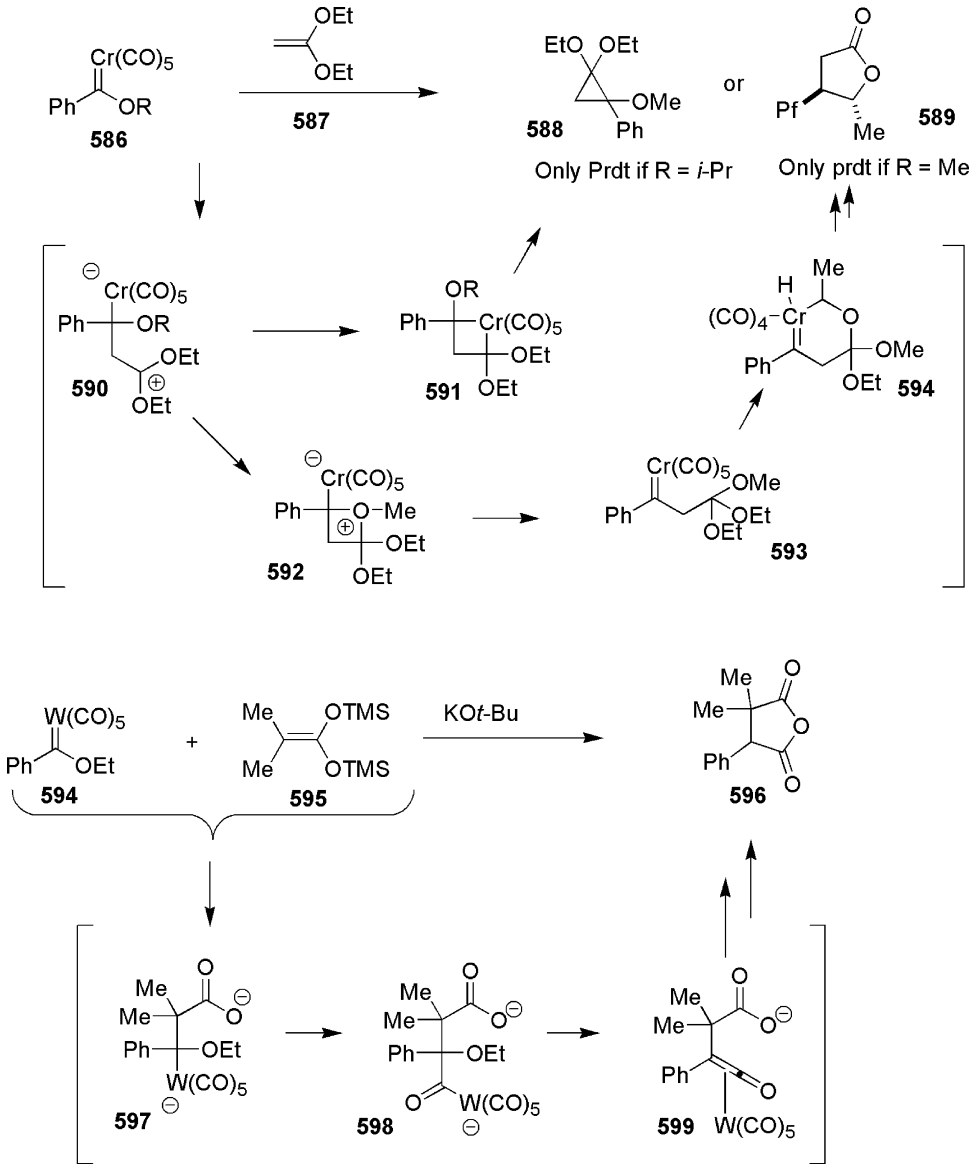
Scheme 52.

complexes are intermediates in base-catalyzed H/D exchange reactions of $MeReO_3$ [732].

Several examples of Group 7 metal–cumulene complexes were reported in 2005 (see Scheme 72). See Scheme 87 for the general reactivity profile of metal vinylidene complexes. Reaction of manganese complex **727** with alkynylstannanes (*e.g.* **728**) and DMPE was reported [733]. Reaction initially afforded the stannylvinylidene complex (**729**), which was converted to the simple vinylidene complex (**730**) upon treatment with fluoride ion. Reaction with two equivalents of ferrocenium ion led to the dimerization product, bis(carbyne) complex **731**, which could be transformed back to the vinylidene complex **730** upon treatment with cobaltocene. When only one equivalent of oxidant was employed, a mixture of carbyne complex **733** and dimeric complex **735** was obtained. A mechanism involving oxidation of complex **730** to radical cation **732**, followed by hydrogen



Scheme 53.



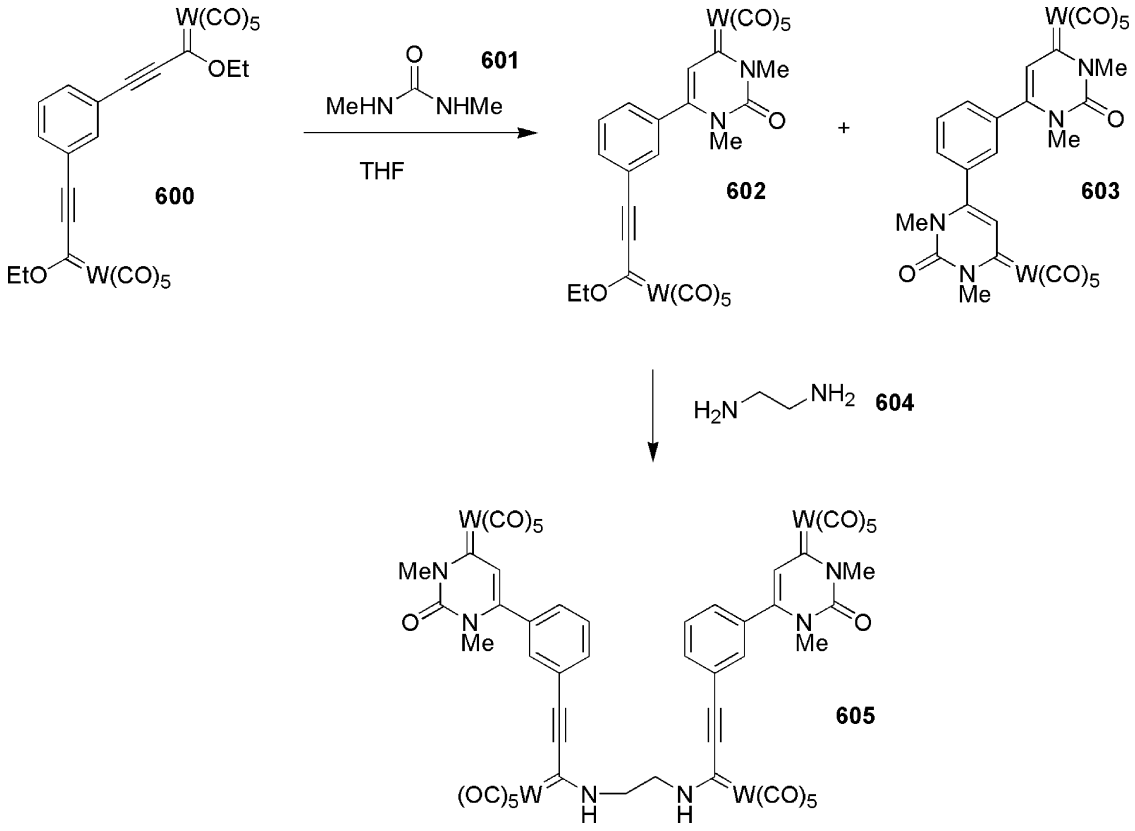
Scheme 54.

abstraction from **730** to generate cationic carbyne complex **733** and alkynyl complex **734** was proposed. Complex **733** dimerizes to bis(carbyne complex) **731**, while alkyne complex **734** dimerizes to bis(carbyne complex) **735**. Related conversion of cycloheptatrienylmanganese complex to bis(metalvinylidene) complex from bis(stannylalkynes) was also reported [734]. Manganese–vinylidene complexes were also generated through protonation of anionic bis(alkynyl)manganese complexes [735]. Coupling of rhenium triflate complex **736** with bis(propargyl alcohol) derivatives (*e.g.* **737**) to form mono- (*e.g.* **738**) and bis(allenylidene-ruthenium) complexes (*e.g.* **739**) was reported [736]. Electrochemical studies were reported for the binuclear complexes. The charge on the one-electron reduction product was found to be delocalized over both rhenium atoms. A manganese vinylidene complex (**741**) was proposed as an intermediate in the conversion of alkynylmanganese complex **740** to complex **742** [737]. Carboranyl–rhenium vinylidene complexes were proposed as intermediates in the coupling of terminal alkynes in the coordination sphere of rhenium [738].

Reaction pathways for oxarhenacyclobutanes (*e.g.* **743**, Scheme 73) were studied computationally [739]. The studies were related to rhenium catalyzed dihydroxylation and whether the initial addition to ethylene proceeds via [2 + 2]-cycloaddition or [3 + 2]-cycloaddition. Pathways involving fragmentation to a carbene complex (**744**) and formaldehyde or fragmentation to a rhenium oxo (**745**) complex and ethylene were evaluated. The reaction pathway involving carbene complex formation was energetically more favorable but kinetically less favorable. More highly substituted analogs were also examined [740].

1.1.3.5. Group 8 metal–carbene complexes.

1.1.3.5.1. Cationic metal–carbene complexes that are not cumulenes. Formation and reactivity of bridging carbyne diiron complexes (*e.g.* **751**, Scheme 74) was reported [741]. Treatment of the bridging carbene complex **750** with acid led to

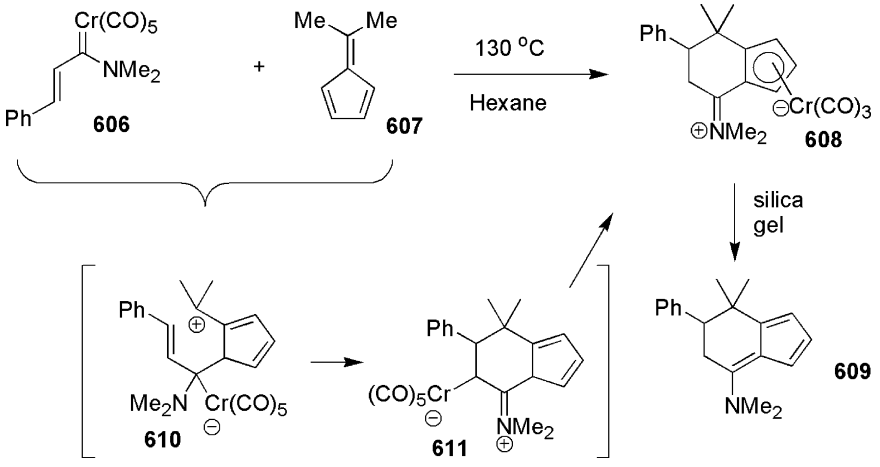


Scheme 55.

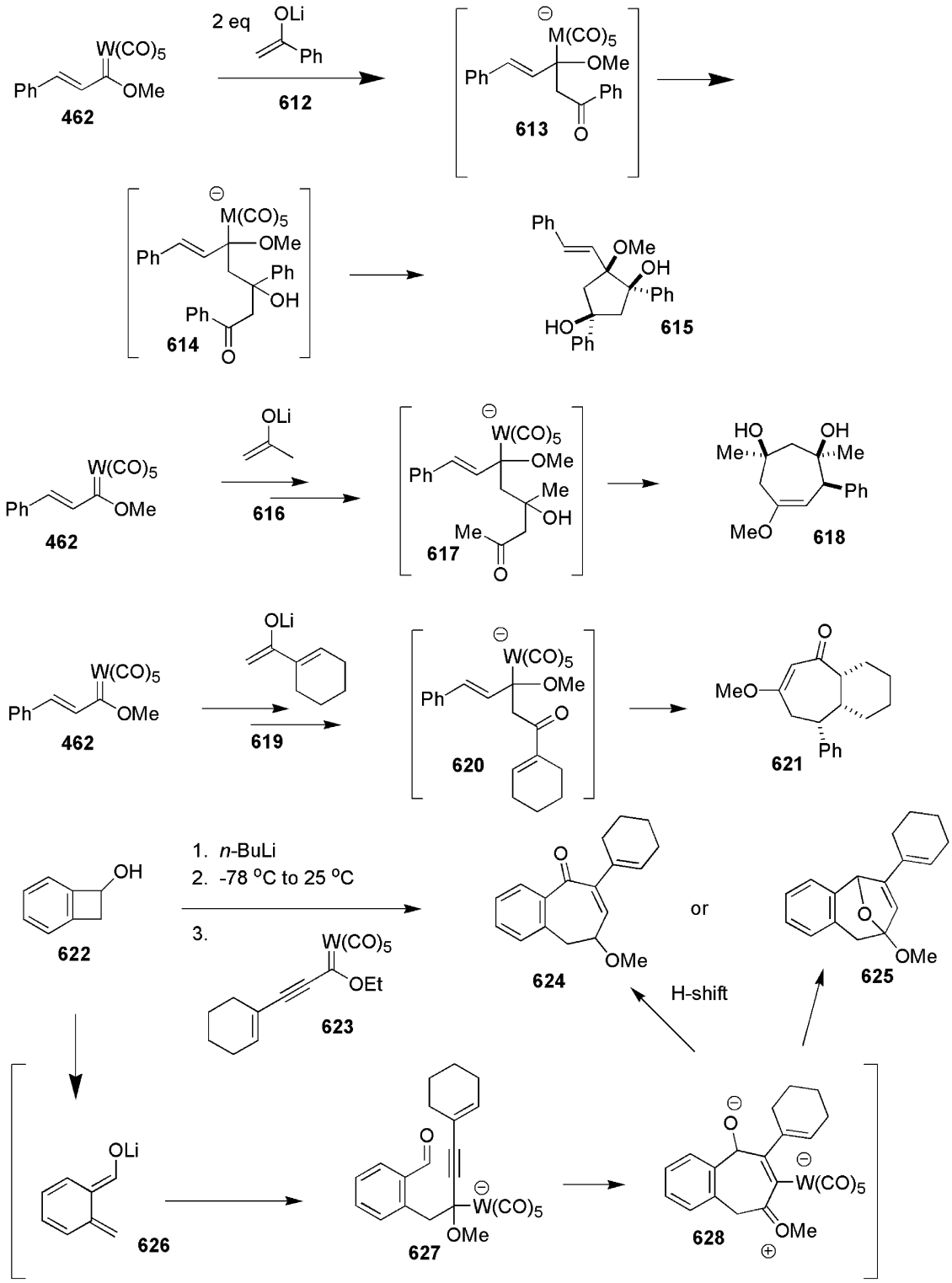
the cationic bridging carbene complex **751**. Reaction of **751** with a variety of nucleophiles led to the bridging carbene complexes (*e.g.* **752–755**). In most cases simple substitution products were obtained. Reaction with the anionic chromium complex **756** led to the trimetallic complex **754**. Reaction with methanethiolate led to the substitution product **755** and the ligand substitution product **757**.

Formation of cationic alkenylcarbene–ruthenium complexes (*e.g.* **759**, Scheme 75) through protonation/dehydration of γ-hydroxy-alkenylruthenium complexes (*e.g.* **758**) was reported [742]. A homochiral iron–carbene complex (**763/764**), generated *in situ* from a homochiral siloxyiron complex **762**, afforded chiral cyclopropanes **765** with a high degree of diastereoselectivity [743]. The conformational properties of the iron carbene complex were studied by low temperature NMR and NOESY spectra. The observed stereoselectivity was attributed to backside attack on the anti isomer of the carbene complex, which is the minor species at equilibrium.

Formation of cationic osmafuran derivatives (*e.g.* **768**, Scheme 76) through hydrogen transfer from complex **766** to enone **767** was reported [744]. Subsequent deprotonation afforded the neutral metallafuran **770**. A less substituted com-



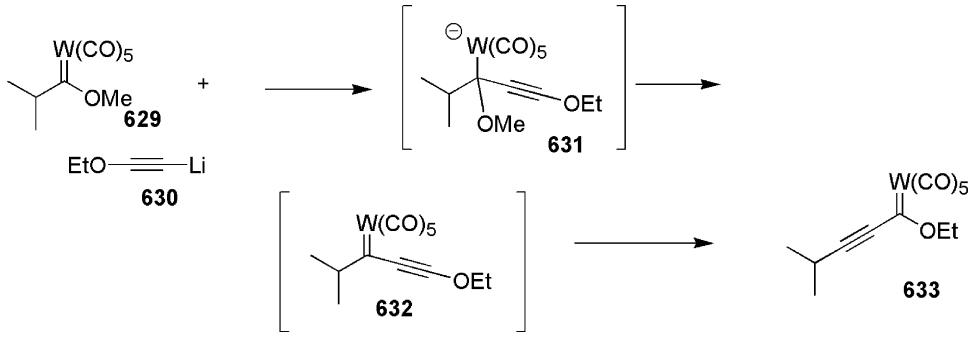
Scheme 56.



Scheme 57.

plex (**771**) afforded an equilibrium mixture (5:1 in favor of metallafuran) of neutral metallafuran **772** and hydridovinylidene complex **773** upon deprotonation.

Additional studies of cationic Group 8 carbene complexes are depicted in Scheme 77 and include: (1) formation of bis(carbene)ruthenium complexes through electrochemical oxidation of alkene-linked diruthenium complexes [745]; (2) a proposal that ruthenium carbene complexes (*e.g.* **775**) are intermediates in the reaction of cationic pincer-ruthenium complexes (*e.g.* **774**) with phenyldiazomethane (or terminal alkynes) to afford bridging carbene–ruthenium complexes (*e.g.* **776** [746]); (3) a proposal that ruthenium carbene complexes are interme-

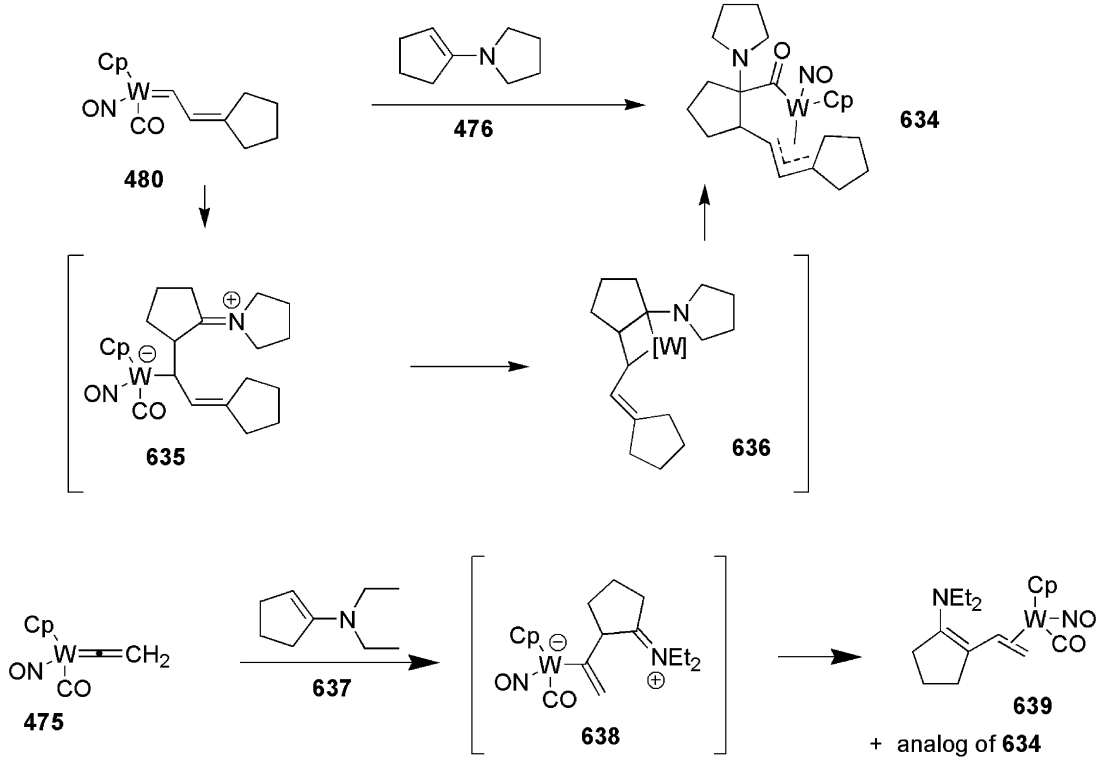


Scheme 58.

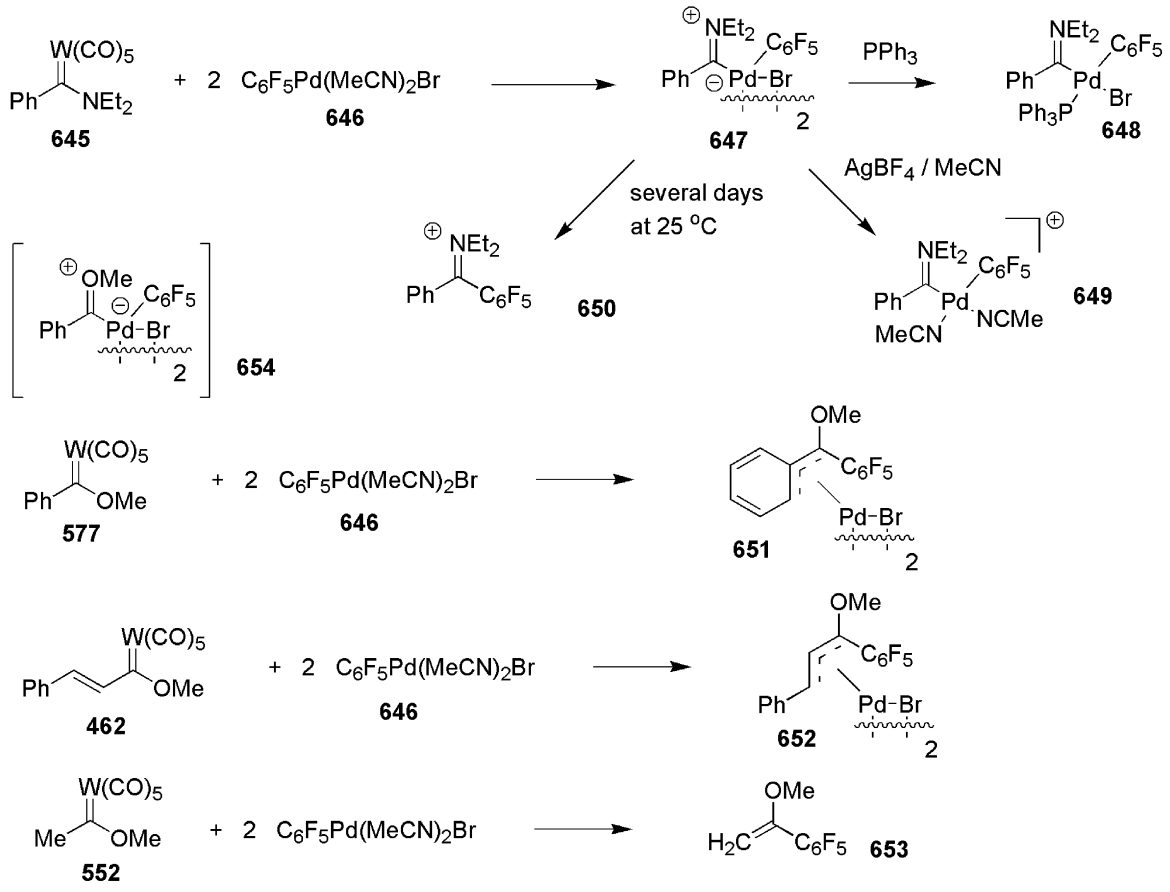
diates in the disproportionation of cationic ruthenium formyl complexes to the corresponding methoxymethyl-ruthenium and carbonyl-ruthenium complexes [747]; (4) discussion of carbene complexes as major contributing resonance form to dicationic ruthenium 4-pyridyl complexes [748].

1.1.3.5.2. Bis(carbene)ruthenium complexes from coupling of two alkynes and a ruthenium complex. The reaction of cationic ruthenium complex **777** (Scheme 78) with bis(alkynes) (*e.g.* **778**) was reported [749]. The complex **781**, which results from breakage of the phosphorus–nitrogen bond, was initially obtained. Thermolysis of this complex led to the tautomerization product **782**. A mechanism involving formation of the bis(carbene) complex (**779**) followed by nucleophilic addition of nitrogen to the carbene ligand was proposed, resulting in intermediate carbene complex **780**. Nucleophilic addition of nitrogen to the carbene carbon followed by breakage of the P–N bond leads to observable complex **781**. Similar reactions were also reported for Cp^* complexes [750].

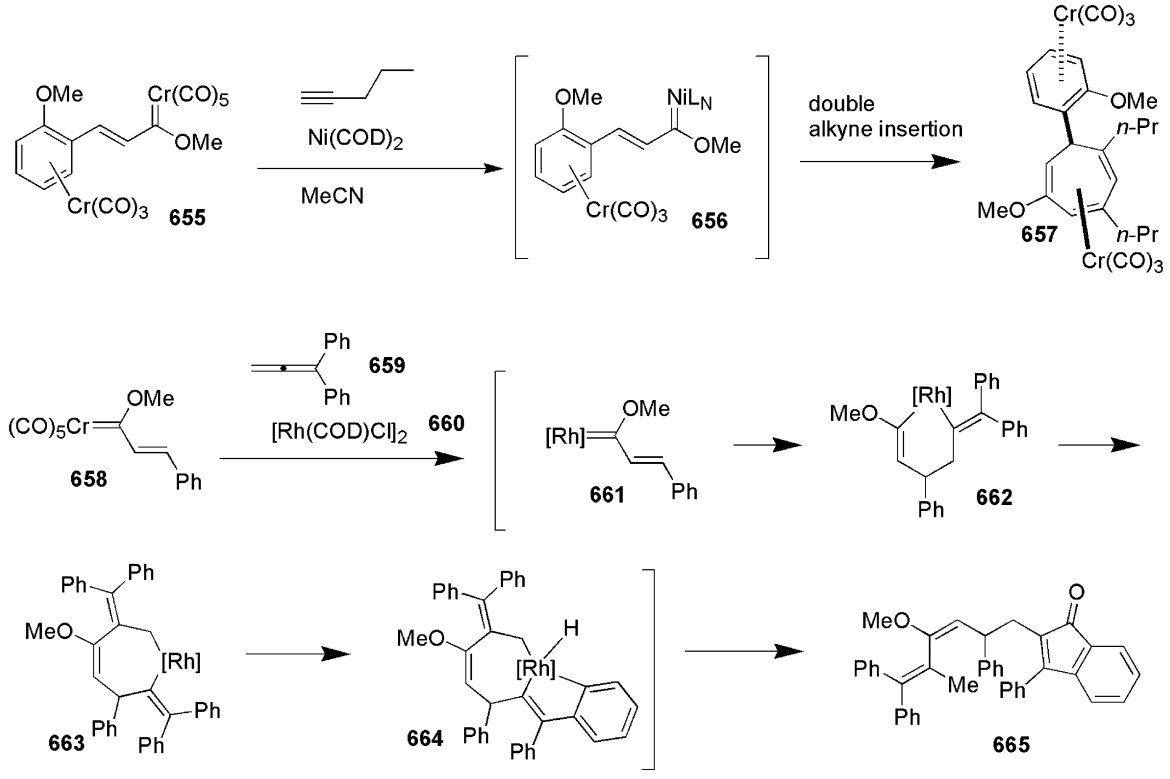
Several variants of ruthenium catalyzed alkyne trimerization, which has been shown to proceed through intermediate bis(carbene) ruthenium complexes, were reported in 2005. Representative examples are depicted in Scheme 79. Coupling of dialkynes (*e.g.* **783**) with nitriles or heterocumulenes in the presence of ruthenium complex **784** was reported [751]. Regiochemistry was attributed to steric influences in the ruthenacyclobutane intermediate derived from addition of the third π-component to the less substituted carbene group of intermediate bis(carbene) complex **785**. Three component coupling of an alkynylborane (*e.g.* **788**), a propargyl alcohol (*e.g.* **789**), and a third alkyne (*e.g.* **790**) was reported [752,753]. The reaction proceeds by *in situ* generation of a dialkyne, followed by formation of a cyclic bis(carbene) complex (**791**)



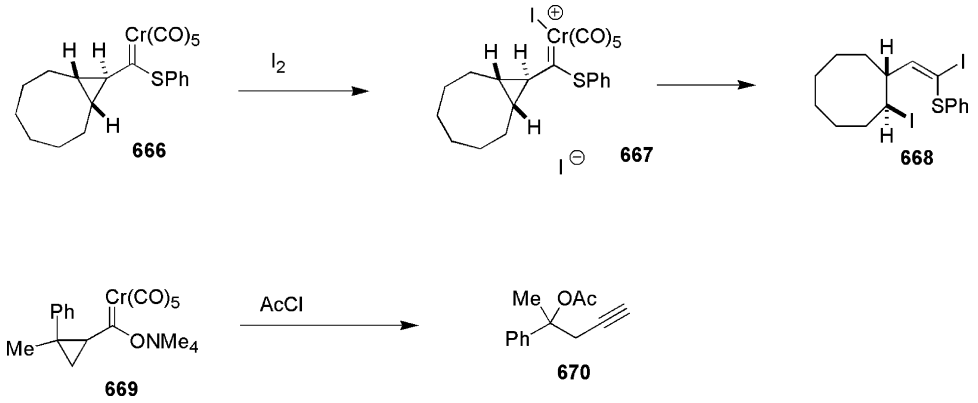
Scheme 59.



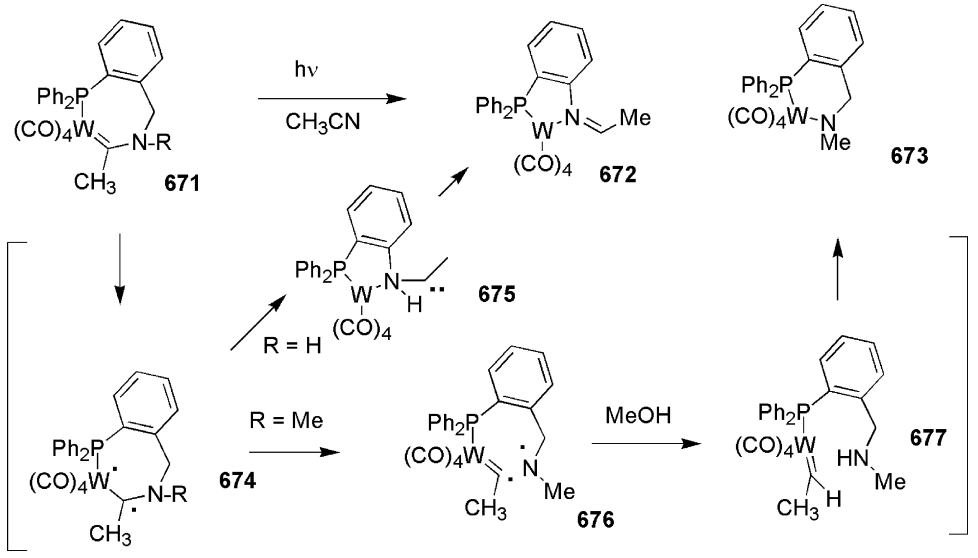
Scheme 60.



Scheme 61.



Scheme 62.

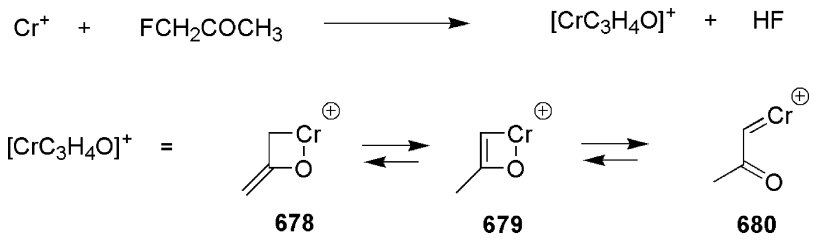


Scheme 63.

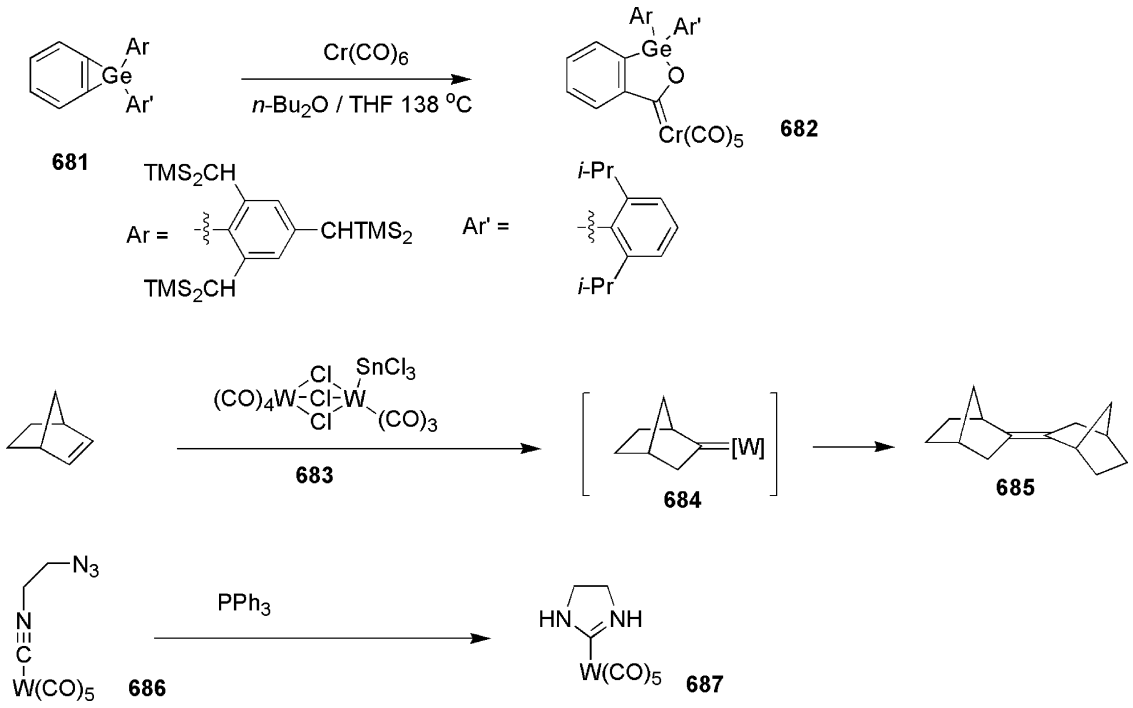
and subsequent reaction with the third alkyne to generate an aromatic ring. A related coupling of bis(alkynes) with alkynylboranes was also reported [754]. Related alkyne trimerizations were also reported [755]. A variant of this reaction occurs in the ruthenium-catalyzed cycloisomerization of bis(alkyne) compound derivatives (*e.g.* **793**) leading to cyclized dienylketone/aldehyde derivatives (*e.g.* **797**) [756]. A related hydrative cycloisomerization was also reported for bis(propargylic) sulfone derivatives [757]. Ruthenium bis(carbene) complexes were proposed as intermediates in [2 + 2]-cycloaddition reactions of propargyl alcohols in acetic acid [758].

1.1.3.5.3. 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.

Ruthenium–carbene complexes (*e.g.* **801**, **804**, Scheme 80) were prepared from the coupling of indenylruthenium complex **800** with diazo compounds [759]. Reaction of these complexes with various organolithium and Grignard reagents was examined. Reaction with methyllithium led to the alkene(hydride)ruthenium complexes (*e.g.* **803**, **805**). Reaction



Scheme 64.



Scheme 65.

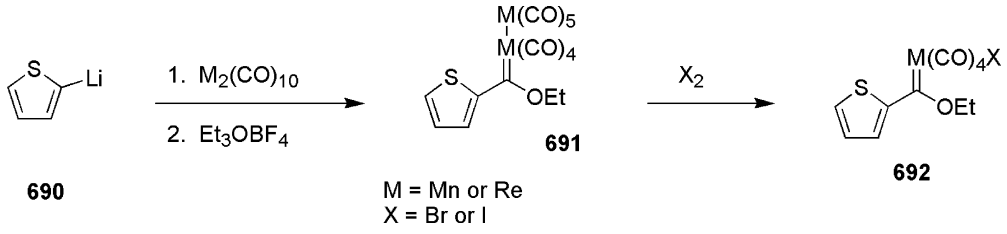
of vinylic and arylmetal reagents led to π-allyl complexes (*e.g.* **802**, **806**). Oxygen-bridged osmium carbene–OEP complexes (OEP = octaethylporphyrin) were obtained from the coupling of (OEP)OsCO with diphenyldiazomethane [760]. Osmium carbene complexes were identified in the FAB Mass Spectrum of osmium porphyrin-catalyzed cyclopropanation reactions [761]. The decomposition of ethyl diazoacetate by ruthenium imine-chelate, well-known cyclopropanation catalysts, was monitored by NMR and IR spectroscopy [762].

Ruthenium carbene complexes featuring a pincer ligand (*e.g.* **808**, Scheme 81) were prepared by deprotonation of cationic ruthenium complexes featuring chelating phosphine sulfide ligands (*e.g.* **807**) [763]. The coupling of related carbene complexes **809** with isocyanides was reported [764]. The reaction leads to the ketimine complexes (*e.g.* **810**).

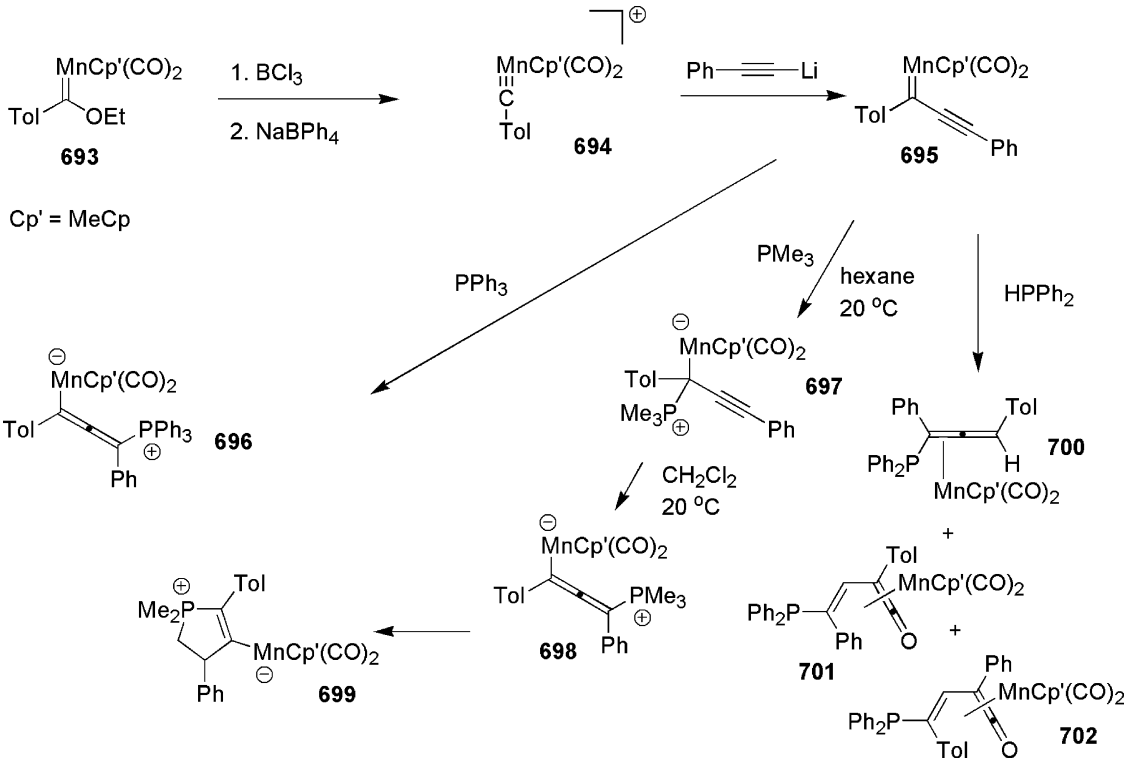
Chelated ruthenium carbene complex **813** (Scheme 82) was prepared by treatment of complex **811** with methyllithium [765]. A mechanism involving formation of unstable but observable methylruthenium complex **812** followed by intramolecular C–H activation, methane reductive elimination, and α-hydride elimination was proposed. CO insertion and pyridine C–H activation reactions were reported for this complex. Treatment of the unstable methylruthenium complex with benzonitrile led to a stable nitrile-coordinated complex **815**.

Ruthenium carbene complexes were proposed as intermediates in the conversion of enynes (*e.g.* **817**, Scheme 83) and trimethylsilyldiazomethane (**818**) to bicyclic compounds (*e.g.* **821**) [766]. After initial formation of the ruthenium carbene complex from reaction of diazo compound with the catalyst, reaction at the alkyne to afford the vinylcarbene complex (**820**) occurs, which then undergoes intramolecular cyclopropanation to afford the eventual product.

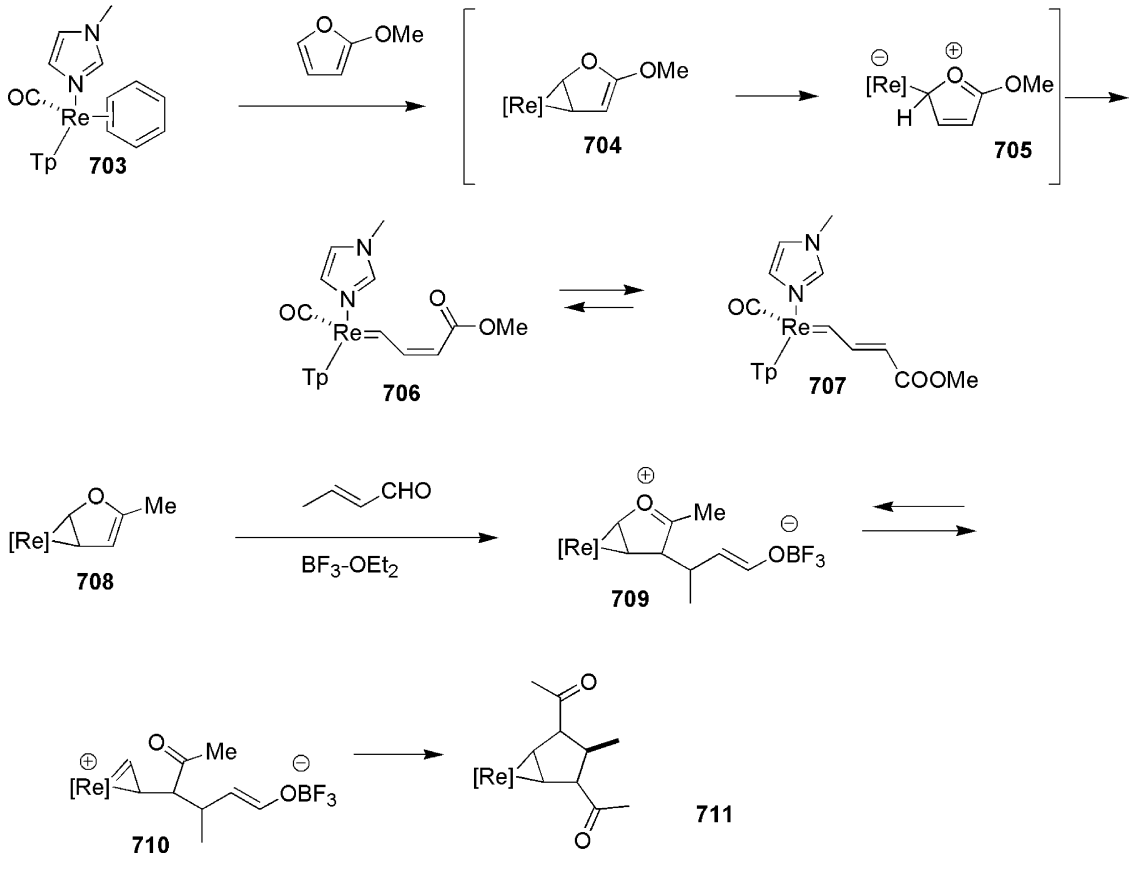
Other studies of carbene complexes in this category include: (1) attempted chelation of a phenylpyridine to a ruthenium carbene complex [767]; (2) formation of ruthenium isocyanide complexes that appear to be better represented as carbene complexes according to the X-ray structure [768]; (3) preparation of chelated β-osmaimine complexes that feature contribution from a osmapyrrole resonance structure [769]; (4) observation of a ruthenium carbene complex from ruthenium-catalyzed cyclopropanation reactions of diazo compounds and alkenes [770].



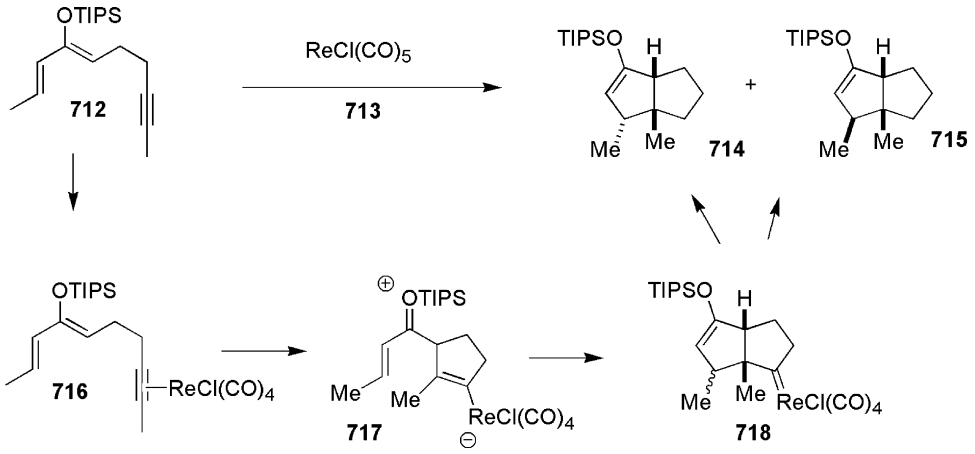
Scheme 66.



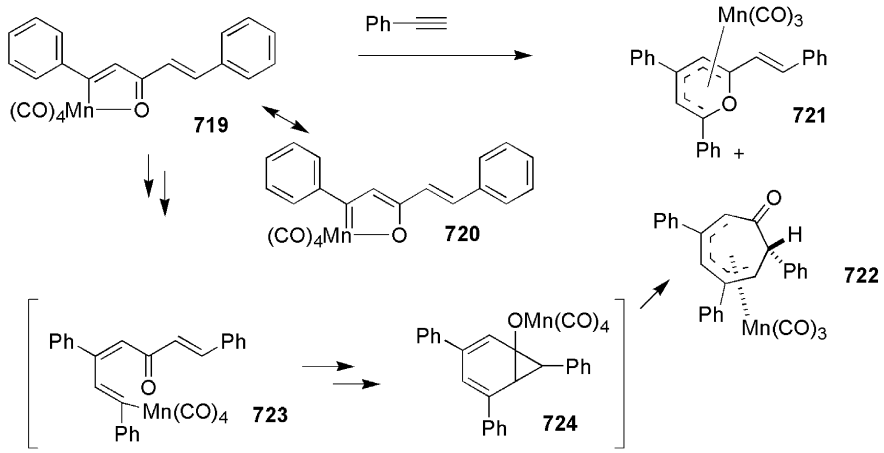
Scheme 67.



Scheme 68.



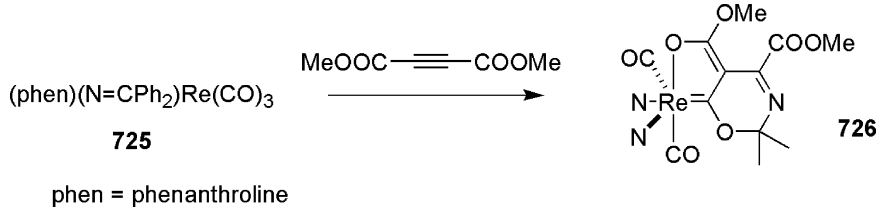
Scheme 69.



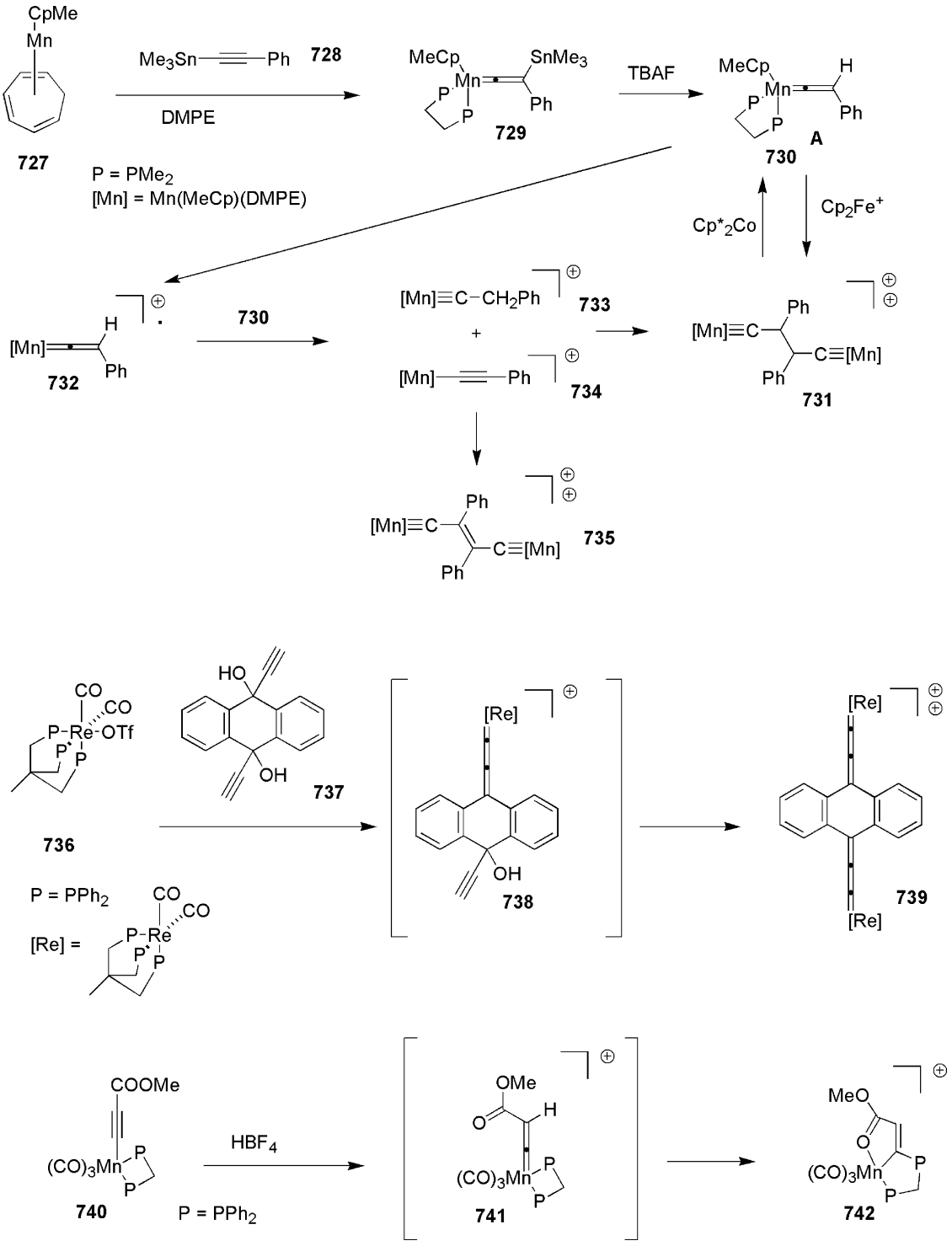
Scheme 70.

1.1.3.5.4. Heteroatom-substituted Group 8 metal–carbene complexes. New synthetic routes to Group 8 metal–carbene complexes featuring heteroatom stabilization are depicted in Scheme 84. Reaction of ruthenium complex **825** with base led to the aminocarbene–ruthenium complex **827** [771,772]. The reaction initially afforded hydride carbene complex **826**, which eventually isomerized to complex **827**. Carbene complex **827** is a fluxional molecule in equilibrium with the metallaaziridine structure **828**. The exchange process was supported by 2D NMR experiments. Treatment of **827**/**828** with PPh_2H led to the aminoalkylruthenium complex **829**. Formation of **829** was attributed to ring opening of the metallaaziridine structure **828**. Coupling of vinylphosphine-osmium complexes (*e.g.* **830**) with imines (*e.g.* **833**) or α,β-unsaturated carbonyl compounds (*e.g.* **831**) led to osmaheteroaromatic species (*e.g.* **832**, **834**) [773].

Several examples of the synthesis and reactivity of bridging carbyne–diiron complexes are depicted in Scheme 85. Ligand exchange reactions were reported for bridging aminocarbene–iron complexes (*e.g.* **835**) with various nitrogen-containing species [774,775]. Reaction with amines and various imines and pyridines led to the ligand exchange products (*e.g.* **837**, **840**). The amine complex **836** afforded the bridging hydride

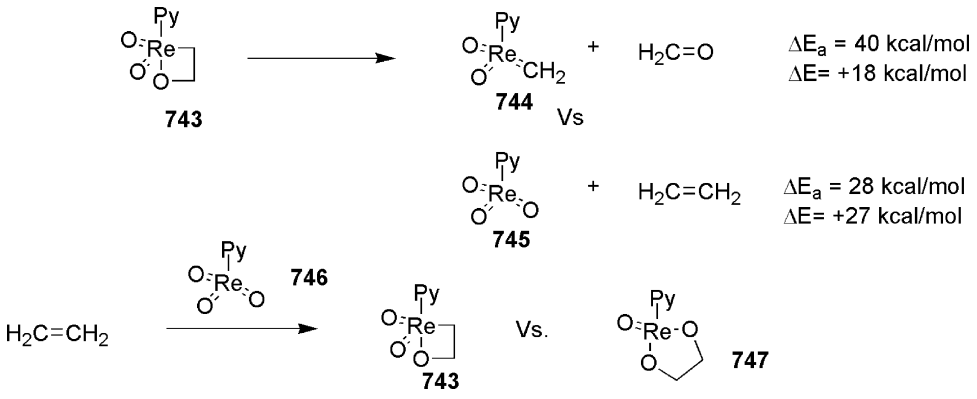


Scheme 71.



Scheme 72.

complex **837** upon treatment with sodium hydride. Reaction with NaNHEt led to the neutral carbamoyl complex **838**. Reaction of the imine complex **840** with an alkynyllithium led to the diaminocarbene complex **842**. A related process was reported for a benzonitrile ligated complex [776]. Bridging aminocarbyne complex **835** was transformed to the Fischer alkynylcarbene complex **843** using the Fischer synthesis [777]. Addition of carbon nucleophiles (cyanide and malonate-type anions were reported for the alkynylcarbene complexes [778]. Addition of cyanide resulted in a reversible diastereoselective addition to the carbene carbon. Stabilized carbanions afforded products from addition to the alkyne carbon (Michael addition). Binuclear carbene complexes (**845**, **846**) were obtained through reduction of bridging alkenylcarbene complexes **844** [779]. The course of the hydride addition was highly dependent on the steric bulk at nitrogen. A dimeric binuclear complex (**848**) was obtained

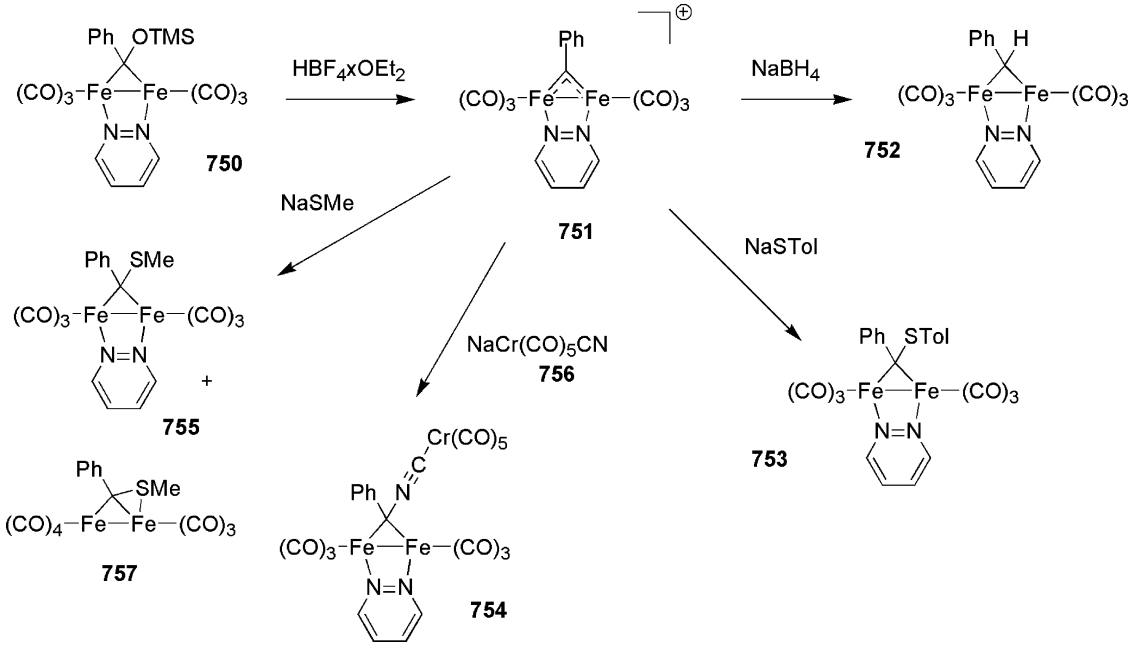


Scheme 73.

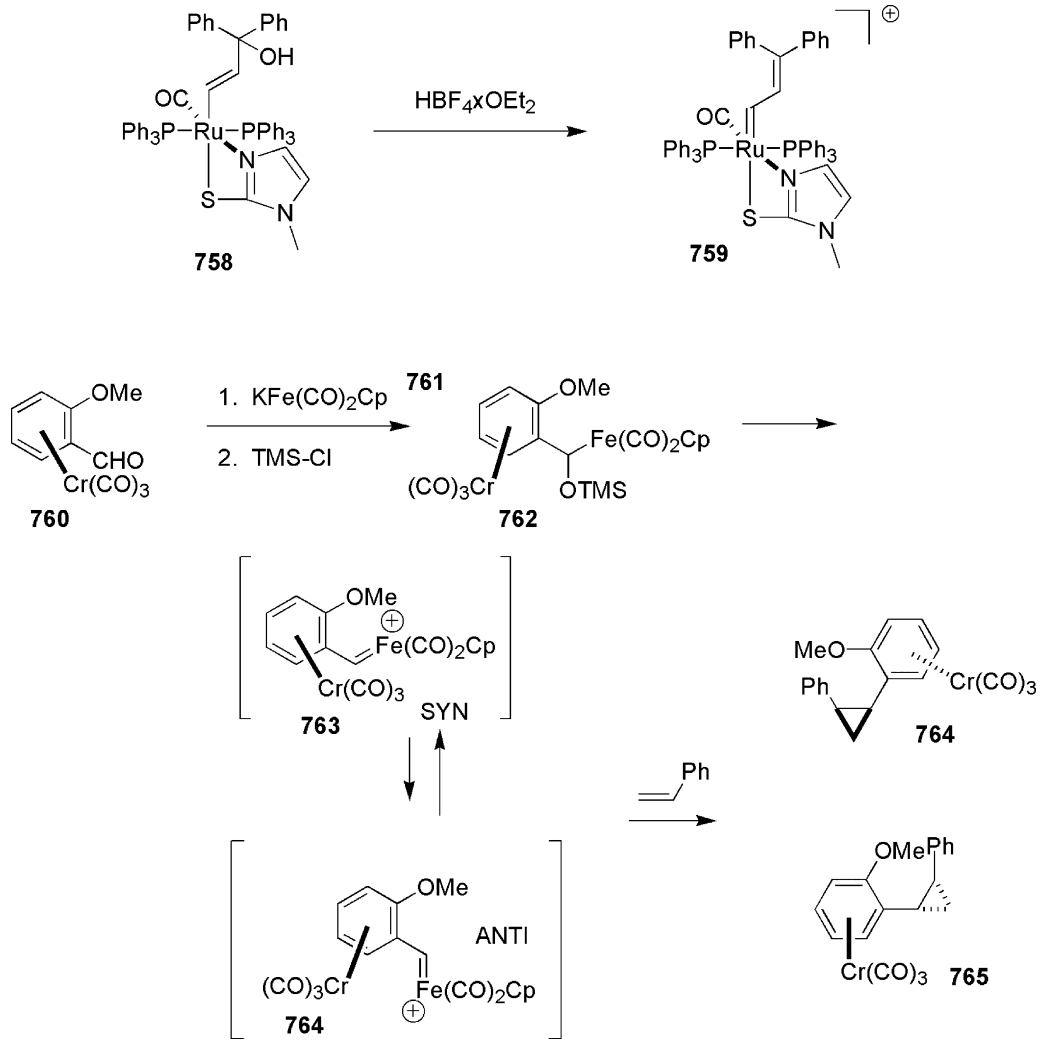
through reaction of complex **847** with sodium hydride [780]. Bridging carbyne-diiron complexes (*e.g.* **849**) were converted initially to the bridging aminocarbene–iron complexes (*e.g.* **851**) upon treatment with aniline derivatives (*e.g.* **850**) [781]. Rearrangement below room temperature led to the non-bridging carbene–diiron complexes (*e.g.* **852**). Subsequent thermolysis afforded a mixture of the iron complexes **853**–**855**. Thermal decomposition of related bridging iron–manganese bimetallic carbynes was also reported [782].

Additional examples of heteroatom-stabilized carbene complexes are depicted in Scheme 86. These include: (1) reaction of pincer carbene complexes (*e.g.* **856**) with alkynes was to form insertion/C–H activation products (*e.g.* **857**) [783]; (2) synthesis and C–H activation reactions for pincer carbene ruthenium complexes (*e.g.* **860**) and DFT studies of the mechanism [784]; (3) preparation of pincer carbene ruthenium complexes that are basic [785]; (4) determination of the thermodynamic and kinetic acidity of $[Cp^*(CO)_2Fe{=}C(OMe)Me]^+$ (pK_a 8.25 in 1:1 water:acetonitrile) [786].

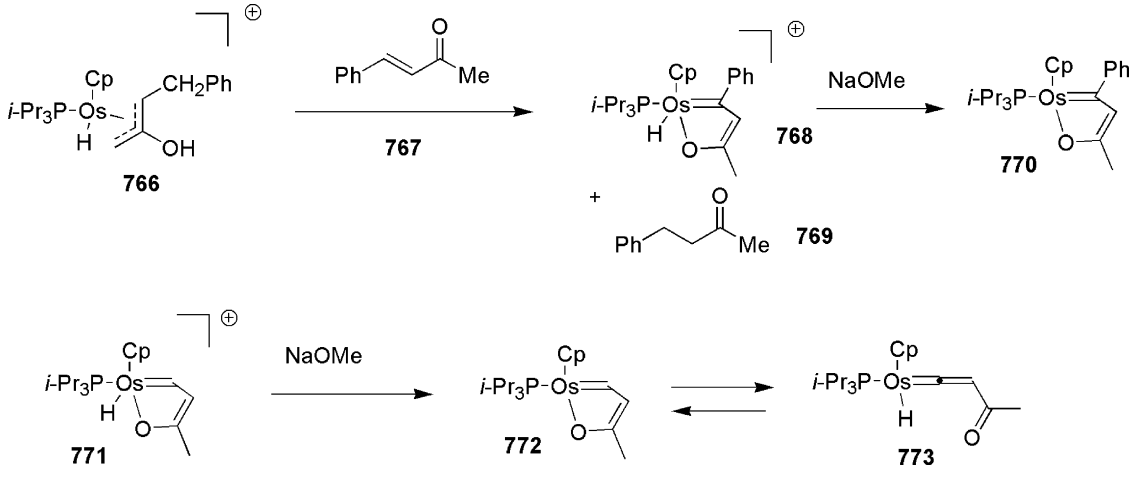
1.1.3.5.5. Group 8 metal–vinylidene complexes. Many examples of the formation of metal–vinylidene complexes (**865**, Scheme 87) via coupling of coordinatively unsaturated Group 8 metal complexes with terminal or silylated alkynes were reported in 2005. Representative examples are depicted in Fig. 12. Common reaction pathways for these complexes include reaction with nucleophiles to form vinylmetal species (**868**), reaction with alcohols (or amines) to form Fischer carbene complexes (**869**) or water to form metal acyls (**867**), and deprotonation at the β-position to form alkynylmetal complexes (**866**). Other common synthetic routes to metal vinylidenes included addition of electrophiles to metal acetylide complexes (*i.e.* the reverse of the reaction synthesizing **866**), and treatment of acylmetal complexes with dehydrating agents (*i.e.* the reverse of the reaction synthesizing **867**).



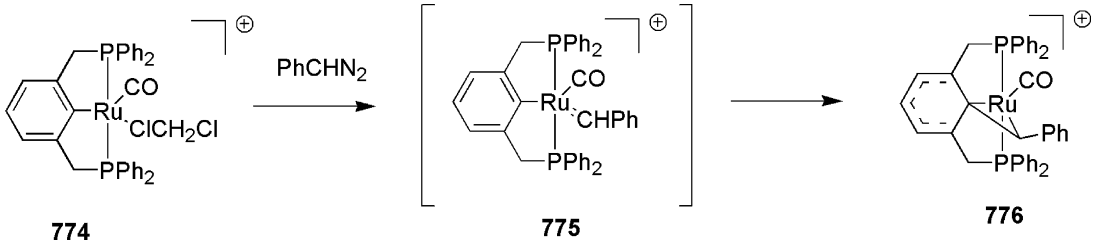
Scheme 74.



Scheme 75.



Scheme 76.



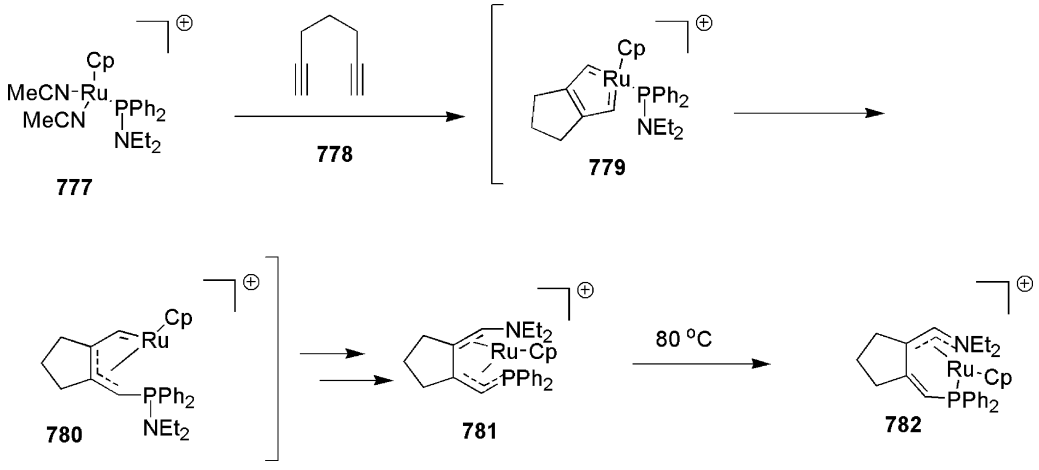
Scheme 77.

Specific reports which highlight the reaction pathways of Scheme 87 are depicted in Fig. 12 and include: (1) formation of cationic iron–vinylidene complexes and subsequent conversion to alkynyliron complexes [787]; (2) formation of ruthenium vinylidene complexes through reaction displacement of the dihydrogen ligand of $Ru(\eta^2\text{-}H_2)(Tp)(PPh_3)[P(OEt)_3]$ with terminal alkynes (and allenylidenes using propargyl alcohols) [788]; (3) formation of ruthenium vinylidene complexes (*e.g.* **870**) and subsequent conversion to the alkynyl complexes [789]; (4) formation of Cp-chelate vinylidene complex (**873**) from complex **872** and subsequent conversion to neutral alkynylruthenium complex [790]; (5) formation of Fischer carbene complex **875** from unstable vinylidene complex **874** and subsequent hydration to afford noncyclic Fischer carbene complex **876** [791]; (6) formation of osmium vinylidene complex **878** from reaction of alkenylphosphine complex **877** with terminal alkynes in the presence of triethylamine [792]; (7) formation of an alkynylvinylidene-linked bis(ruthenium) complex (**879**) [793]. Ruthenium vinylidene complex **881** was a catalyst for the *Z*-selective addition of trimethylsilylacetylene to arylacetylenes [794]. The formation and bonding properties of various ruthenium- and osmium-vinylidene complexes and analogs where one of the vinylidene carbons were replaced by other Group 14 elements were examined computationally [795]. Niobium- and tantalum vinylidene complexes were similarly examined. The conversion of H–Ru–C≡CX derivatives (X = H, Me, or SiH_3) derivatives to Ru=C=CHX complexes and the conversion of X–Ru–C≡CH derivatives to Ru=C=CHX complexes were studied computationally [796].

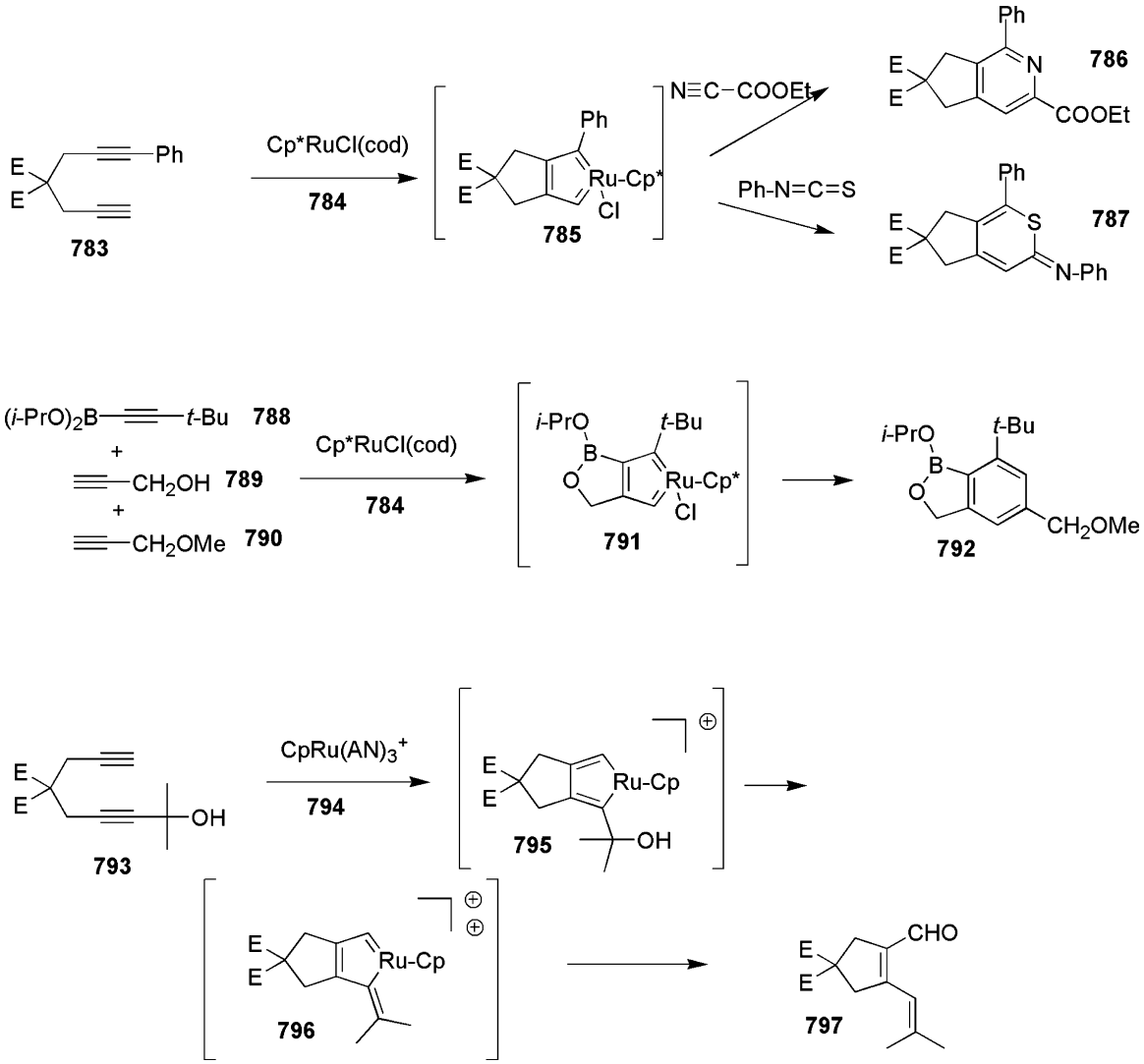
The formation of hydridoruthenium vinylidene complexes (*e.g.* **883**, Scheme 88) and subsequent conversion to simple carbene complexes (*e.g.* **884**) was reported [797]. Reaction of dihydrogen complex **882** with terminal alkynes led to the hydridovinylidene complex **883**. Protonation led to the carbene complex **884**. Simple carbene complexes **884** could also be prepared in one step by treatment of **882** with an alkyne in the presence of tricyclohexylphosphonium chloride. Several derivatives of **884** were prepared and tested in their ability to catalyze the RO-CM of cyclopentene with allyl alcohol.

Ruthenium vinylidene complexes and bis(vinylidene-ruthenium) complexes (*e.g.* **886**, Scheme 89) the contain DPPM ligands were prepared and their reactions with base examined [798]. The bis(vinylidene-ruthenium) complex **886** was prepared by oxidative dimerization of ethynylruthenium complex **885**. Reaction of bis(vinylidene-ruthenium) complex **886** with DBU resulted in conversion to the butadiyne-bridged bis(ruthenium) complex **887**. Reaction with KO*t*-Bu resulted in the bis(alkynylruthenium) complex **887** accompanied by the complexes **888** and **889**, which result from deprotonation of the DPPM ligand followed by addition of the carbanion to the carbene carbon. The electrochemistry of these complexes was also studied.

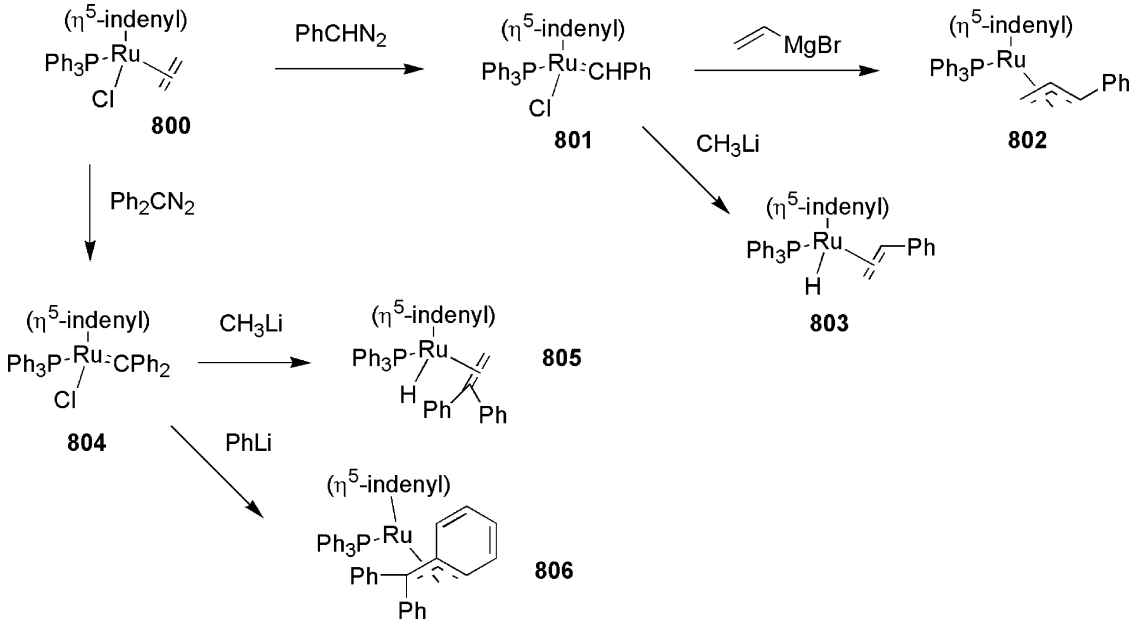
Ruthenium–vinylidene complexes were proposed as intermediates in numerous reaction processes that result in the



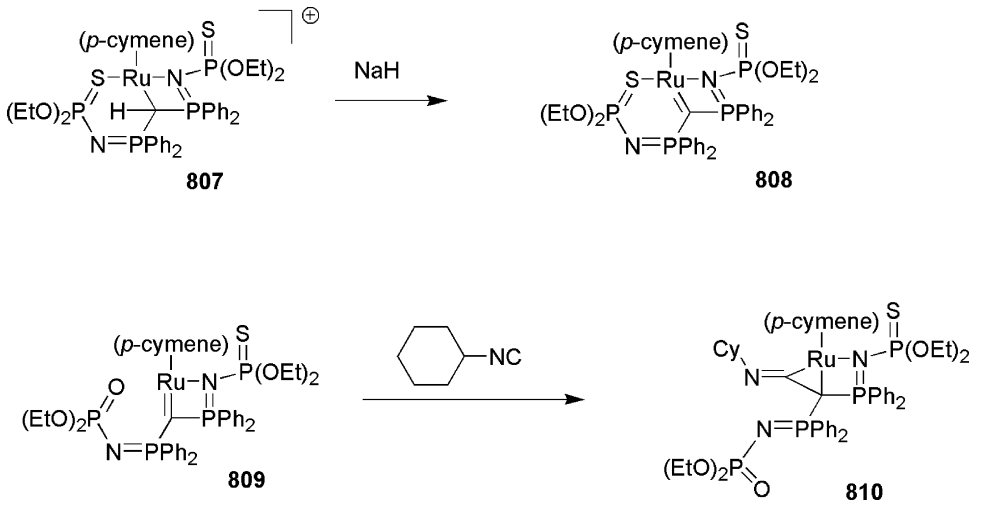
Scheme 78.



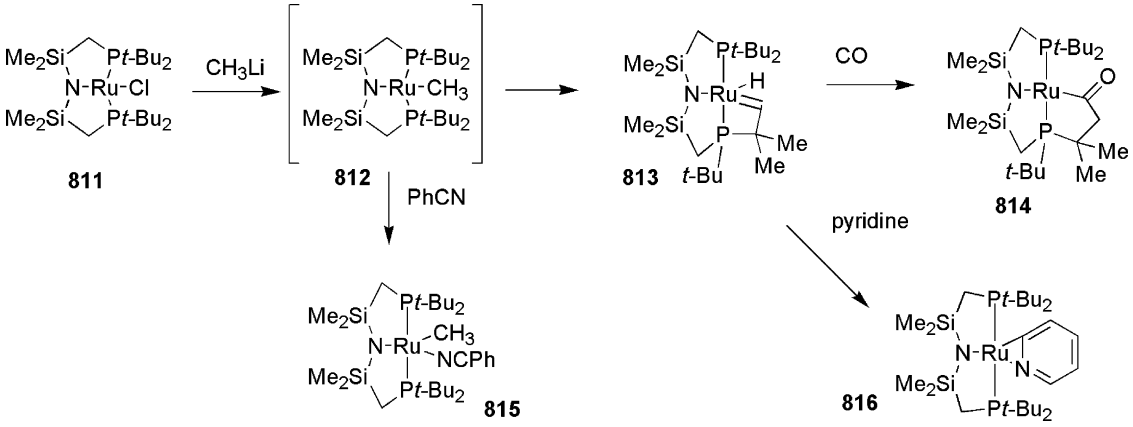
Scheme 79.



Scheme 80.

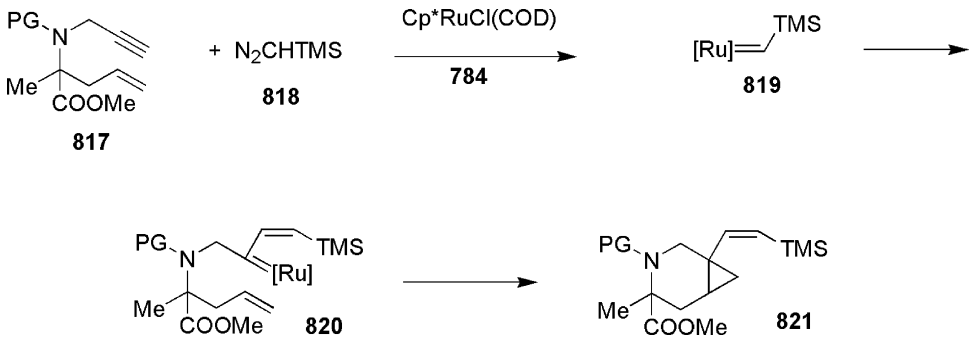


Scheme 81.

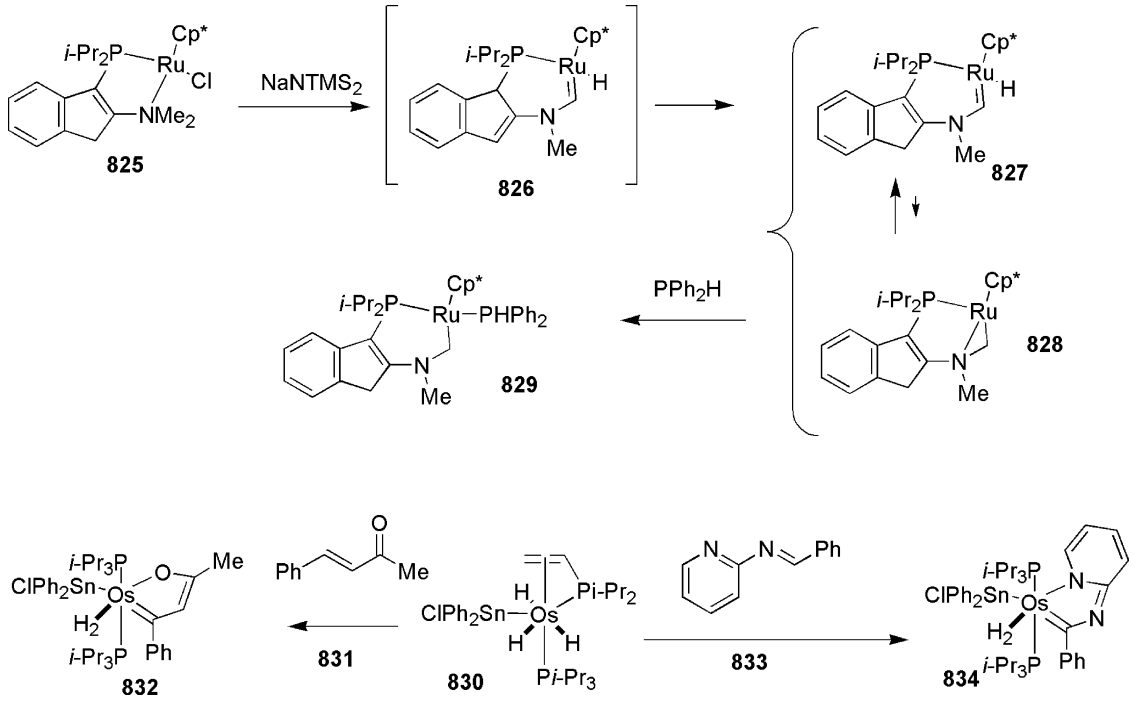


Scheme 82.

formation of carbocyclic compounds from conjugated alkynes; examples are depicted in Scheme 90. The ruthenium-catalyzed conversion of various arylvinylacetylenes and various alkynylbiphenyls (*e.g.* **890**) to polynuclear aromatic compounds (*e.g.* **893**) via cationic ruthenium vinylidene complexes (*e.g.* **892**) was reported [799]. Ruthenium vinylidene complexes (*e.g.* **895**) were proposed as intermediates in ruthenium-catalyzed cycloaromatization reactions where conjugated dienynes (*e.g.* **895**) are converted to highly rearranged annulated benzene derivatives (*e.g.* **900**) [800]. Ruthenium vinylidenes were proposed as intermediates in ruthenium-catalyzed conversion of 1,2-bis(alkynyl)benzene derivatives (*e.g.* **901**) to substituted naphthalenes (*e.g.* **904**, **905**) [801]. The reaction proceeds through formation of a vinylidene complex (**902**) which under-



Scheme 83.



Scheme 84.

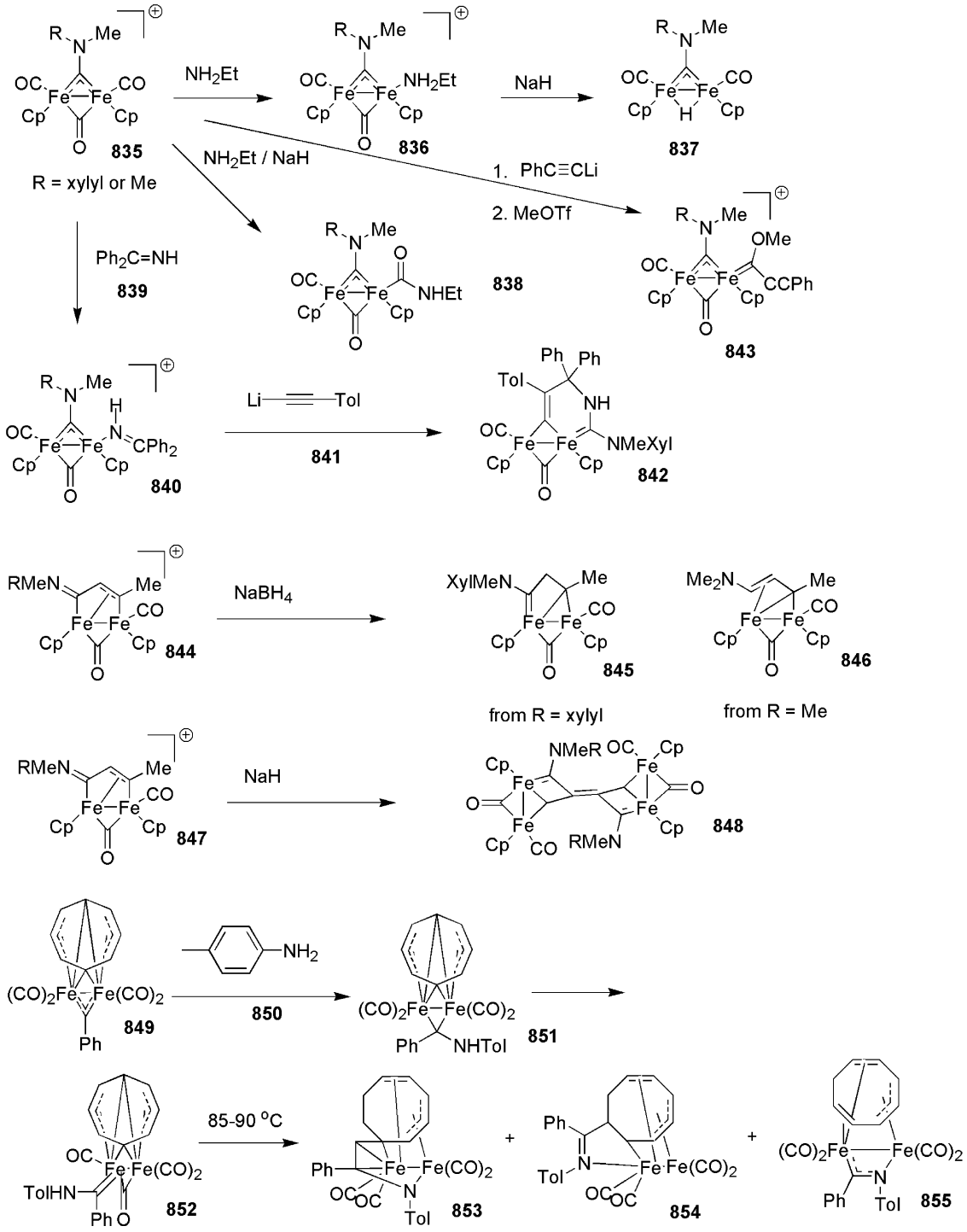
goes a metalla-Moore cyclization to afford a free carbene intermediate (**903**), which then affords carbene-derived products. A related process was employed for the conversion of iodoethynylphenyl epoxides (*e.g.* **906**) to naphthalenols (*e.g.* **907**) or benzoxepines (*e.g.* **908**) [802]. The course of the reaction was highly solvent dependent. The naphthalenes were derived from a vinylidene intermediate (*e.g.* **909**) pathway. The benzoxepines were formed through a π-alkyne complex (*e.g.* **913**). Related ruthenium vinylidene complexes were proposed as intermediates in the cyclization of propargyl alcohol derivatives or conjugated enyne derivatives into cyclopentene/cyclopentadiene derivatives catalyzed by complex **891** [803].

Ruthenium–vinylidene complexes (*e.g.* **918**, Scheme 91) were proposed as intermediates in rutheniumcatalyzed hydrative alkyne cyclization of alkyne-enones (*e.g.* **916**) [804]. A mechanism that involves formation of a vinylidene **918** followed by hydration to form the acylruthenium complex **919** followed by cyclization was proposed.

Osmium–vinylidene complexes (*e.g.* **923**, **924**, Scheme 92) were suggested as intermediates in the conversion of alkynylosmium complex **921** to the dihydronaphthalene complex **922** upon treatment with acid [805]. A mechanism involving protonation to afford the vinylidene (**923**), followed by oxidative addition into the vinylic C–H bond to form the hydridovinylidene complex (**924**), followed by hydrogen migration, C–H oxidative addition into the arene C–H bond, alkene insertion, reductive elimination, and complexation was proposed.

1.1.3.5.6. Group 8 metal complexes of higher cumulenes. Metal-higher cumulene complexes (**928**, **933**, Scheme 93) are produced from the coupling of coordinatively unsaturated Group 8 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 (**932**). A variety of reaction processes of Group 8 metal–cumulene complexes were reported in 2005. Common reaction pathways for these complexes include reaction with nucleophiles at the γ-position, resulting in alkynylmetal complexes (**930**), or attack at the γ-position, resulting in allenylmetal complexes (**931**). Reaction with alcohols or amines can lead to α,β-unsaturated Fischer carbene complexes (**929**). Representative examples of this class of compounds are depicted in Fig. 13.

Specific reports which highlight the reaction pathways depicted in Scheme 93 are depicted in Fig. 13, and include: (1) formation of ruthenium allenylidene complexes containing pyrimidene ligands (*e.g.* **934**), which proved to be inactive for metathesis [806]; (2) formation of (bis) and (tris)-allenylidene complexes linked through conjugating groups (*e.g.* **935**) and subsequent electrochemical studies [807]; (3) formation of iron allenylidene complex **936** and subsequent electrochemical studies and reaction with nucleophiles [808]; (4) formation of chiral ruthenium allenylidene complex **937** and subsequent diastereoselective addition of nucleophiles to the γ-carbon of chiral ruthenium allenylidene (*e.g.* reaction with acetophenone enolate to afford alkynylruthenium complex **938**) [809]. Several processes reported in 2005 invoke metal-higher cumulene complexes as intermediates, including: (1) ruthenium catalyzed propargyl substitution reactions (which involves allenylidene complexes, *e.g.* **939**) [810–812]; (2) generation of an allenylidene complex (**941**) from alkynyl complex **940** and subsequent reaction with nucleophiles [813]. A computational study of ruthenium-catalyzed propargyl substitution

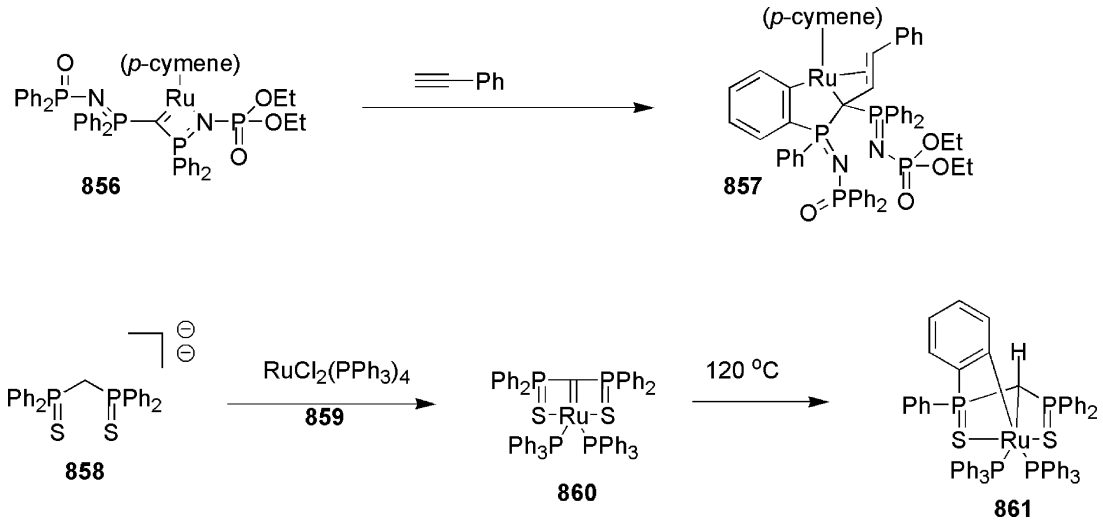


Scheme 85.

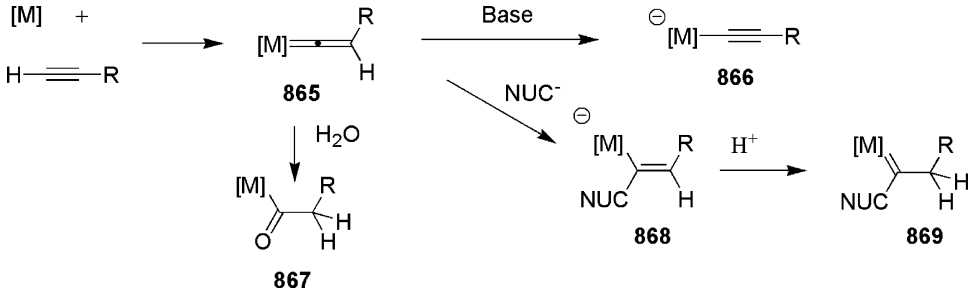
reactions was reported [814]. The cumulene–bridged bis(iron) complex **942** was generated through two-electron oxidation of bis(alkyliron) complex **941** [815]. A compilation of electrochemical data for a variety of carbene, vinylidene, allenylidene, alkynyl, and carbyne complexes was reported [816].

The coupling of cationic ruthenium complexes (*e.g.* **944**, Scheme 94) with propargyl alcohol derivatives (*e.g.* **945**) to form allenylidene complexes (*e.g.* **946**) was reported [817]. At higher temperature allenylidene complex **946** underwent an intramolecular [2 + 2]-cycloaddition to afford alkenylcarbene complex **947**. Treatment of the resulting alkenylcarbene complex with base led to the alkynylruthenium complex **948**.

The reaction of cationic ruthenium allenylidene complexes (*e.g.* **949**, Scheme 95) with alkenyl Grignard reagents was reported [818]. Reaction with Grignard reagents leads to alkynylruthenium complexes (*e.g.* **951**). Protonation of the vinyl



Scheme 86.



Scheme 87.

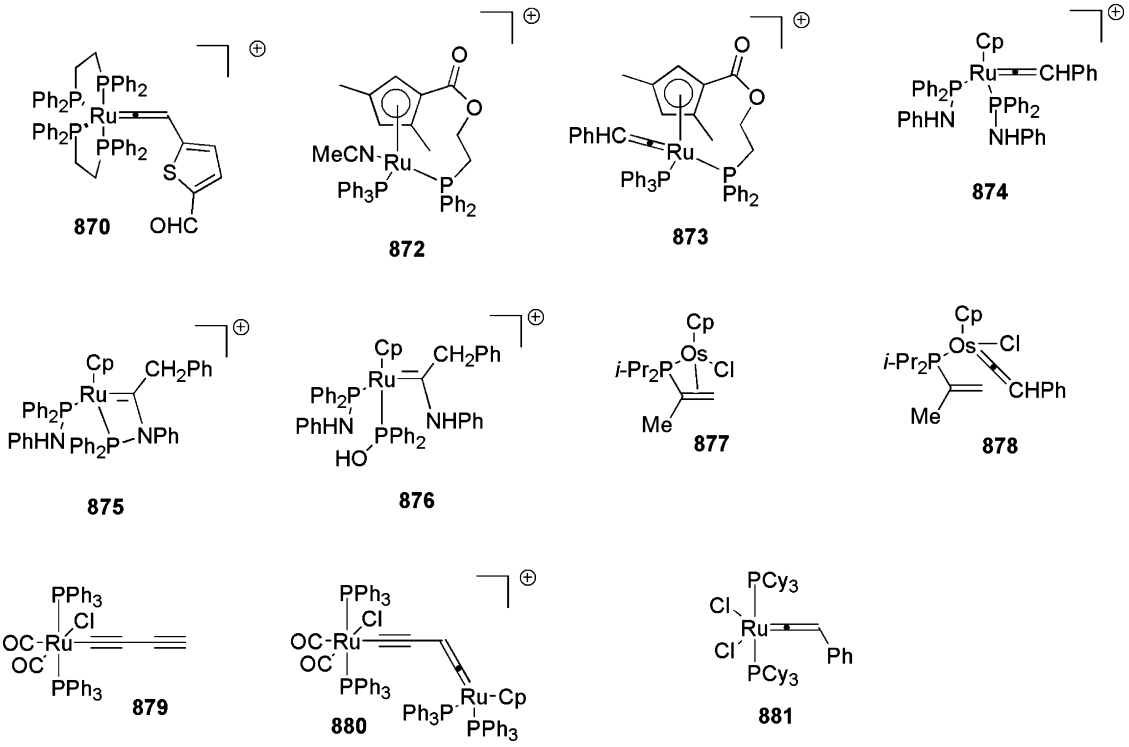
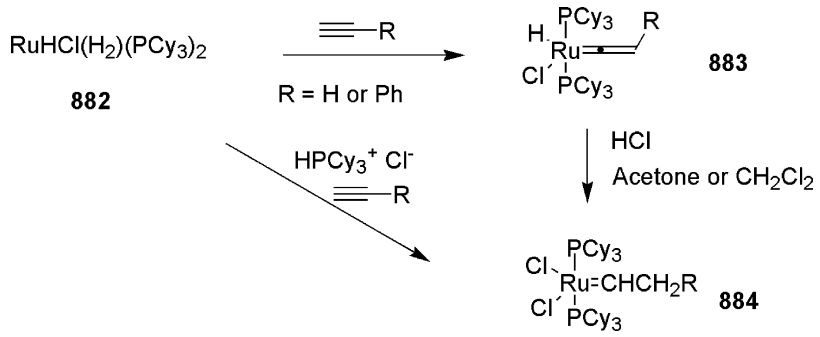


Fig. 12. Representative Group 8 metal–vinylidene complexes, precusors, and reaction products reported in 2005.



Scheme 88.

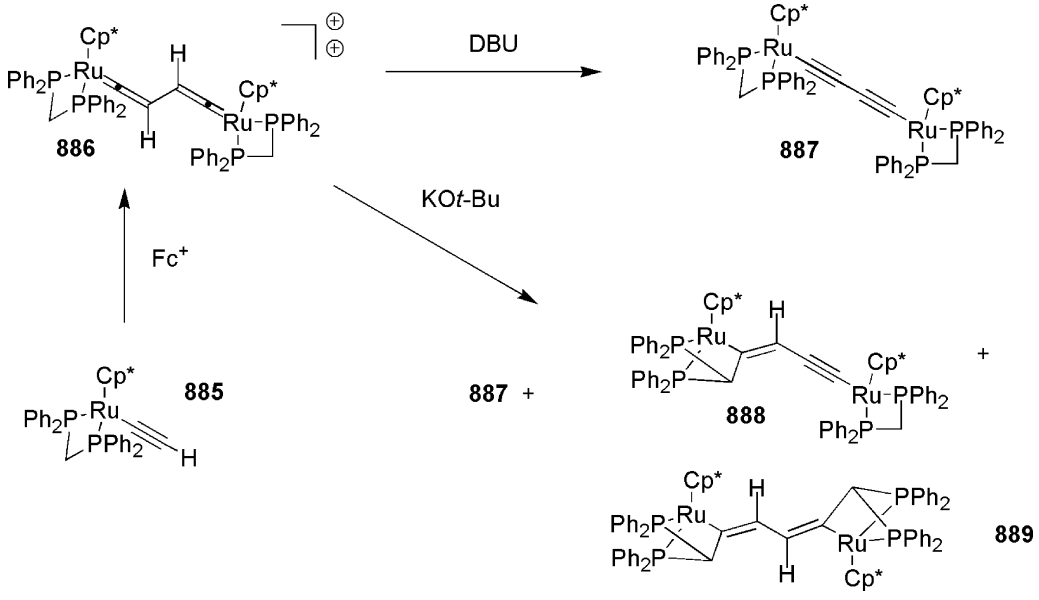
adduct followed by reflux in acetonitrile led to a mixture of the simple enynes (**953**) and rearranged enynes (**954**). The mechanism for formation of the rearranged enyne involves intramolecular [2 + 2]-cycloaddition to afford bicyclic carbene complex **955** followed by retrocycloaddition the other direction. Protonation of the 2-propenyl adduct led to the cyclic allene–ruthenium complex **959**. A mechanism involving cyclization of intermediate vinylidene complex **957** to form carbocation **958** followed by 1,2-hydride shift was proposed.

Allenylidene–ruthenium complexes (*e.g.* **963**, Scheme 96) were suggested as intermediates in the isomerization of propargyl alcohols (*e.g.* **960**) to α,β-unsaturated aldehydes (*e.g.* **964**) [819]. If the process was performed in the presence of acetone, aldol products (*e.g.* **962**) were observed. Allenylidene complex **967** was proposed as an intermediate in the cyclodimerization of diphenylpropargyl alcohol resulting in ruthenium complex **967** [820].

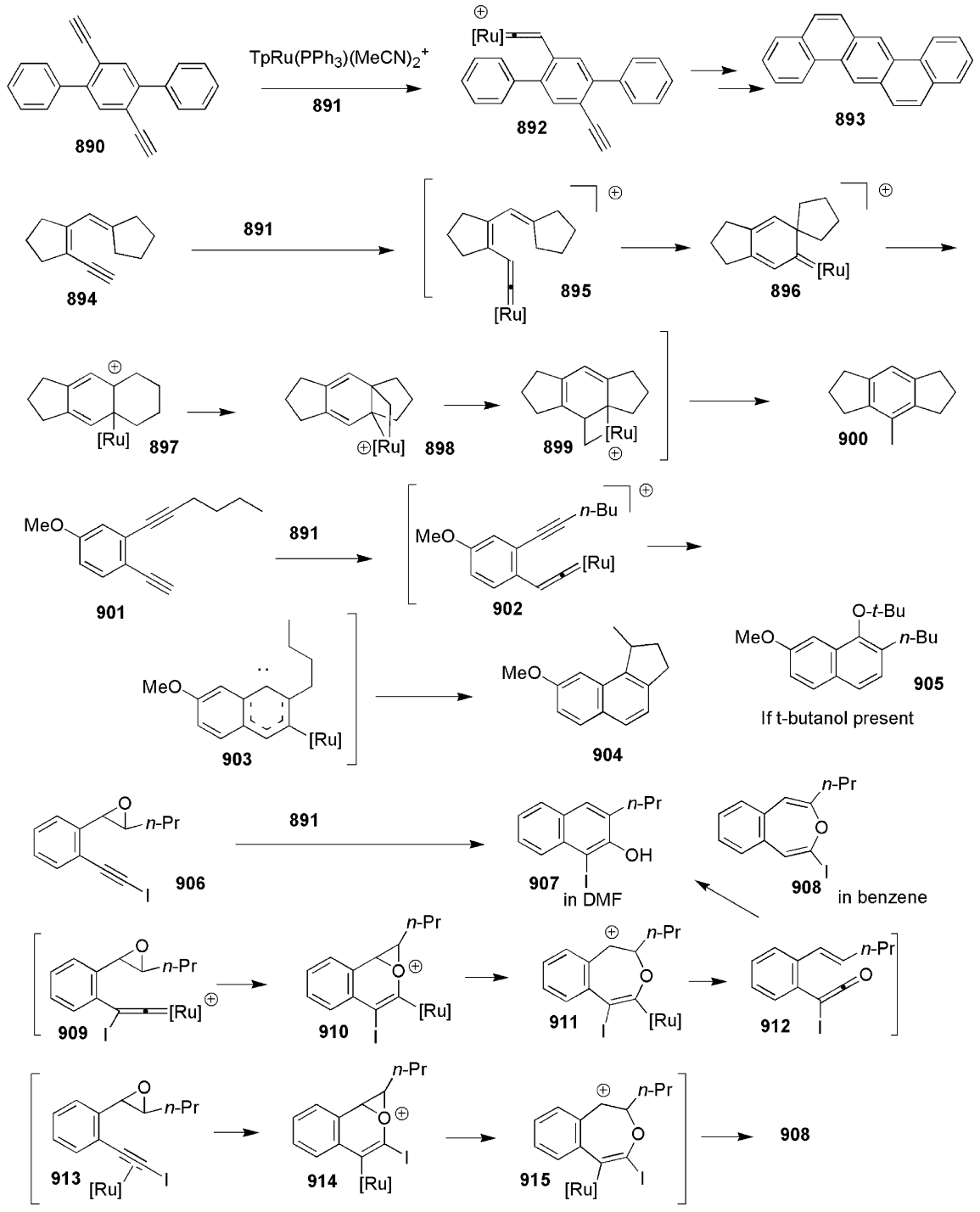
The chemistry and electrochemistry of ruthenium–butatrienylidene complexes (*e.g.* **970**, Scheme 97) was reported [821]. The complex was generated through the reaction of dialkyne **969** (R = H or TMS) with ruthenium halide **968** in the presence of NH_4PF_6. The reaction of complex **968** with the silylated alkyne in the presence of methanol led to the alkynyl ketone complex **971**, presumably through addition of water to the butatrienylidene complex. Additional products, dimeric compound **972/973** and [2 + 2]-cycloaddition product **974**, were also obtained from this reaction. Formation of the dimeric compound was attributed to addition of the methanol adduct **975** to the butatrienylidene complex followed by isomerization. Treatment of the disilylated alkyne with **968** and NH_4PF_6 led to the iminium salt–alkynyl complex **976**, presumably through addition of ammonia to the butatrienylidene complex.

1.1.3.6. Group 9 metal–carbene complexes.

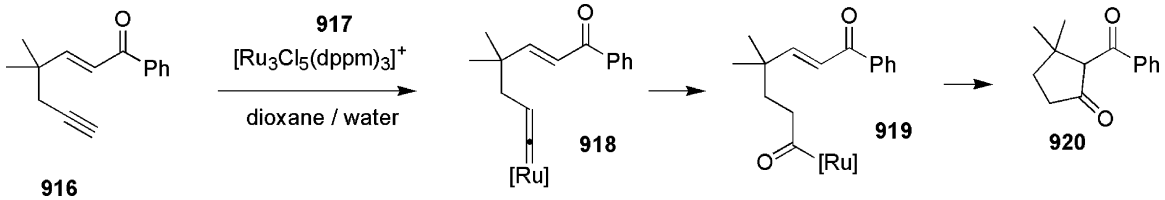
1.1.3.6.1. Simple carbene complexes. Several manuscripts emphasizing the synthesis of Group 9 metal carbene complexes appeared in 2005; representative examples are depicted in Scheme 98. A variety of carbene complexes (*e.g.* **982**, **984**) were prepared by reaction of sulfur ylides with various transition metal complexes [822]. The reaction could also be extended to ruthenium complexes as well; Grubbs catalyst I was prepared



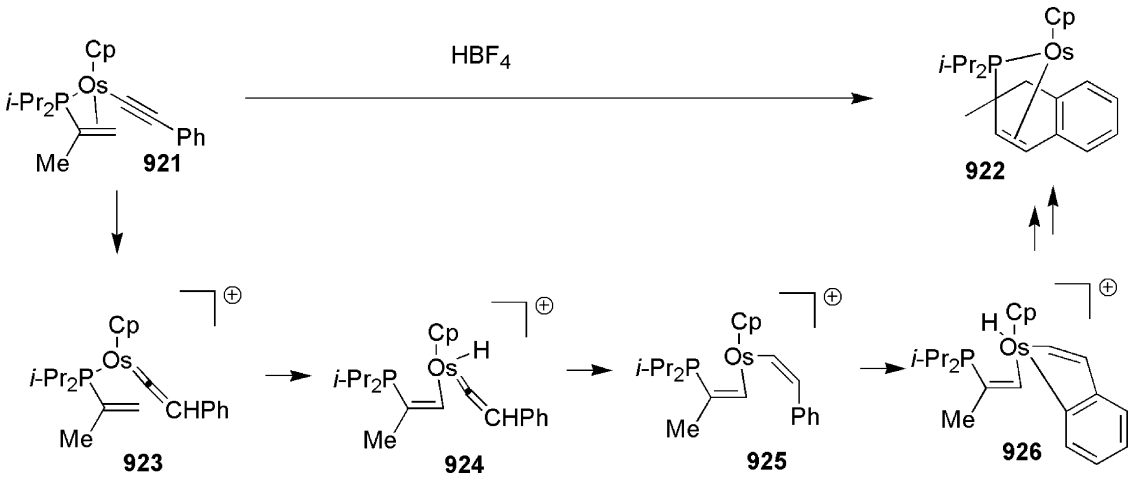
Scheme 89.



Scheme 90.



Scheme 91.



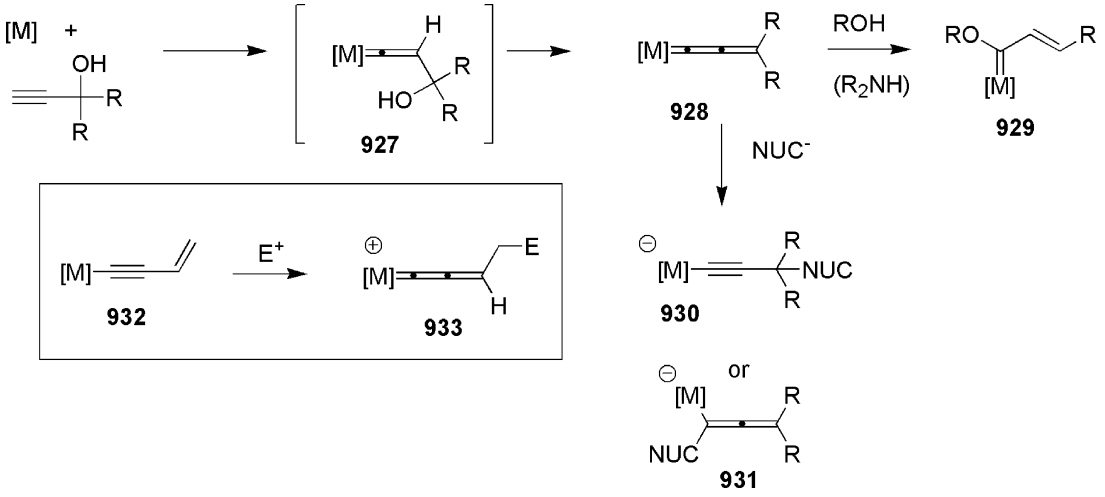
Scheme 92.

using this methodology. Iridium carbene complexes (*e.g.* **986**) were obtained from treatment of tetrairidium complex **985** with epoxides [823]. Iridium fluorocarbene complexes (*e.g.* **988**) were produced in the reduction of difluoroalkyliridium complexes (*e.g.* **987**) [824]. The initially formed complex **988** was converted to the iridium-protonated complex **989** upon protonation. Treatment with the iodide salt led to the HI addition product **990**. A cobalt Fischer carbene complex was produced in the reaction of oxalamide derivatives (*e.g.* $Et_2NCOCONEt_2$) with dicobalt octacarbonyl and higher clusters [825].

The coupling of iridium complex **992** (Scheme 99) with the organolithium reagent derived from iodide **991** led to iridabenzvalene **993/994** [826]. Thermolysis or extended reaction time at room temperature led to the iridabenzene derivative **995** and the iridium-substituted Cp complex **996**. The Cp complex is believed to arise from the alternative regioisomeric iridabenzene **997** since higher temperature thermolysis is required for the conversion of iridabenzene **995** to the Cp complex. The PMe_3 iridabenzene complexes (**999**, **1000**) were more stable and both of the regioisomeric complexes could be isolated.

Cobalt carbene complexes (*e.g.* **1003**, Scheme 100) were detected as intermediates in the conversion of cyclobutadienylcobalt complex **1002** to the pentadienyl complex **1004** [827]. The carbene complex could be intercepted with various reagents. Reaction with pyridine or triphenylphosphine led to the carbene addition products (*e.g.* **1005**, **1006**). Reaction with cyanide or isocyanides led to substituted cobaltocenes (*e.g.* **1007**). Reaction with triethylamine led to the deprotonation product **1008**.

Group 9 metal carbene complexes were proposed as intermediates in several transformations; representative examples are depicted in Scheme 101. Rhodium carbene complexes (*e.g.* **1010**) were proposed as intermediates in the rhodium-catalyzed coupling of diazoesters, aldehydes, and titanium alkoxides [828]. The C–C bond forming event was suggested to occur between a rhodium carbene complex (**1010**) and a titanium-complexed aldehyde (**1011**). Rhodium carbene complexes are likely intermediates in rhodium-catalyzed methylenation of



Scheme 93.

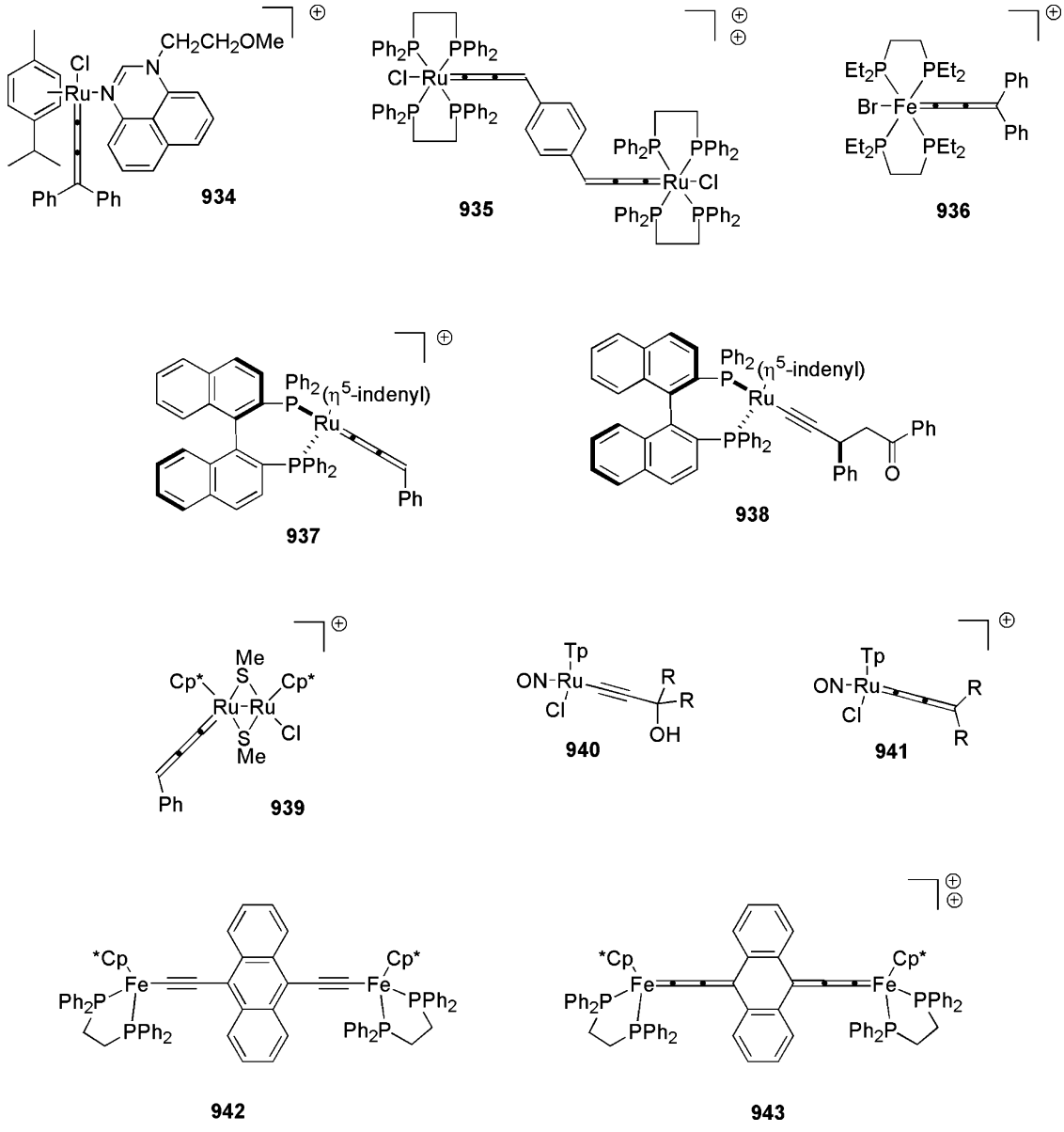
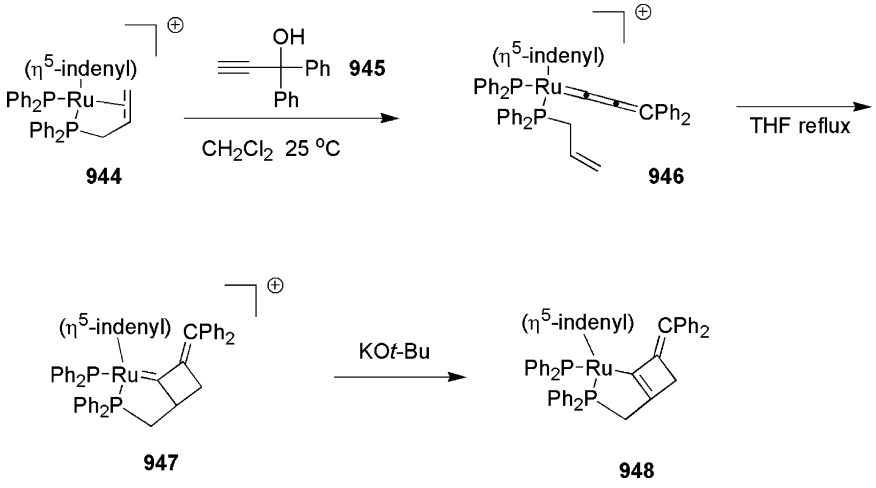
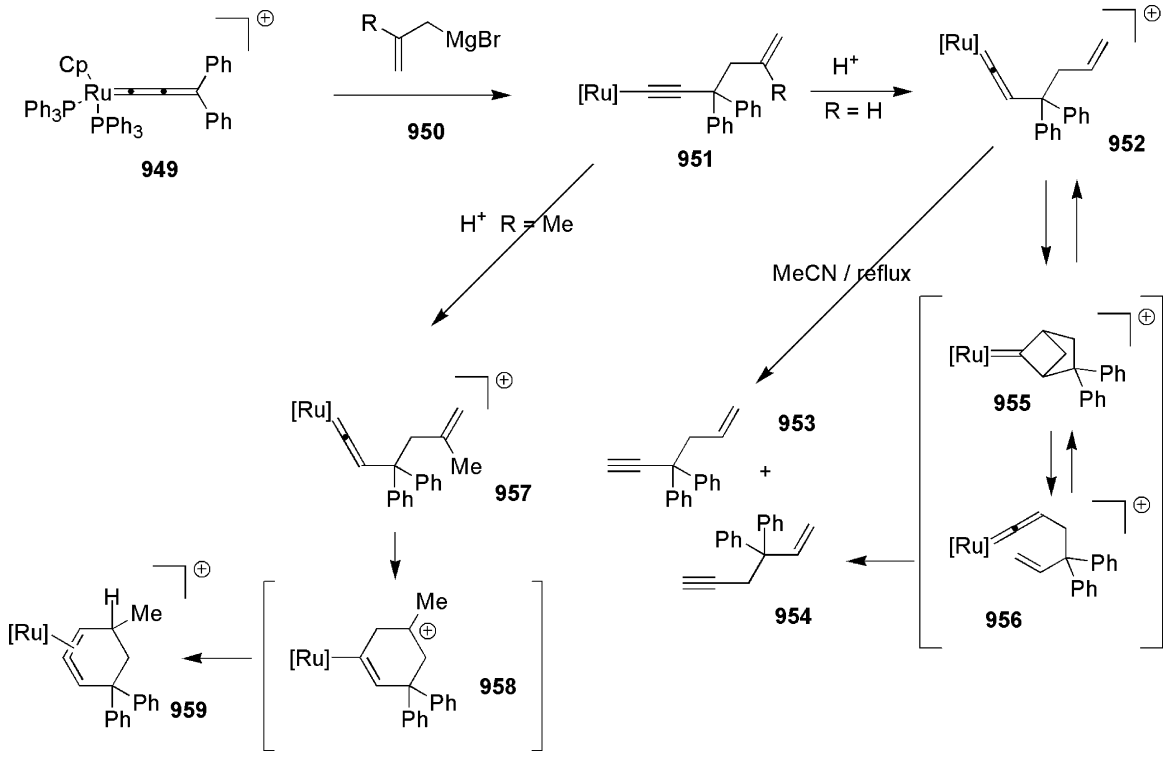


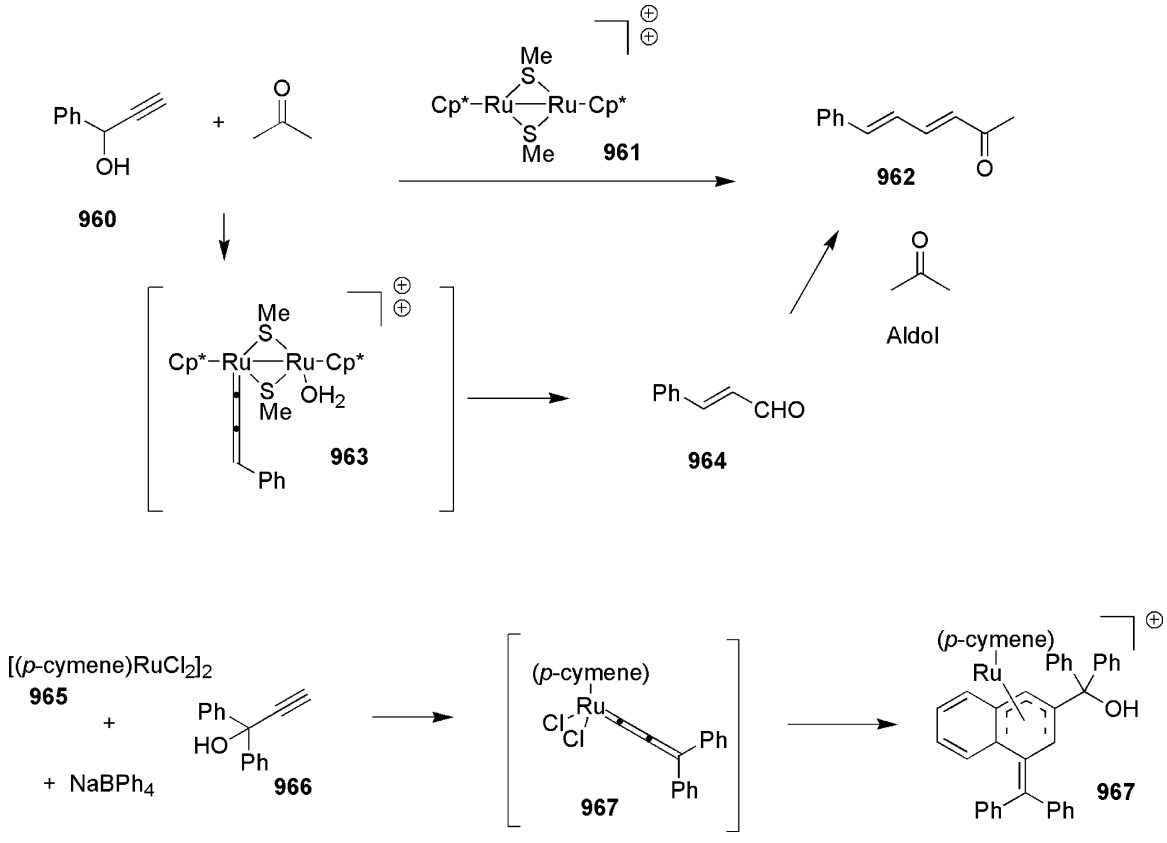
Fig. 13. Representative Group 8 metal–higher cumulene complexes and products derived therefrom reported in 2005.



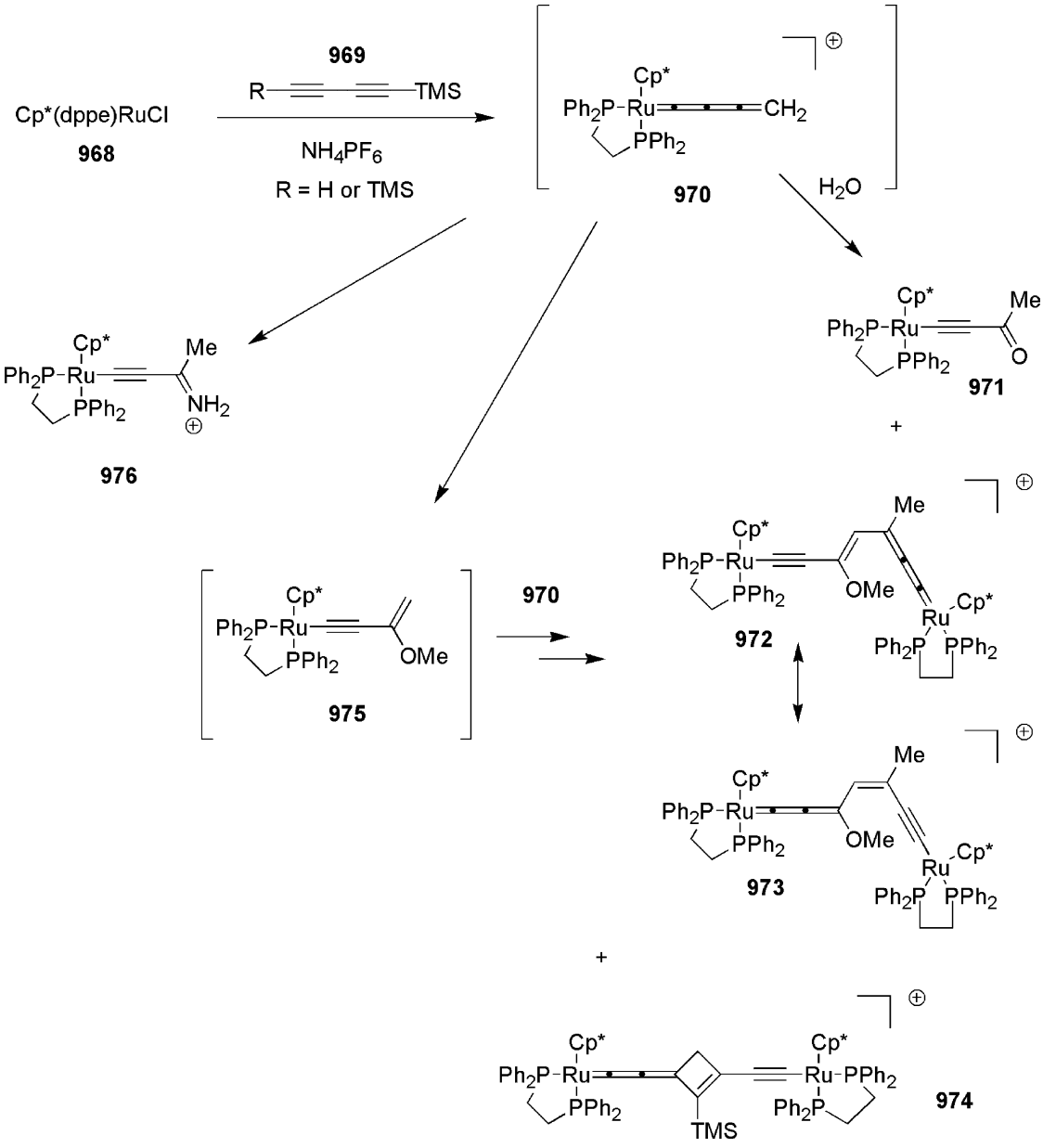
Scheme 94.



Scheme 95.



Scheme 96.



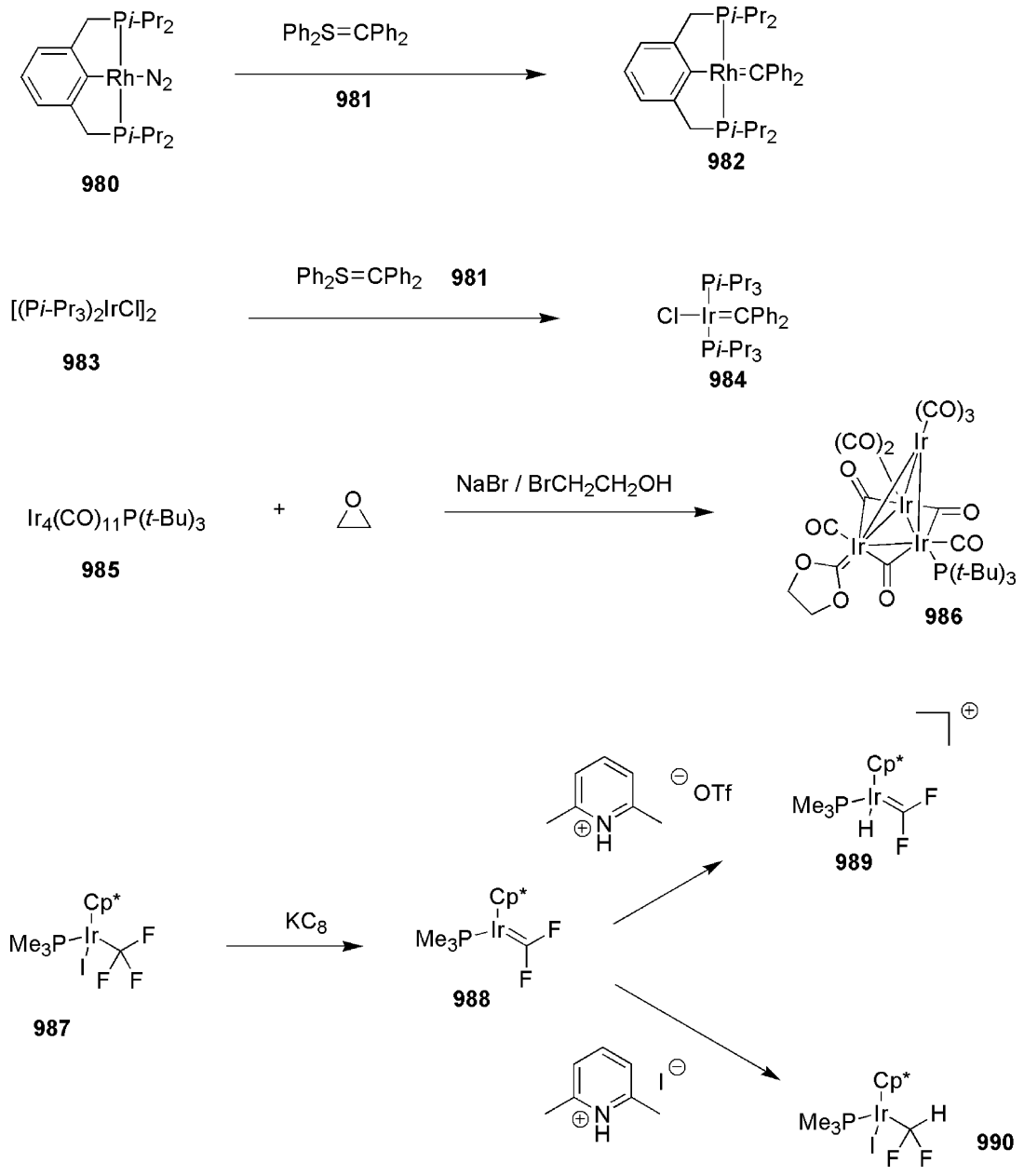
Scheme 97.

aldehydes using trimethylsilyl diazomethane and triphenylphosphine [829]. Iridium carbene complexes (*e.g.* **1016**) were proposed as intermediates in the cycloisomerization of enyne derivatives (*e.g.* **1013**) [830]. Formation of the bicyclic compound **1017** was proposed to proceed through formation of an iridium-alkyne complex (**1015**) followed by concomitant shift of a hydrogen and formation of a carbene complex (**1016**), followed by intramolecular cyclopropanation. Iridium carbene complexes (*e.g.* **1019**) were proposed as intermediates in the conversion of bis(thiophene) complex **1018** to complex **1020** upon protonation [831].

Other studies of Group 9 metal–carbene complexes (excluding cumulenes) include: (1) formation of a chelated arylrhodium–carbene complex [832]; (2) mechanistic studies of rhodium-catalyzed aziridination of imines [833]; (3) mechanistic studies of rhodium catalyzed aziridination of imines and the steric influences in the carbene complex intermediate that can explain enantioselection [834]; (4) a suggestion that cobalt carbene complexes are intermediates in the addition of carbenes to cobalt 1,2-dithioketone complexes [835].

1.1.3.6.2. Cumulene complexes. Similar synthetic procedures and reactivity patterns were generally observed for Group 9 and Group 8 metal–cumulene complexes (Schemes 87 and 93).

The synthesis and reactivity of alkynylrhodium–vinylidene complexes (*e.g.* **1021**, Scheme 102) was reported [836]. Reaction of vinylidene complex **1021** with CO led to the enynyl complex **1022**. Reaction with HCl led to the enyne π-complexes **1024**. Protonation of **1021** at low temperature afforded an observable vinyl complex (**1023**) from protonation at the vinylidene ligand, which converts to enyne complex **1024** upon



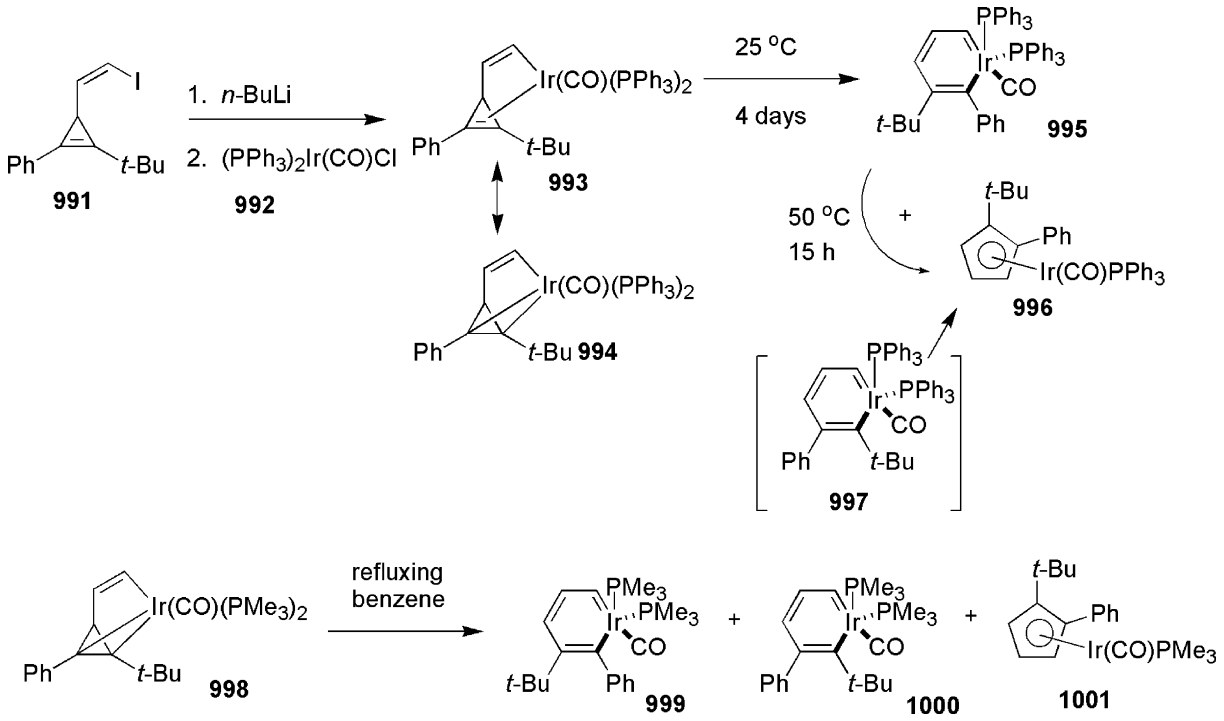
Scheme 98.

warming to room temperature. Reaction with acetic acid led initially to observable oxidative addition product **1025**, which subsequently afforded the enyne derivative **1027** upon warming to room temperature.

Bis(vinylidene-iridium) complexes (*e.g.* **1029**, Scheme 103) were prepared through the reaction of complex **1028** with bis(trimethylsilyl)acetylene [837]. This complex can also serve as a catalyst for alkyne dimerization and trimerization. Coupling with silyl(alkyl)acetylene derivatives led to products from alkyne insertion into the Ir–H bonds.

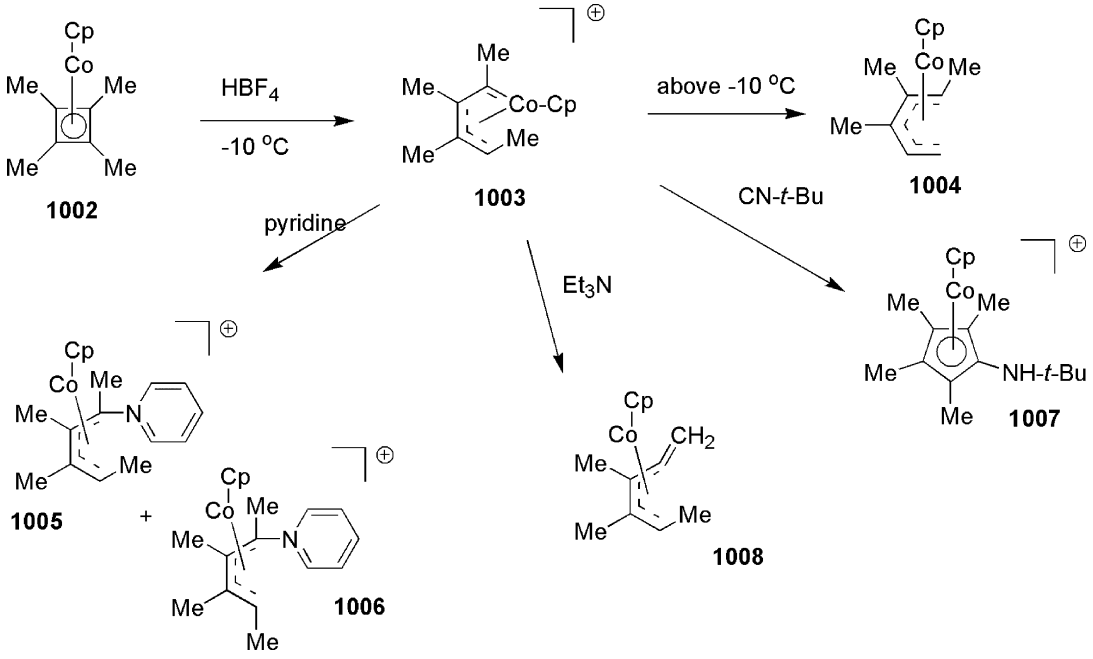
Rhodium–vinylidene complexes were proposed as intermediates in several carbon–carbon bond forming processes involving alkynes; representative examples are depicted in Scheme 104. Cycloisomerization of enynes (*e.g.* **1032**) was proposed to occur through vinylidene intermediates (*e.g.* **1034**) [838]. An unusual feature of the reaction is that even internal alkynes participate and afford alkyl migrated products. Rhodiumvinylidene complexes (*e.g.* **1037**) were proposed as intermediates in the cyclodimerization of arylacetylenes catalyzed by ruthenium porphyrin complexes [839]. After formation of a vinylidene complex (**1037**), Diels–Alder reaction and hydrogen shifts afford the cyclodimerization product **1039**. Rhodium–vinylidene complexes were proposed as intermediates in the dimerization of alkynes induced by $(CO)(PPh_3)_2RhCl_2$ [840].

Iridium–vinylidene complexes (*e.g.* **1042**, Scheme 105) were proposed as intermediates in alkyne coupling reactions using iridium complex **1040** [841]. This mechanism was supported

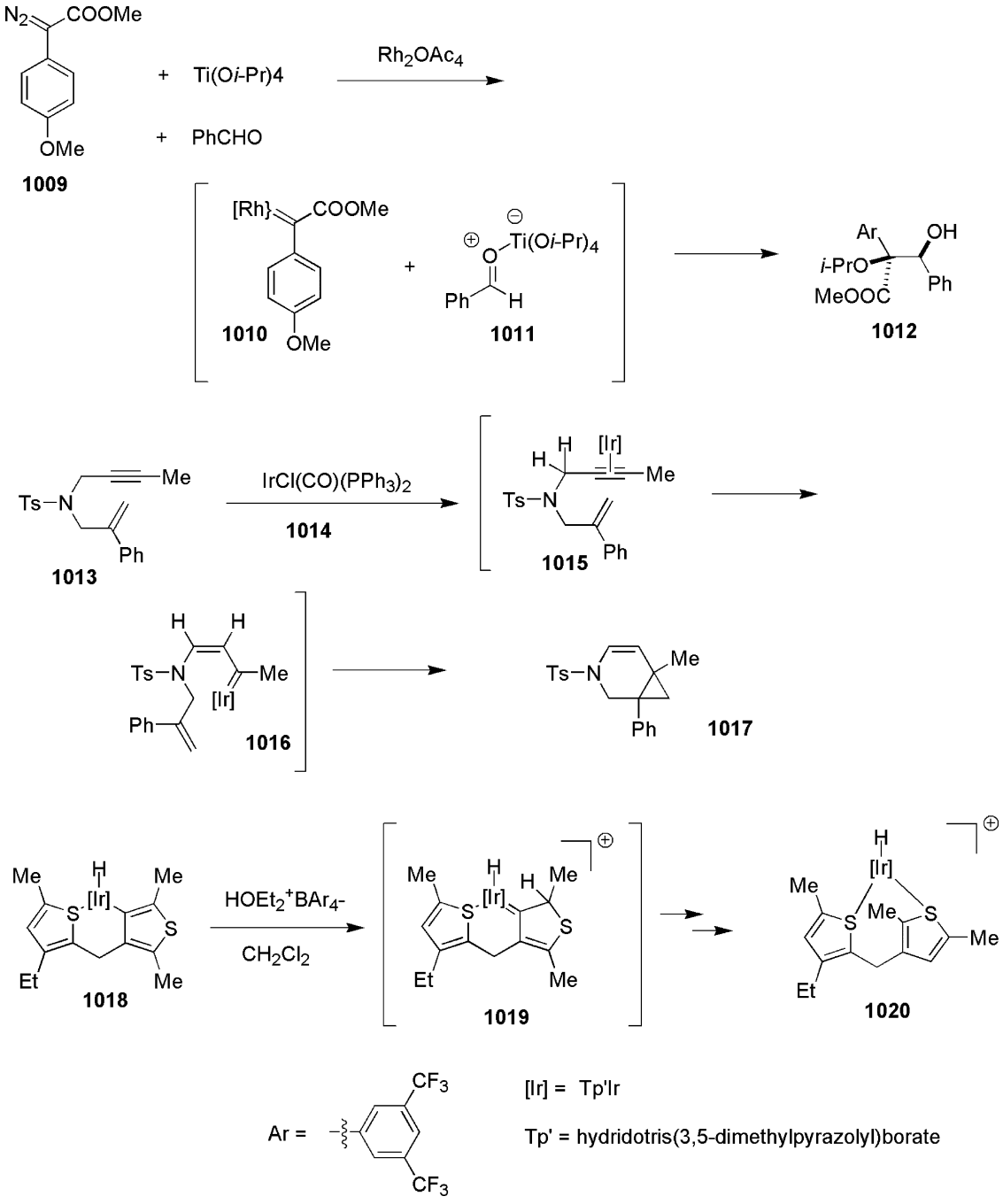


Scheme 99.

through deuterium labeling studies and through observation of cyclic carbene complexes (*e.g.* **1045**) derived from metal vinylidene complexes. Related carbene complexes (*e.g.* **1050**) were proposed as intermediates in the formation of cyclization/oxygen transfer product **1047** from coupling of complex **1040** with nitro-alkyne **1046** [842]. The proposed mechanism involves nucleophilic addition of the nitro group oxygen to the iridium–alkyne complex **1048**, to afford cyclized intermediate **1049**, followed by formation cleavage of the N–O bond resulting in formation of carbene complex **1050**, followed by cyclization of the resulting carbene complex-nitroso compound. Iridium–vinylidene complexes were proposed as intermediates in the formation of bis(alkynyl)iridium complexes from an η^2-acetatoiridium complex and terminal alkynes [843].



Scheme 100.

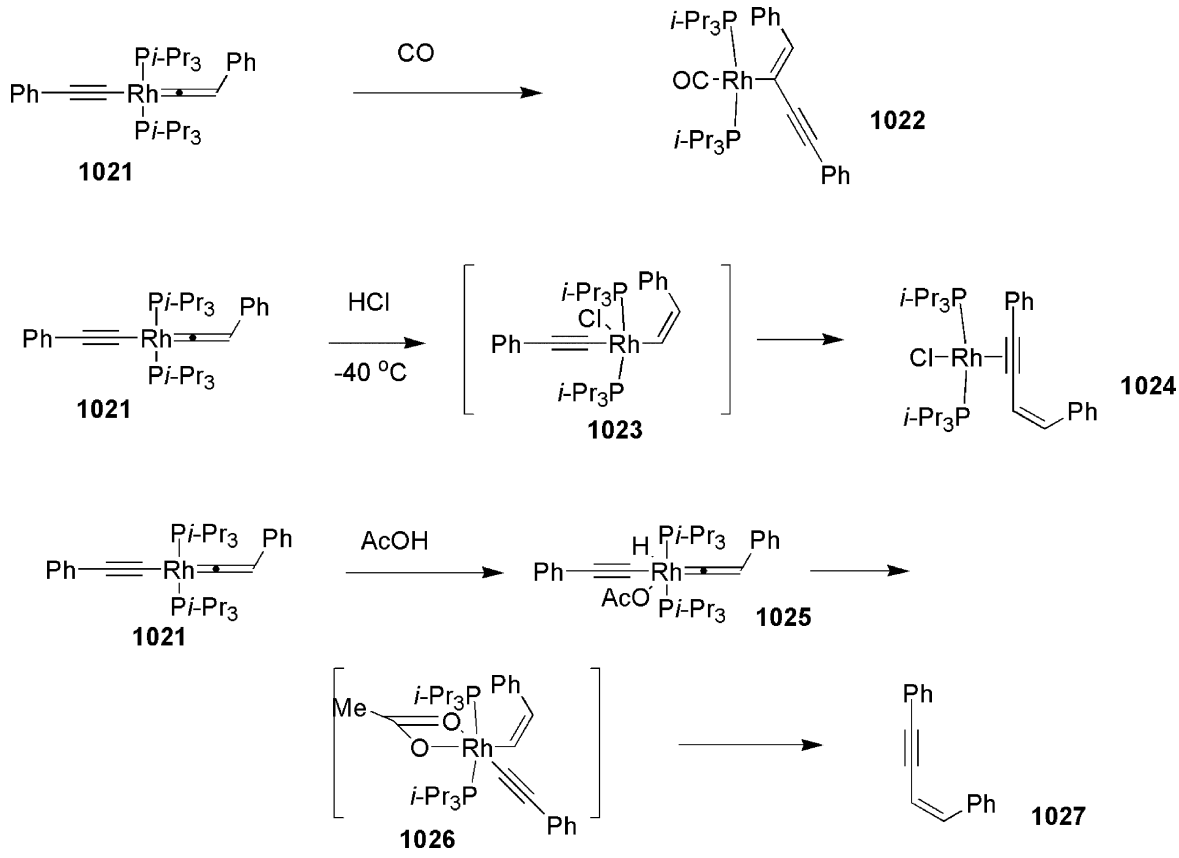


Scheme 101.

Iridabenzenes (*e.g.* **1053**, Scheme 106) were prepared through coupling of iridacyclopentadienes (*e.g.* **1051**) with terminal alkynes [844]. In the first step a (dienyl)(alkynyl)iridium complex (**1052**) is produced, which transforms to the iridabenzene upon protonation. A mechanism involving formation of the cationic vinylidene complex (**1054**), followed by cyclization to generate iridacycle **1055**, followed by 1,3-hydrogen shift was proposed. Deuterium labeling studies support this mechanistic proposal.

A variety of mono-N-heterocyclic carbene complexes of rhodium and platinum were reported [845,846]. Both types of complexes feature strong agostic interactions with axial hydrogens of an adjacent cyclohexane ring of the NHC ligand.

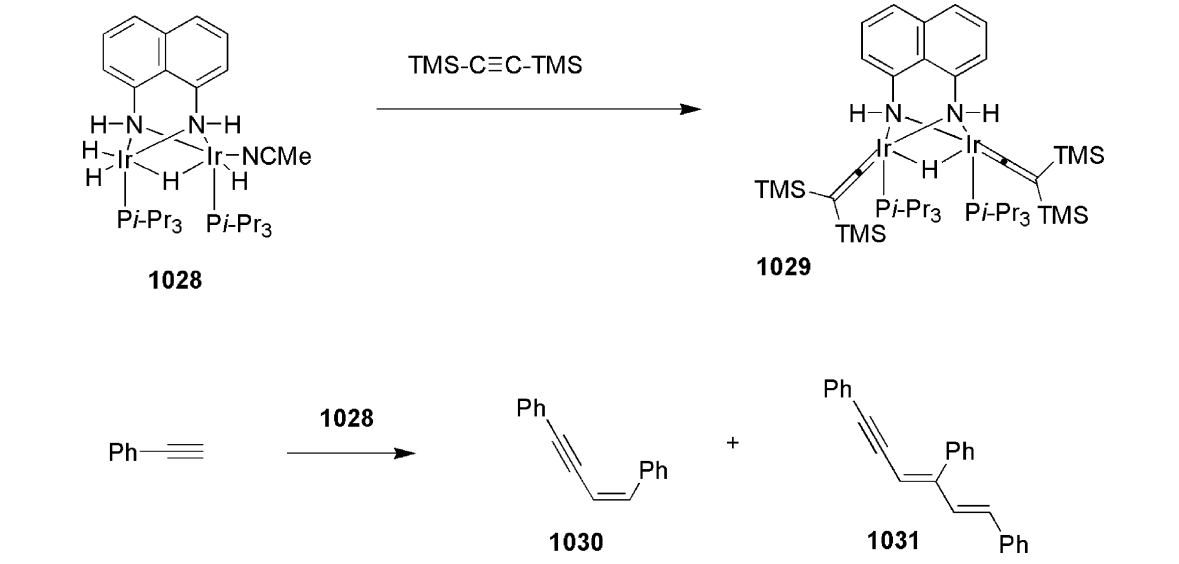
1.1.3.7. Group 10 metal–carbene complexes (includes platinum and gold-catalyzed alkyne cycloisomerizations). Several manuscripts emphasizing the synthesis of Group 10 metal carbene complexes appeared in 2005; representative examples are depicted in Scheme 107. Palladium–carbene complexes (*e.g.* **1062/1063**) were prepared from the coupling of chloro-substituted iminium salt **1060** with $Pd(PPh_3)_4$ [847]. Palladium



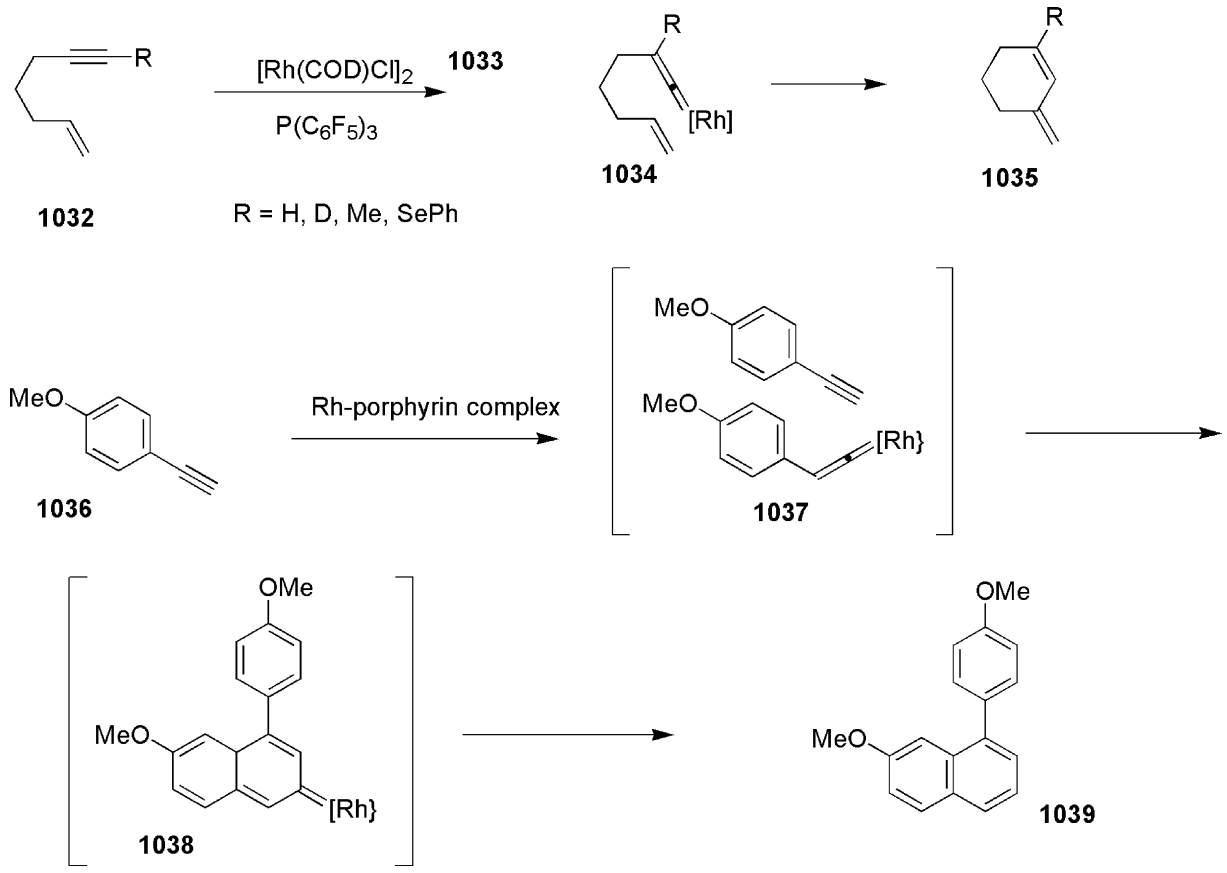
Scheme 102.

carbene complexes (*e.g.* **1066**) were synthesized through coupling of (tripyrrinato)palladium(II) complex **1064** with diazo compounds [848]. The preparation of platinum carbene complexes through reaction of bis(acyl)platinum dimer with aminopyridine derivatives was reported [849]. Several related five-membered ring cyclic carbene complexes were evaluated through DFT calculations and the degree of π-bonding of the Pt–carbene bond was determined.

The synthesis and reactivity of platinum carbene complexes featuring pincer ligands (*e.g.* **1070**, Scheme 108) was reported [850]. Platinum carbene complex **1070** was best represented by resonance form **1071**. Methylation led to phosphorus-iminium



Scheme 103.



Scheme 104.

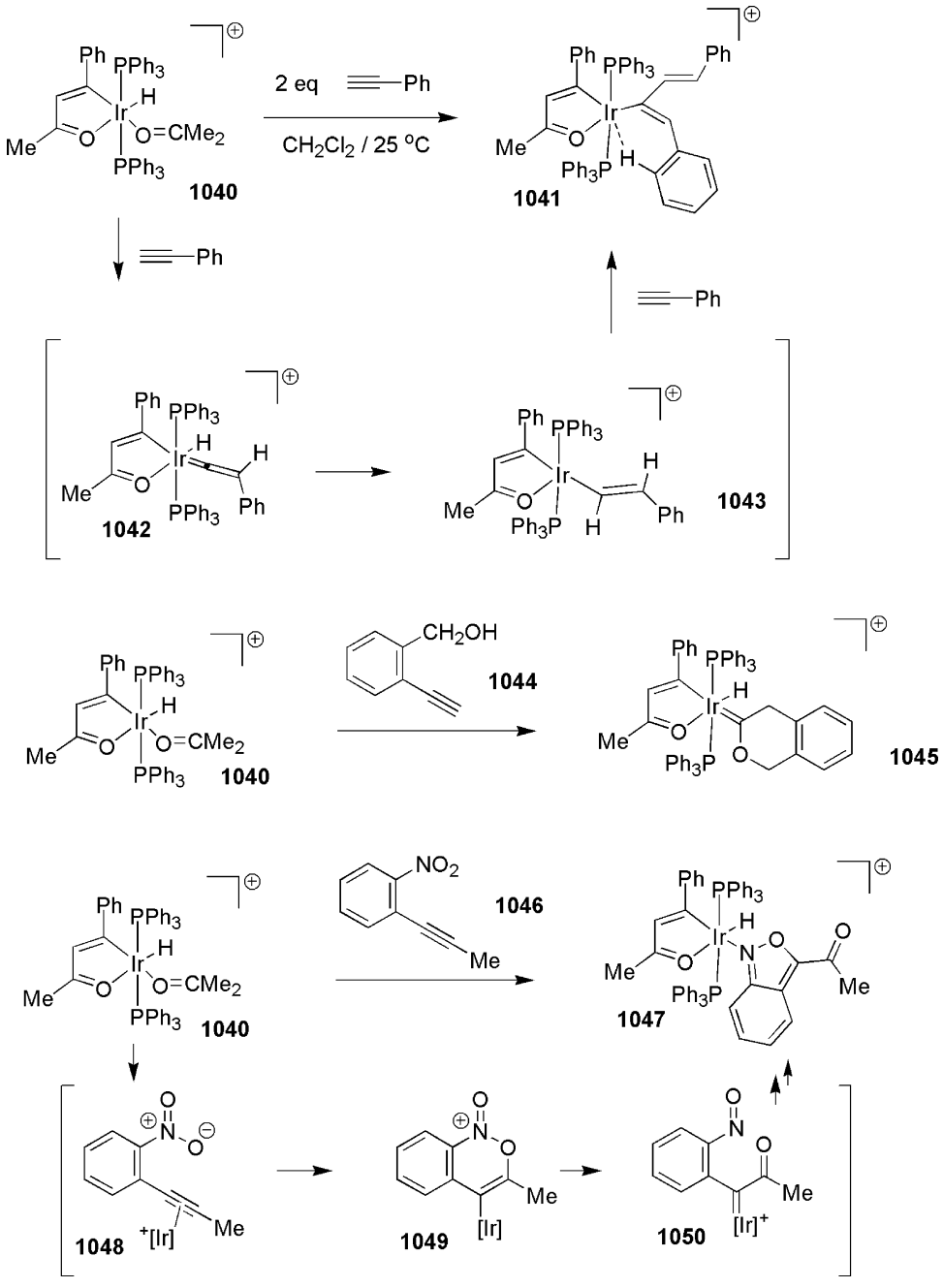
salt **1072**, which afforded cyclic compound **1074** upon treatment with water. The protonated compound **1073** could be identified spectroscopically as an intermediate in the formation of **1074**.

The preparation of nickelacyclopentadienyl complexes (*e.g.* **1077**, Scheme 109) from the reductive coupling of nickelocene with stilbenes (*e.g.* **1075**) was reported [851]. A mechanism involving reduction to produce CpNi, followed by oxidation addition into the alkene C–H bond to afford alkenylnickel species **1080**, followed by intramolecular C–H activation of the ortho-aromatic H to form metallacycle **1081**, followed by complexation of nickel to the CpNi was proposed.

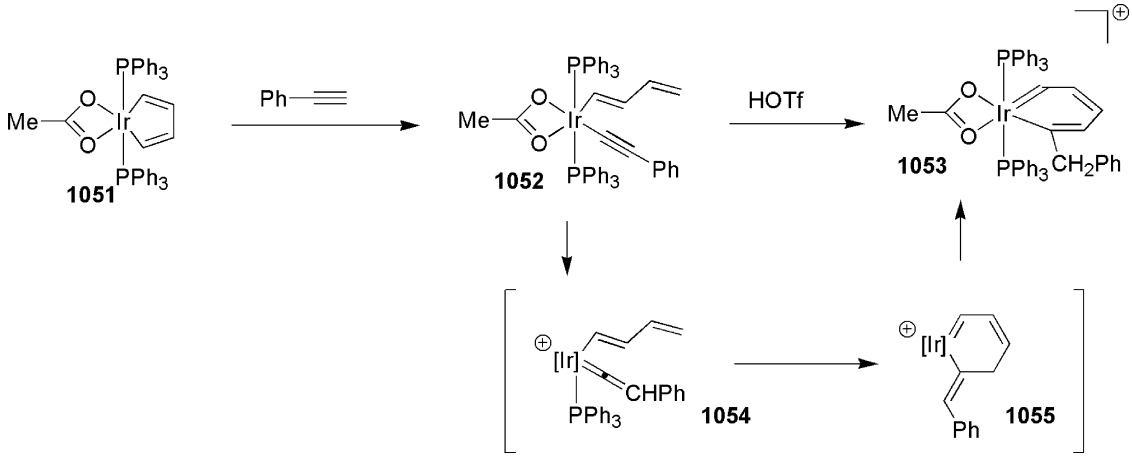
DFT studies of the structure of cationic bis(platinum)carbene complexes [*e.g.* Pt–Pt=CH_2^+] and platinum–gold carbene complexes and their reaction with ammonia by hydrogen loss was reported [852]. The bis(platinum) complex is more stable as a bridged structure. The mixed platinum-gold complex has two energy minima, a singlet open-chain structure and a bridged structure. The bis(platinum) complex reacts with ammonia to afford (NH_3)Pt–Pt$(CH_2)^+$ which undergoes consecutive isomerizations to eventually afford (NH_3)Pt–PtC^+ and H_2. The mixed platinum–gold complex reacts with ammonia to afford Pt–Au–$CHNH_2^+$.

Palladium carbene complexes (*e.g.* **1086**, Scheme 110) were proposed as intermediates in the reaction of benzyl bromide with ethyl diazoacetate to afford cinnamate esters (*e.g.* **1084**) [853]. Formation of a palladium carbene complex (**1086**) from the coupling of oxidative addition product **1085** and the diazo compound, followed by benzyl group migration and β-hydride elimination was proposed. Palladium vinylidene (*e.g.* **1089**) and allenylidene (*e.g.* **1092**) complexes were proposed as intermediates in the vinylidenation (or allenylidenation) of norbornadiene using terminal alkynes [854]. New copper and palladium cyclopropanation catalysts were developed and carbene complexes were proposed as reactive intermediates [855]. Platinum carbon double bonded intermediates (*e.g.* **1096**) were suggested as intermediates for the decomposition of platinadiazomethane derivatives (*e.g.* **1094**) [856]. A palladium carbene complex was suggested as contributing resonance forms for a chelating 4-palladapyridinium complex [857].

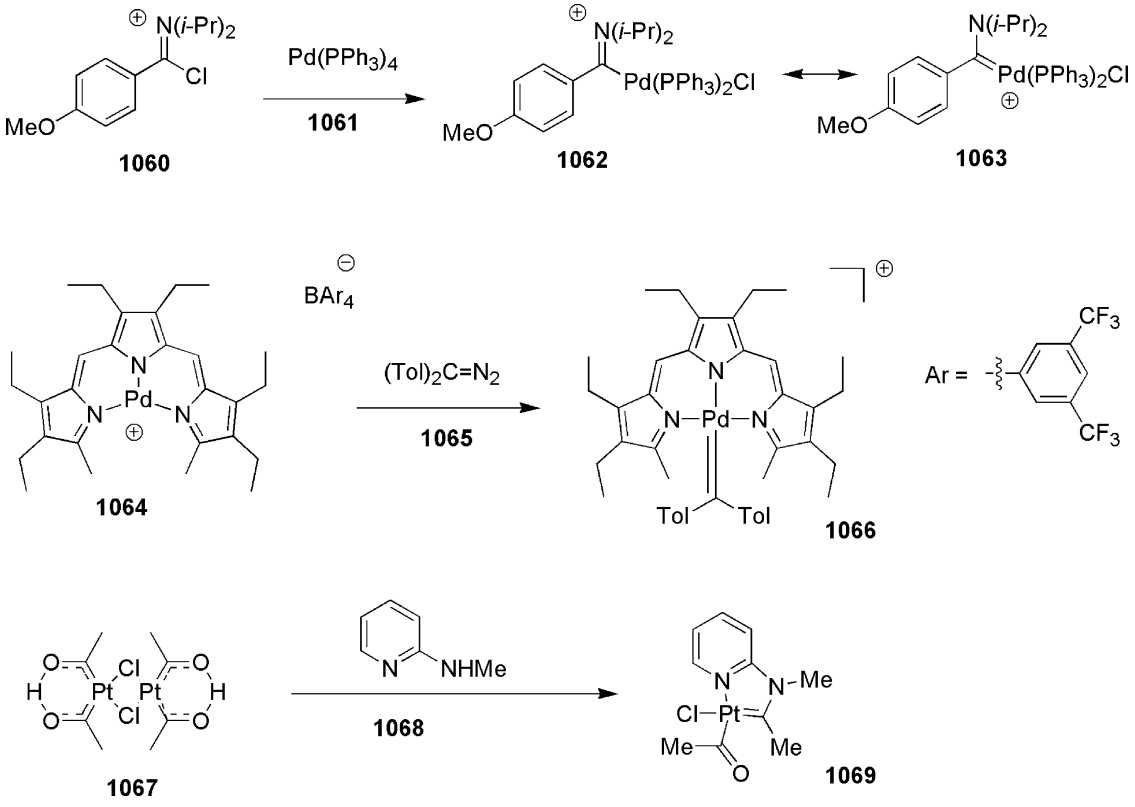
Several papers report the development of new reaction processes using carbene intermediates generated through the reaction of enyne derivatives with platinum or gold complexes; representative examples are depicted in Scheme 111. Net intramolecular cycloaddition of conjugated enynes and alkenes was observed upon treatment of dienynes (*e.g.* **1098**) with catalytic amounts of gold(I) cations (*e.g.* **1099**) [858]. A mechanism that involves formation of a cyclopropylcarbene–gold complex (**1100**) followed by ring expansion was proposed. Reaction of enynes (*e.g.* **1103**) with gold catalysts (*e.g.* **1104**) led to either enyne metathesis products (*e.g.* **1106**) using terminal alkynes or intramolecular cycloaddition products (*e.g.* **1107**) using arylacetylenes [859]. Cyclopropylcarbene–gold



Scheme 105.

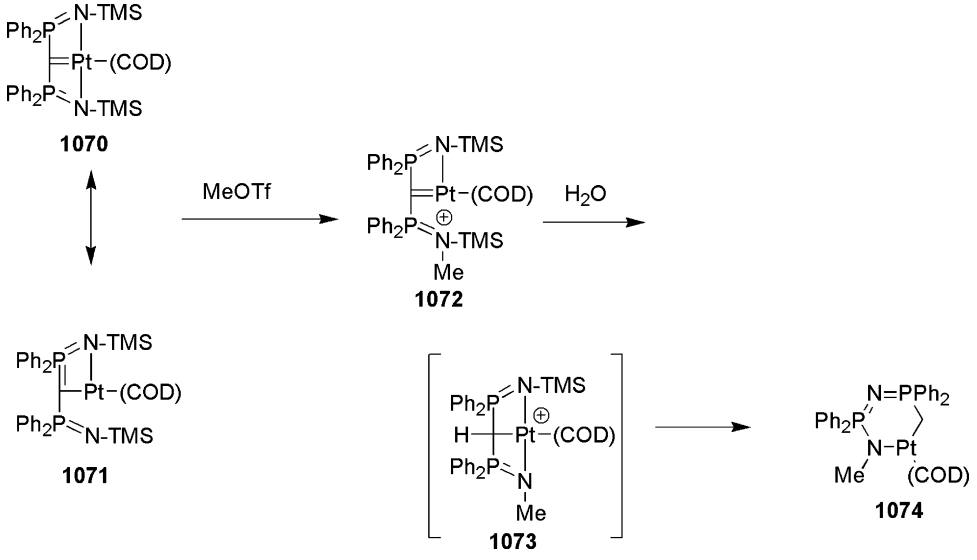


Scheme 106.

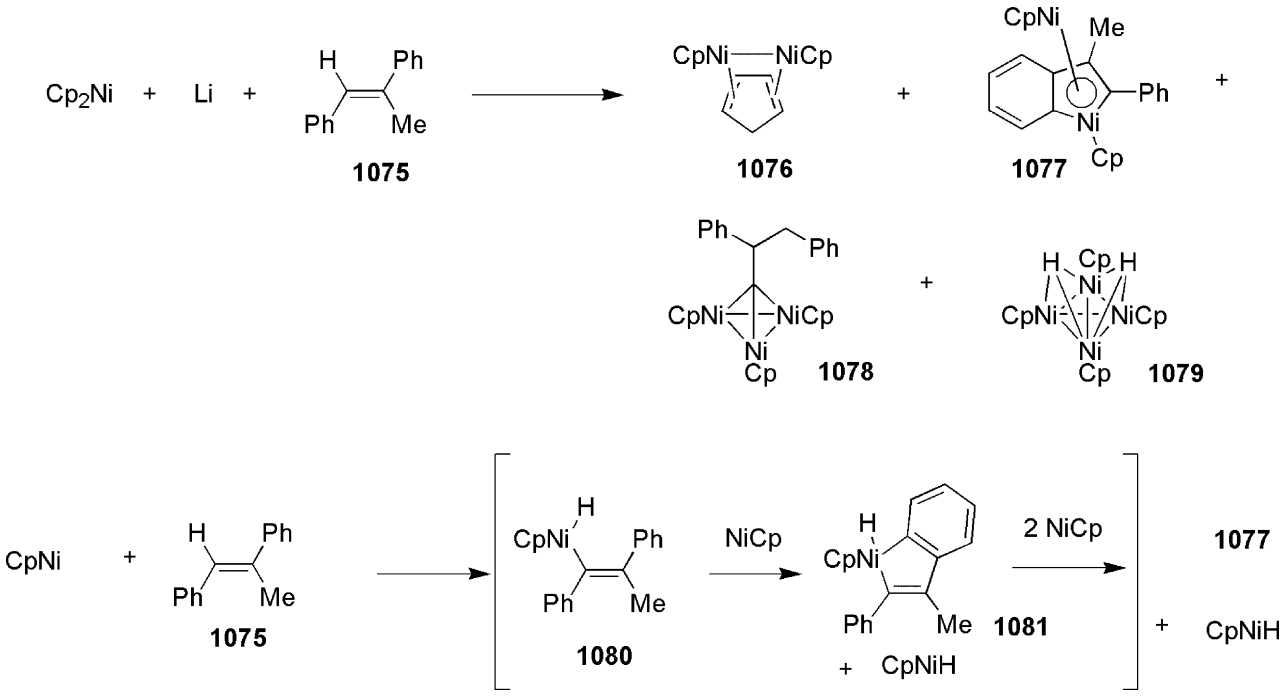


Scheme 107.

complexes (*e.g.* **1105**) were suggested as intermediates. Tandem enyne cycloisomerization/ether formation was observed upon treatment of enyne alcohols (*e.g.* **1108**) with gold(III) chloride [860]. The key step involves generation of a cyclopropylcarbene complex (**1109**) followed by intramolecular attack of oxygen on the electrophilic cyclopropane derivative. Computational studies of platinum-catalyzed enyne cycloisomerization and enyne metathesis were also reported, which also support the intermediacy of cyclopropylcarbene complexes [861]. Cyclization of alkyne-arenes using platinum and gold complexes was studied computationally and the calculations are supportive of the intermediacy of cyclopropylcarbene complexes [862]. Mechanistically related processes involving the synthesis of alkenylnaphthalenes through



Scheme 108.



Scheme 109.

metal catalyzed enyne cycloisomerization were also reported [863].

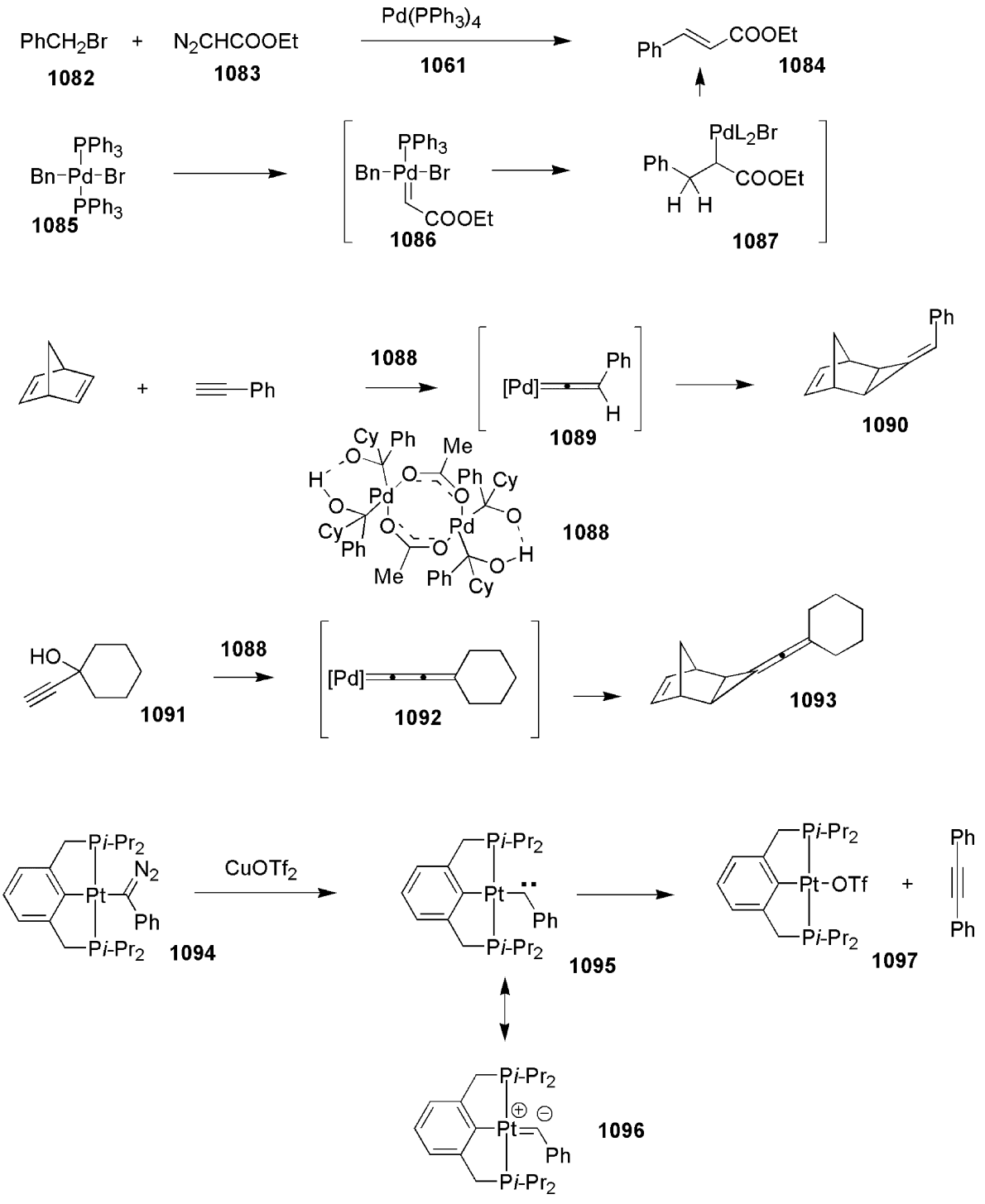
Heterocyclizations were also reported using functionalized alkyne derivatives and gold- or platinum complexes; examples are depicted in Scheme 112. Pyrroles (*e.g.* **1117**) were produced in the reaction of homopropargyl azide derivatives (*e.g.* **1113**) with gold complexes (*e.g.* **1114**) [864]. A mechanism involving cyclization to a vinylgold–diazonium salt (**1115**), followed by nitrogen loss and gold carbene complex (**1116**) formation, followed by demetallation was proposed. Bromofuran (*e.g.* **1119**) formation was observed upon treatment of enyne-ketones (*e.g.* **1118**) with gold(III) chloride [865]. A mechanism involving a gold carbene complex (**1119**) was proposed, which affords the bromofuran derivative after 1,2-shift of bromine and demetallation. Dialkynylbenzaldehyde derivatives (*e.g.* **1121**) afforded benzotropones (*e.g.* **1122**) upon treatment with gold(III) bromide [866]. A mechanism involving formation of a carbonyl ylide–carbene complex (**1123**), followed by intramolecular cycloaddition, oxygen bridge opening, and hydride shift was proposed.

Platinum and gold-catalyzed cycloaddition reactions were also reported. Reaction of furan-alkyne derivative **1125** (Scheme 113) with gold(I) chloride led to indenol **1131** [867]. The proposed mechanism involves formation of a cyclopropylcarbene–gold complex (**1126**) followed ring opening to an aldehyde–carbene complex (**1127**), followed by formation of an oxepine-gold species (**1128**), which undergoes rearrangement to the aromatic oxide derivative followed by epoxide ring opening. Several papers report on computational modeling of these and related processes [868].

Carbene complexes were also generated from 1,2-shift of propargyl ester derivatives in the presence of platinum and gold complexes (see Scheme 114). Esters of propargylic–allylic alcohols (*e.g.* **1132**) cyclized to cyclopentenone derivatives (*e.g.* **1134**) upon treatment with gold(I) derivatives [869]. A related process was observed upon treatment of internal alkyne-propargyl esters with gold(I) species [870]. Cyclopropanation was observed in the reaction of propargyl ester derivatives (*e.g.* **1135**) with styrene derivatives in the presence of gold(I) salts [871]. An intramolecular version of this reaction was also reported [872]. Indole annulation was effected by treatment of indole-propargyl ester derivatives (*e.g.* **1140**) with platinum(II) chloride complex **1141** [873]. Enyne cycloisomerizations involving propargyl-functionalized compounds (*e.g.* **1144**) were also evaluated computationally [874,875]. The computations suggest that the 1,2-shift of propargyl oxygens may occur after the cyclization event (pathway B) instead of the generally accepted route involving initial conversion to an alkenylcarbene complex (pathway A).

Several other reaction processes were reported from the reaction of alkynes and platinum or gold complexes that might involve carbene complex intermediates. Several papers reported on platinum- and gold-catalyzed enyne metathesis in 2005, which may involve metal carbene complex intermediates. A theoretical study of gold-catalyzed enyne metathesis suggested that cyclopropylcarbene complexes are key intermediate in both enyne metathesis and in [2 + 2]-cycloaddition [876]. Similar intermediates have also been proposed for platinum-catalyzed [2 + 2]-cycloaddition of enynes [877].

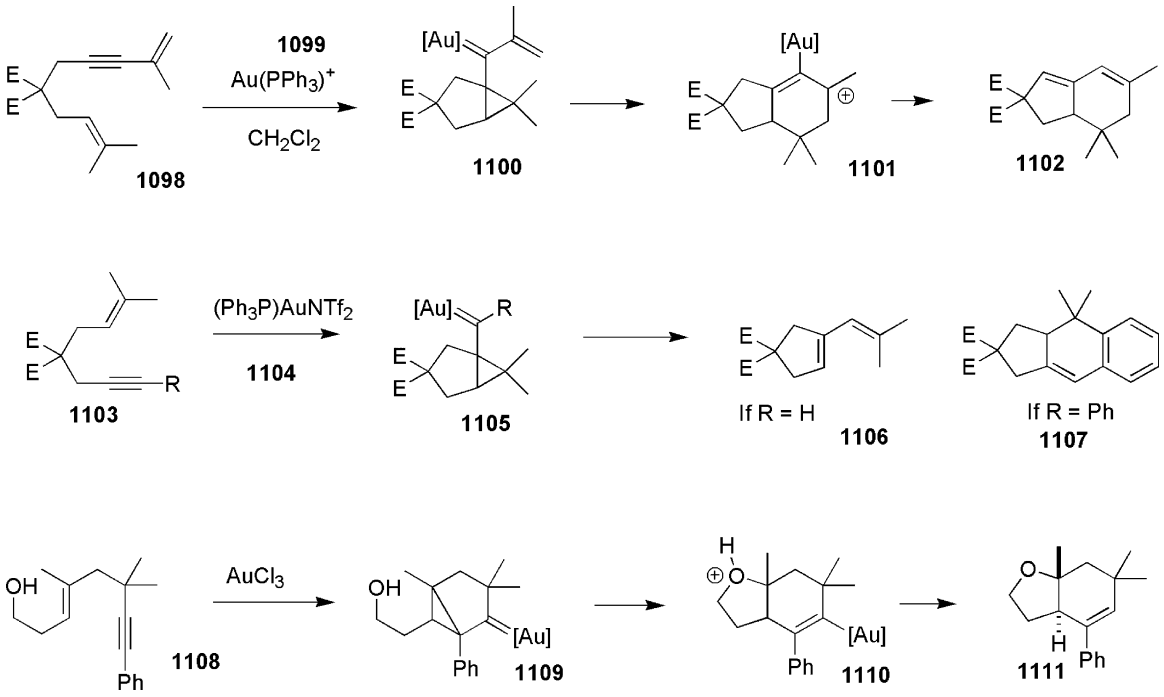
1.1.3.8. Group 11 carbene complexes. The structure, synthesis, and electrophilic reactivity of discrete copper carbene complexes (*e.g.* **1152**, Scheme 115) was reported [878]. Mononuclear copper carbene complexes are generated at equilibrium through



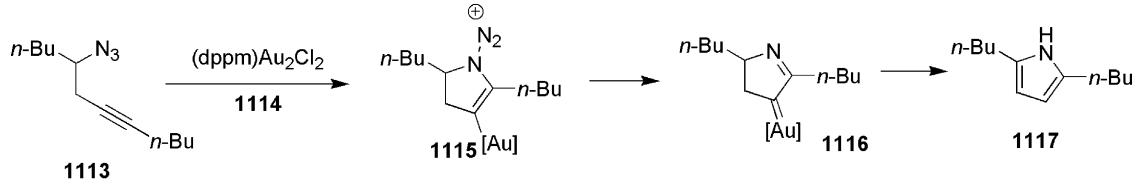
Scheme 110.

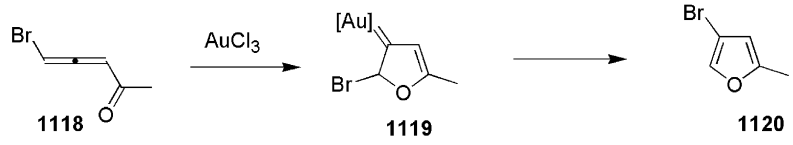
treatment of bridging dicopper carbene complex **1151** with arenes. The mononuclear complex was comparatively less stable and decomposed to tetraphenylethylene. Reaction of the dicarbene/monocarbene complex mixture with isocyanides led to the carbene dimerization product **1153**. Reaction with triphenylphosphine led to the ylide **1155**. Reaction with alkenes led to cyclopropanes (*e.g.* **1157**). All of the reactions were proposed to proceed through the mononuclear complex.

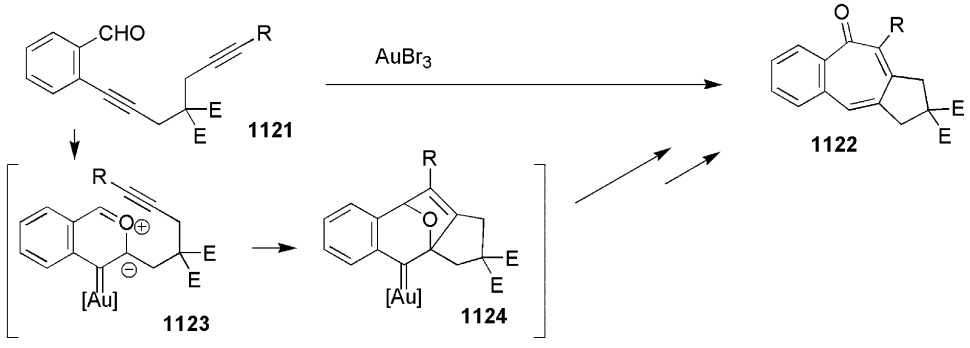
Various species featuring a double bond to copper were evaluated computationally [879]. The authors suggested that $Cp_2Cu{=}CH_2$ derivatives are stable enough to be prepared. The same paper also studied cerium carbene and carbyne complexes. The role of copper versus rhodium catalysts in the conversion of α-diazoamides to β-lactams (N–H insertion) or α,β-unsaturated amides (β-hydride elimination) was studied computationally [880]. The intermediacy of



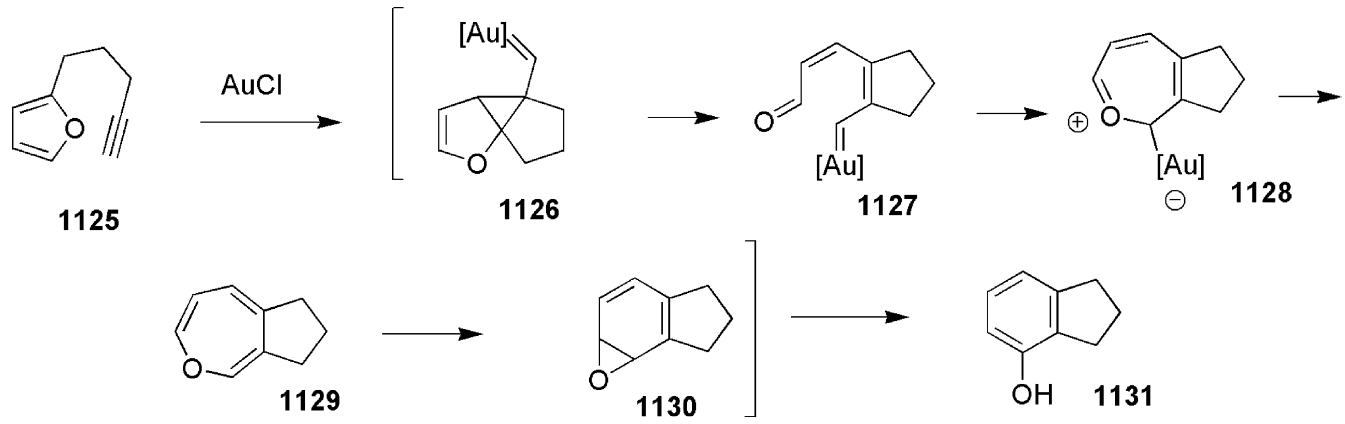
Scheme 111.



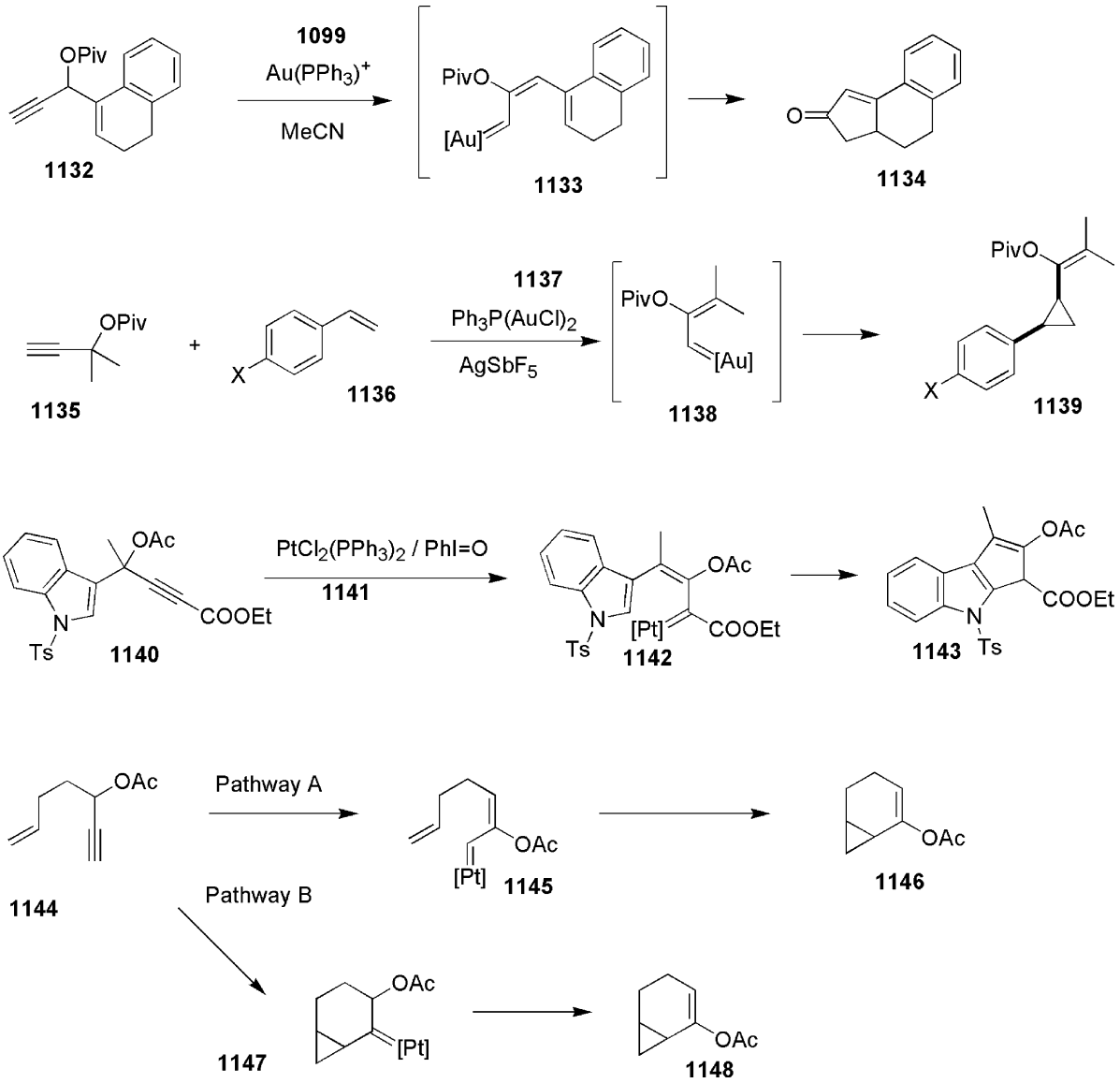




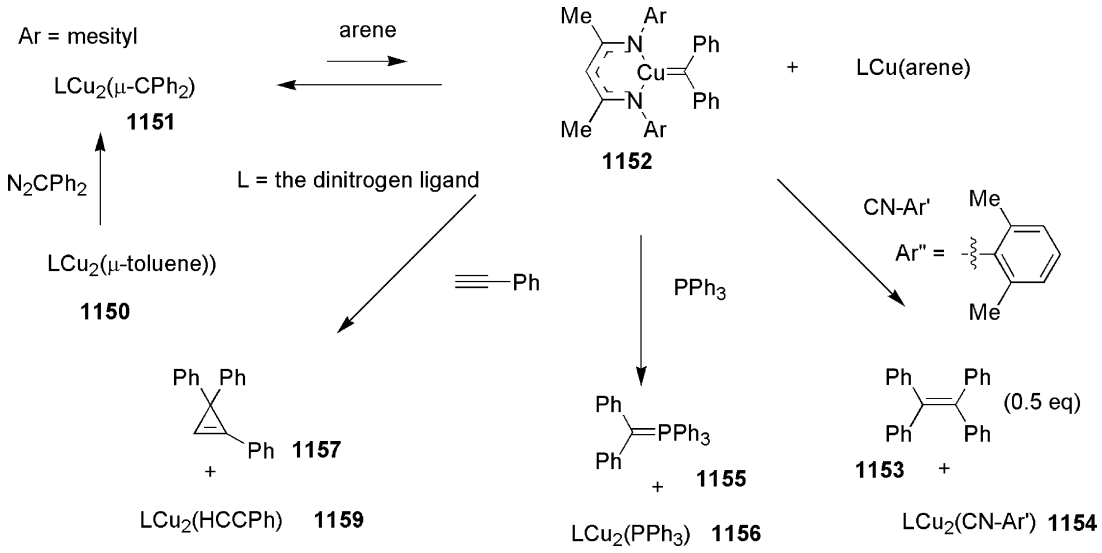
Scheme 112.



Scheme 113.



Scheme 114.



Scheme 115.

gold–carbene complexes in the NHC-gold catalyzed reaction of ethyl diazoacetate with aromatic compounds was discussed [881].

1.1.3.9. Lanthanide and actinide carbene complexes. Samarium carbene complexes (*e.g.* **1162**, **1164**, Scheme 116) were reported [882]. A bimetallic complex **1162** was obtained when the reaction was performed in toluene. An anionic monometallic complex **1164** was produced from the coupling of dianionic ligand **1160** and samarium(III) iodide–THF complex in toluene/THF. The bimetallic complex featured a shorter C–Sm bond more consistent with a carbene complex structure. The carbene complexes behave like Schrock carbene complexes. Reaction of either carbene complex with benzophenone led to carbonyl olefination product **1163**.

Thorium–carbene complexes were generated through the interaction of laser-ablated thorium atoms with methane [883]. The infrared of transient intermediates were compared with calculated IR spectra.

1.2. Metal–carbyne or metal–alkylidyne complexes

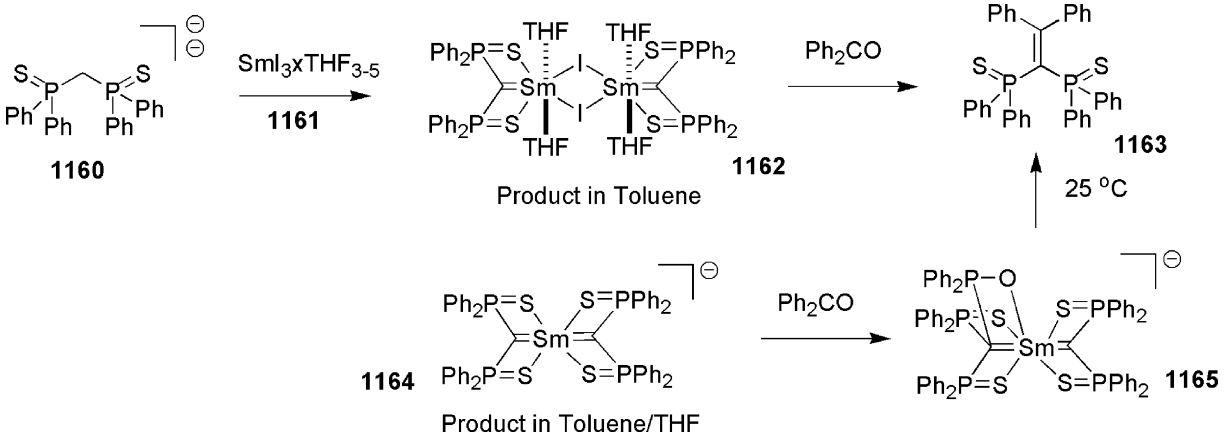
1.2.1. Review articles

Review articles featuring metal carbyne complexes which appeared in 2005 include: (1) a review of alkyne metathesis [884,885], and (2) electronic spectroscopy and photophysics of metal–carbyne complexes [886]. Some of the reviews of carbene complexes feature both carbene and carbyne complexes [90,109,122].

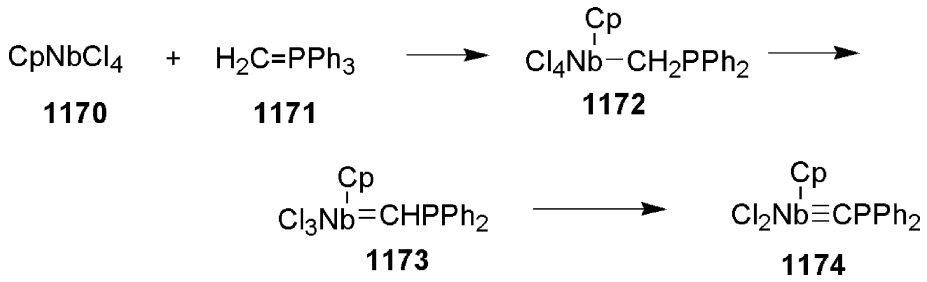
1.2.2. Synthesis and/or generation

Niobium carbyne complexes (*e.g.* **1174**, Scheme 117) were generated the reaction of niobium complex **1170** with methylenetriphenylphosphorane [887]. A mechanism involving nucleophilic addition followed by sequential elimination of two moles of HCl was proposed.

Several examples of the preparation of tris(amido)amine molybdenum–carbyne complexes (*e.g.* **1178**, **1182**, Scheme 118) from molybdenum halide complex **1175** was reported

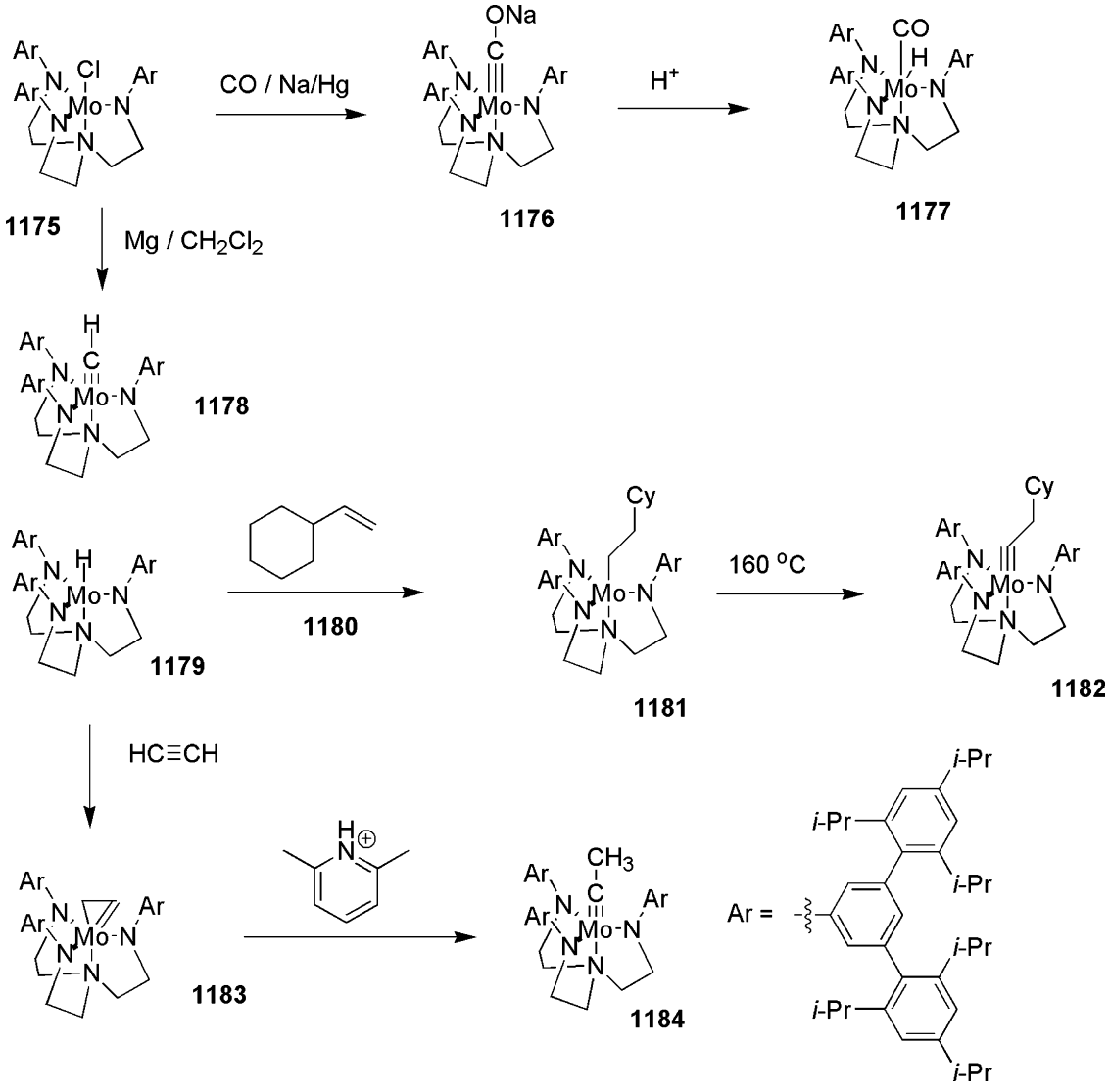


Scheme 116.

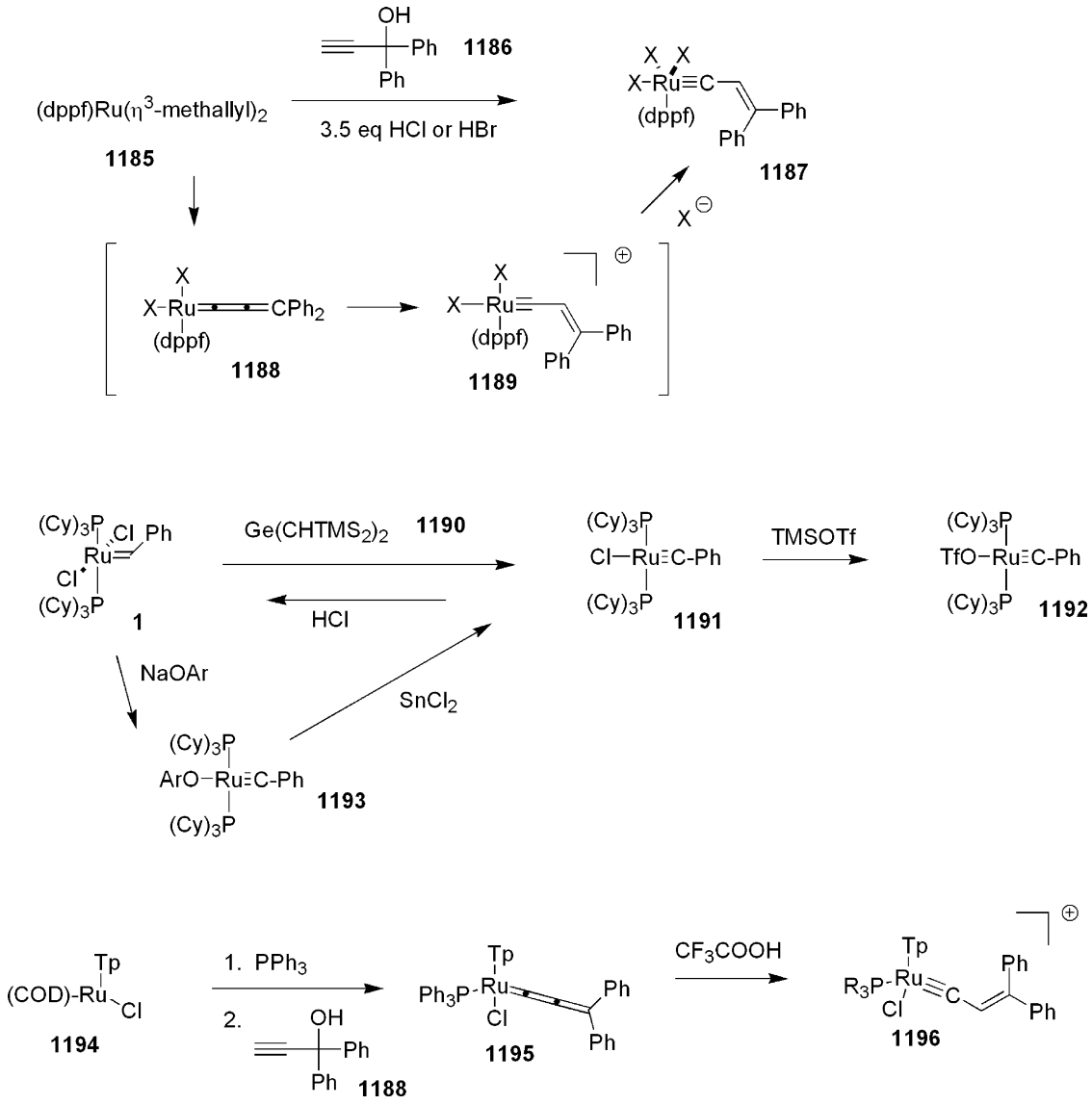


Scheme 117.

[888]. Reduction of the complex **1175** followed by reaction with CO led to the anionic CO complex **1176**, which is best represented by the carbyne complex resonance form. Protonation afforded the neutral hydrdido carbonyl complex **1177**. The terminal carbyne complex **1178** was obtained upon reduction of **1175** in the presence of dichloromethane. The hydrido complex **1179** led to the η^2-alkenyl complex **1183** upon treatment with acetylene. Protonation of complex **1183** led to the terminal carbyne complex **1184**. Reaction of molybdenum hydride **1179** with terminal alkenes led to the alkylmolybdenum complexes (*e.g.* **1181**), which afforded the carbyne complexes (*e.g.* **1182**) upon heating to 160 °C.

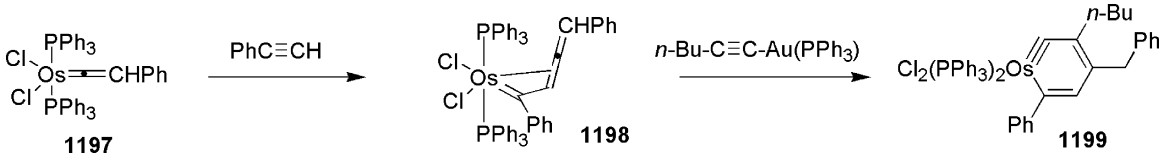


Scheme 118.

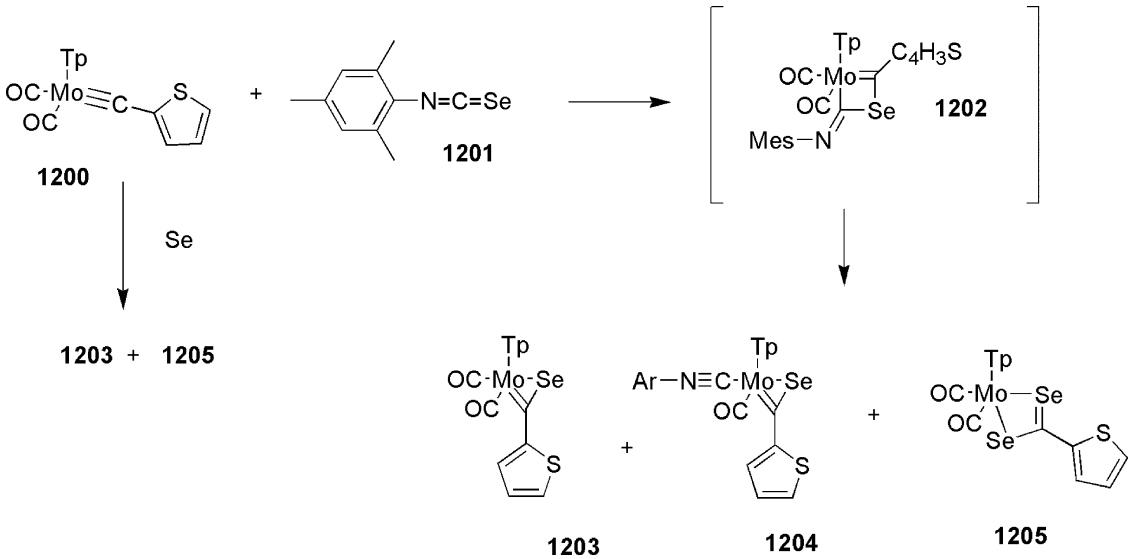


Scheme 119.

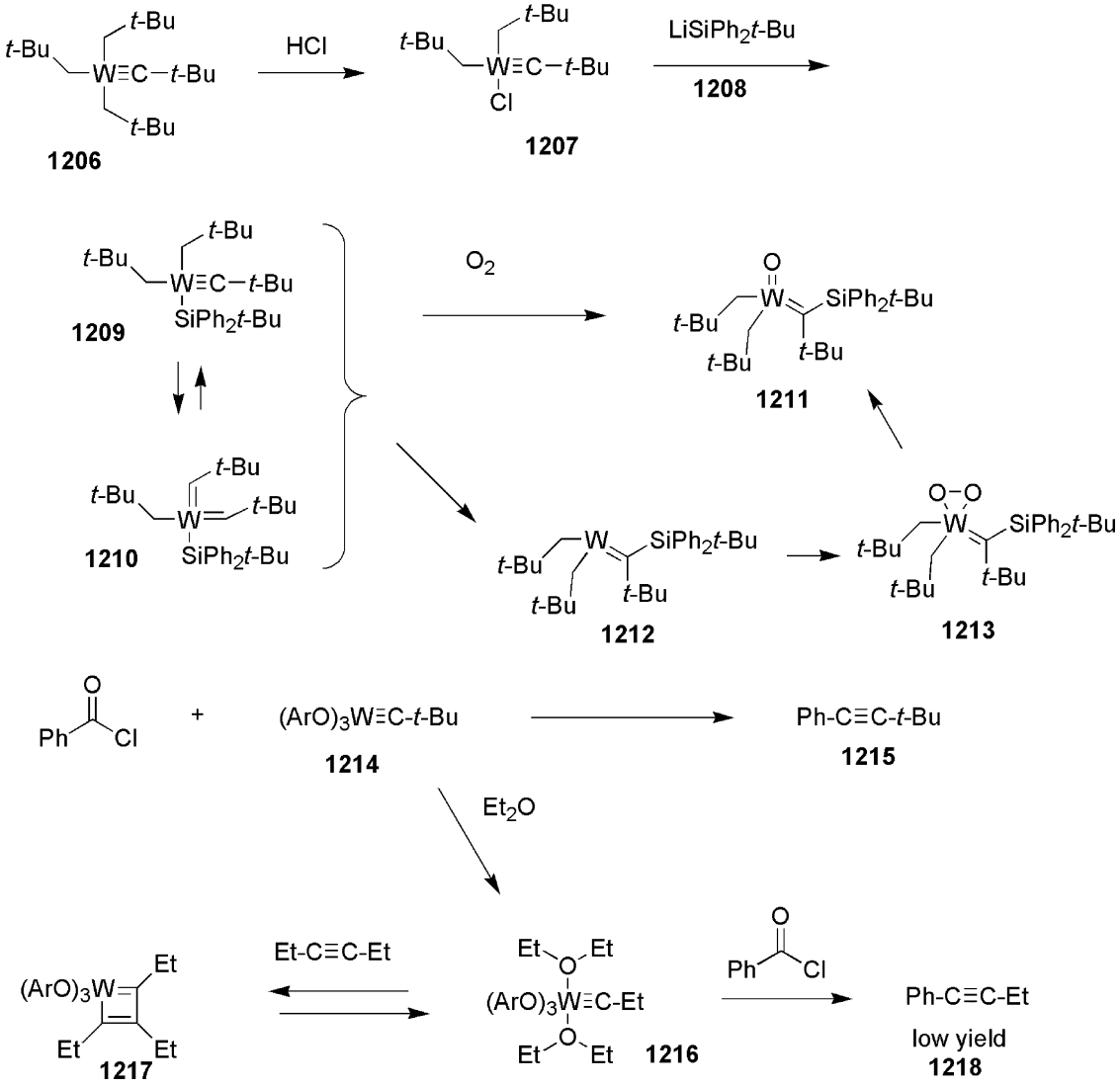
Ruthenium carbyne complexes (*e.g.* **1187**, Scheme 119) were prepared through the coupling of propargylic alcohols (*e.g.* **1186**) with ruthenium complex **1185** in the presence of acid [889]. A mechanism involving formation of the allenylidene complex **1188** followed by protonation was proposed. A dicationic cyclic dimer was obtained upon halide abstraction from carbyne complex **1187** using $AgSbF_6$. Ruthenium carbyne complexes (*e.g.* **1191**) were generated from Grubbs catalyst I [890]. Reaction of Grubbs catalyst I with germylene derivative **1190** led to the carbyne complex **1191**. Alternatively this same carbyne complex could be generated in a two step sequence involving treatment of Grubbs catalyst I with *p*-*t*-butylphenoxide to generate carbyne complex **1193** followed by ligand exchange using stannous chloride. Treatment of carbyne complex **1191** with HCl resulted in regeneration of Grubbs catalyst I. Reaction of carbyne complex **1191** with TMS-OTf led to triflate complex **1192**. Similar reactions were reported for alkylidene analogs of Grubbs catalyst I. Formation



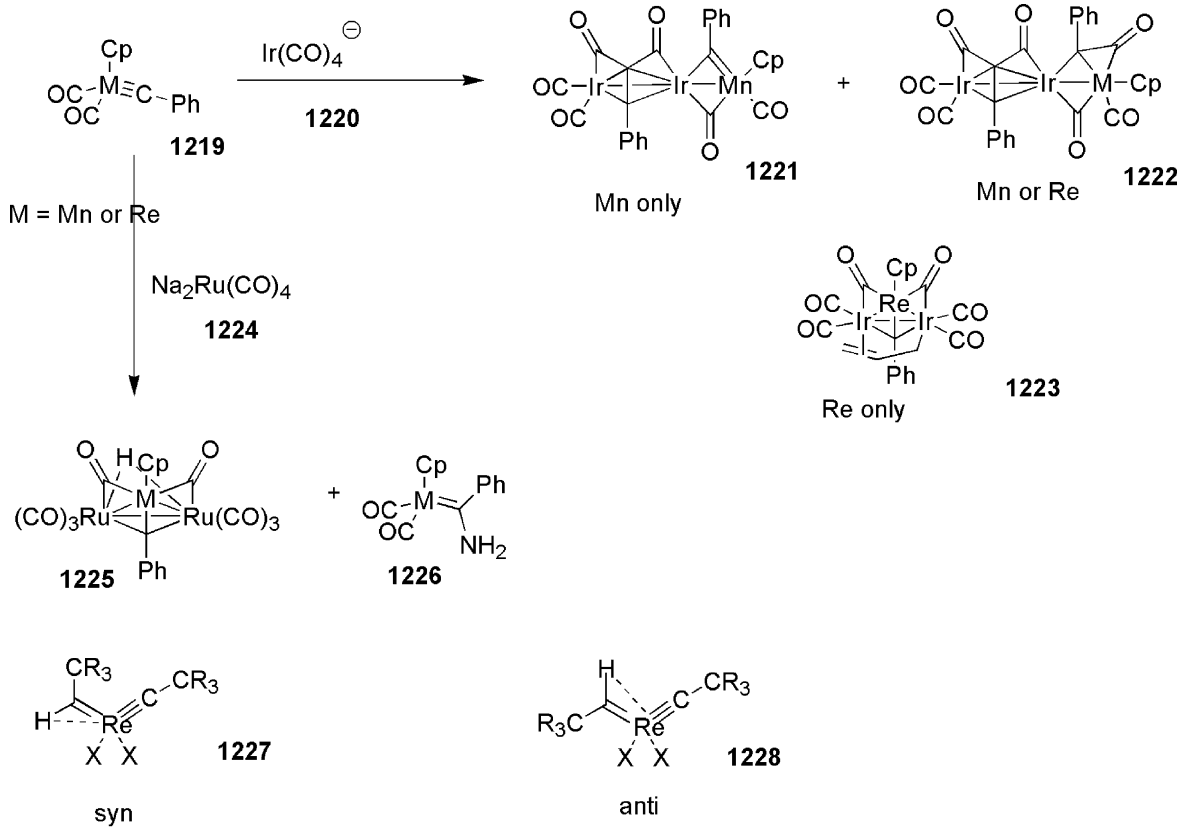
Scheme 120.



Scheme 121.



Scheme 122.

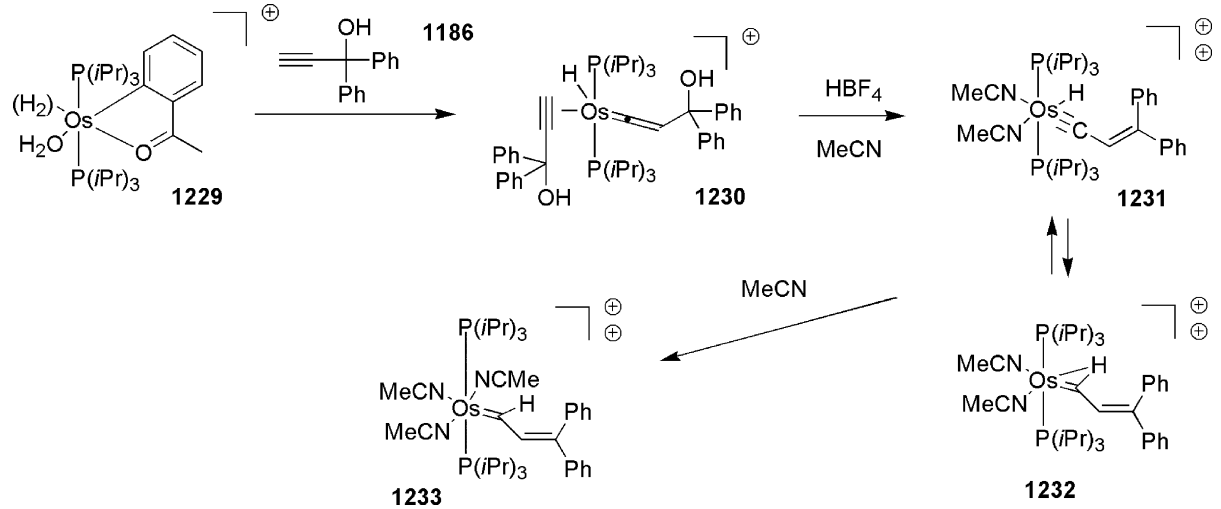


Scheme 123.

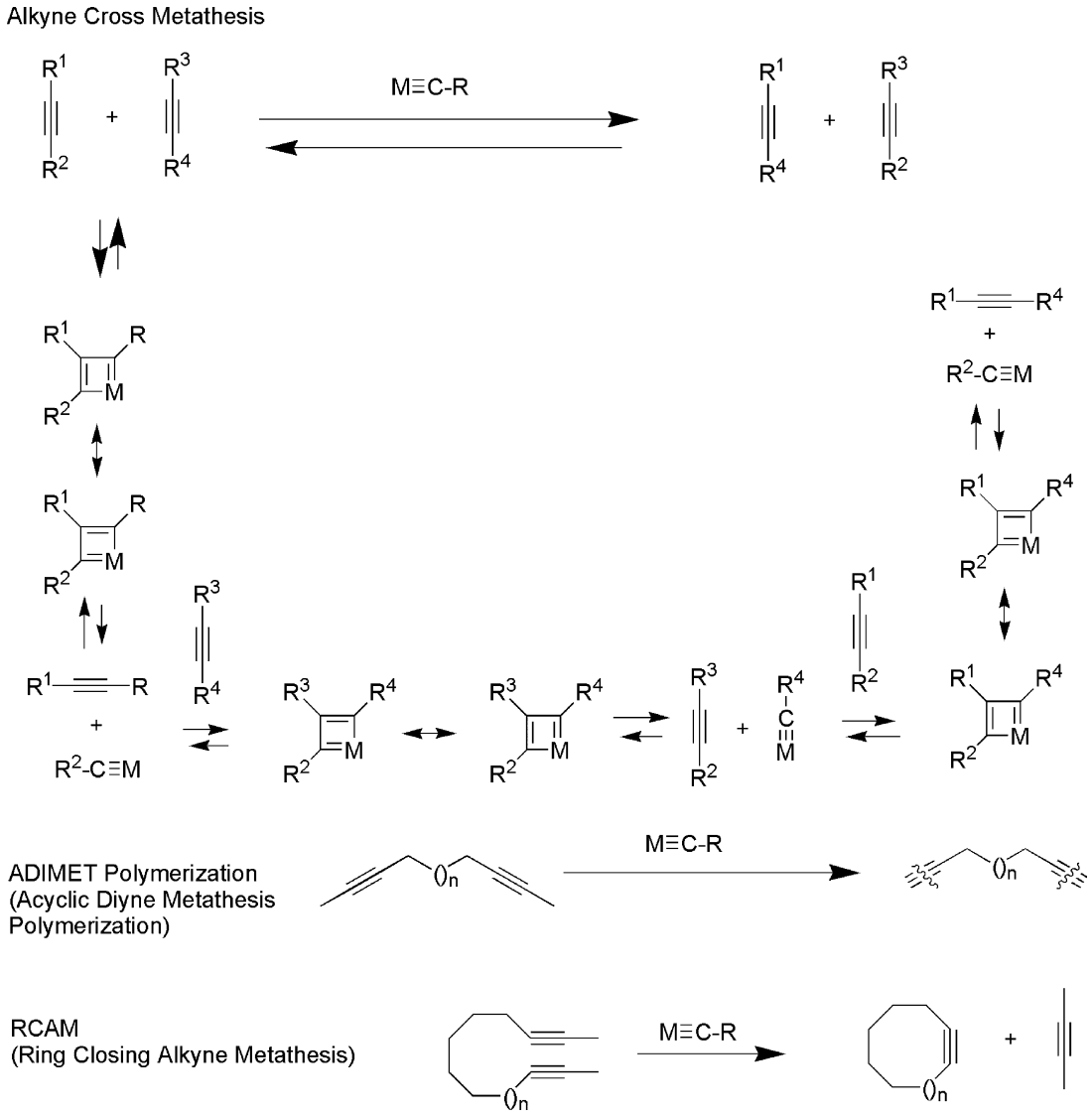
of ruthenium vinylidene, allenylidene (*e.g.* **1195**), and carbyne complexes (*e.g.* **1196**) was reported [891,892]. These complexes were prepared from coupling of ruthenium chloride complex **1194** with simple alkynes or propargyl alcohols (*e.g.* **1186**) according to the pathways of Schemes 87 and 93. Formation of cationic ruthenium carbyne complexes (*e.g.* **1196**) occurred upon protonation of ruthenium cumulene complexes (*e.g.* **1195**).

The stepwise formation of osmabenzyne complexes (*e.g.* **1199**, Scheme 120) was reported [893]. The allenylcarbene complex **1198** was formed by the coupling of the osmium vinylidene complex **1197** with phenylacetylene. Subsequent addition of terminal alkyne anion equivalents led to the osmabenzyne complex.

The generation of carbyne–molybdenum hydride complexes and carbene hydride complexes through reaction of laser-ablated



Scheme 124.



Scheme 125.

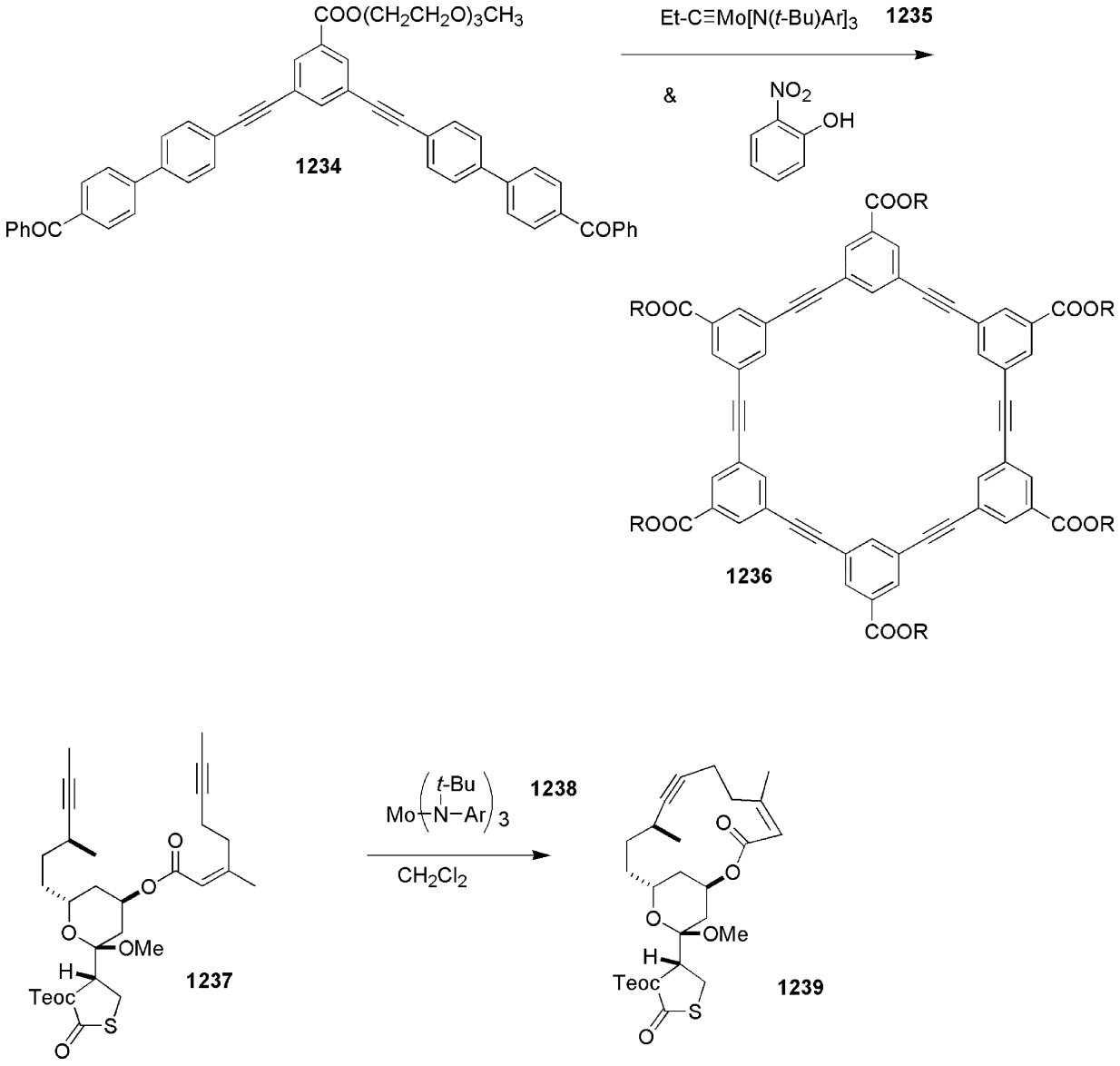
molybdenum atoms with methane and comparison of calculated IR spectra with observed spectra was reported [894].

Some papers in the carbene section feature significant segments on carbyne chemistry. These studies include references [599,600,724,733].

1.2.3. Reactivity

1.2.3.1. Addition reactions of metal–carbyne complexes. Selenation of molybdenum–carbyne complexes (*e.g.* **1200**, Scheme 121) was reported [895]. Reaction of the carbyne complex with mesityl isoselenocyanate (**1201**) led to the carbyne-selenium addition products, η^2-selenoacyl complexes **1203** and **1204**, accompanied by the diselenocarboxylate complex **1205**. The selenoacyl complexes were proposed to arise through [2 + 2]-cycloadduct **1202**. The isocyanide complex **1204** could not be prepared by a ligand exchange of **1203** with mesityl isocyanide. Reaction of carbyne complex **1200** with elemental selenium led to the dicarbonyl selenoacyl complex **1203** and the diselenocarboxylate complex **1205**.

Generation of tris(neopentyl)tungsten–carbyne complex **1206** (Scheme 122) followed by addition of HCl led to carbyne complex **1207** [896]. Treatment with a silyllithium reagent (*e.g.* **1208**) afforded an equilibrium mixture of carbyne complex **1209** and bis(carbene) complex **1210**. Treatment of this mixture with oxygen led to the carbene(oxo) complex **1211**. The mechanism of the oxidation process was evaluated computationally. The most reasonable pathway is silicon migration followed by reaction with oxygen. The interconversion of RCH_2–M≡CR and RCH=M=CHR complexes was studied computationally [897]. Binding of carbyne complex **1206** to silica and subsequent use of the resulting complex for heterogeneous alkene metathesis [898] and alkane metathesis [899] was reported. Alkynylation of acid chlorides using tungsten–carbyne complexes (*e.g.* **1214**) was reported [900]. The high-yielding reaction was limited to formation of *t*-butyl acetylenes. Some alkynylation success was observed if the reaction was performed in diethyl ether, which occurs through bis(ether)carbyne complex **1216**. Reaction of carbyne complex **1216** with



Scheme 126.

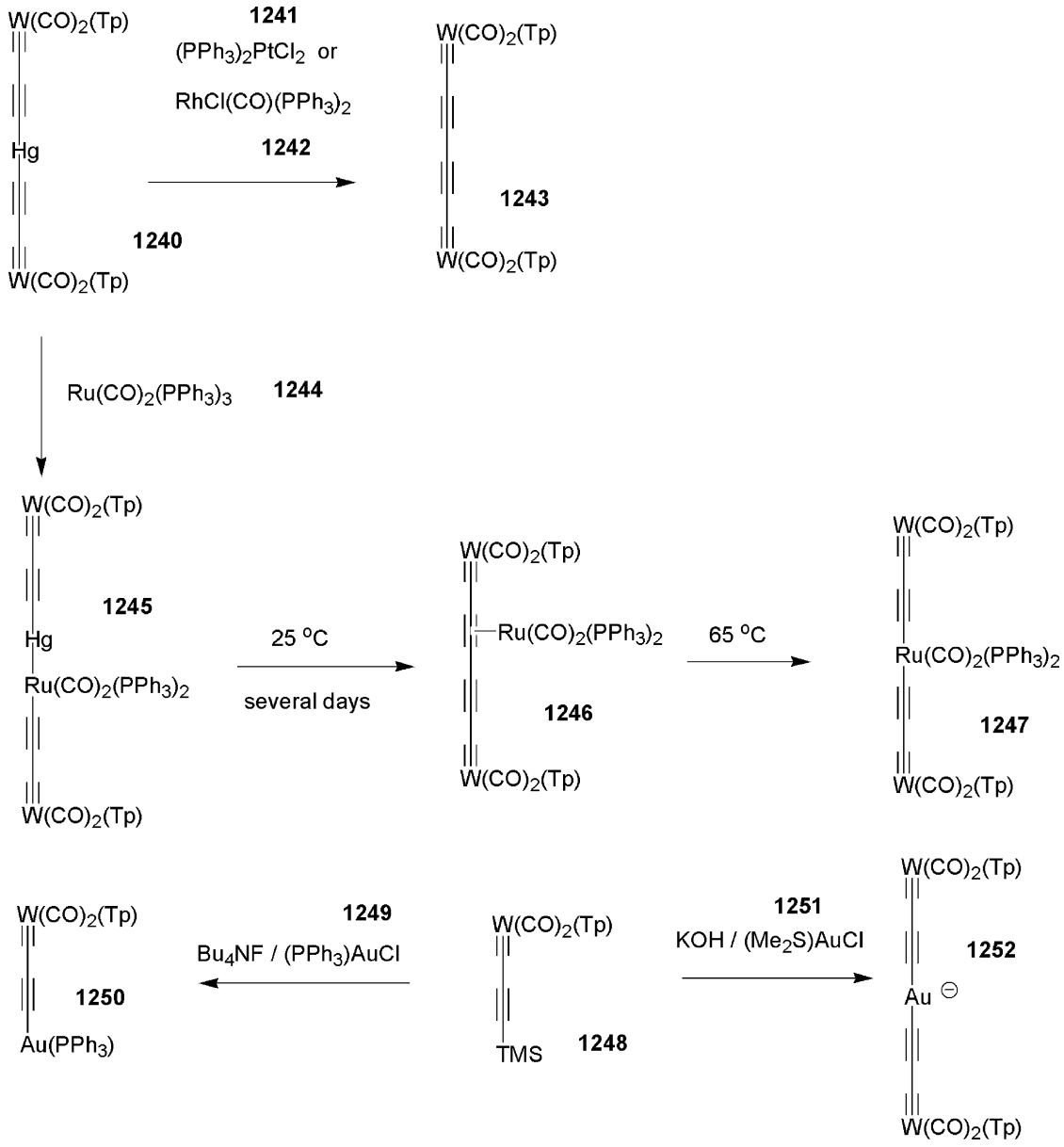
alkynes led to reversible metallacyclobutadiene (*e.g.* **1217**) formation.

The addition of metal carbonyl anions (*e.g.* **1220**, **1224**, Scheme 123) to carbyne complexes **1219** was reported [901]. Reaction with $Ir(CO)_4^-$ (**1220**) led to tri- and tetrametallic compounds **1221**–**1223**. Complex **1222** was obtained from either the manganese or the rhenium carbyne complexes. The manganese carbyne complex also afforded complex **1221**. The rhenium carbyne complex also afforded complex **1223** in addition to **1222**. The allyl ligand in complex **1223** was suggested to arise from the Cp ligand. Coupling with $Ru(CO)_4^{2-}$ (**1224**) led to complex **1226** and a tetranuclear complex, accompanied by aminocarbene complex **1226**. The aminocarbene complex was determined to arise from addition of $NaNH_2$ (an impurity in the metal carbonyl dianion) to the starting carbyne complex. The interconversion of syn and anti-rhenium-carbene(carbyne) complex **1227/1228** was evaluated computationally [902]. The degree of agostic interaction was highly dependent on the identity of the X groups. The agostic interaction was minimal for complexes that feature π-donating X groups. Syn and anti-interconversion occurs through simple bond rotation.

Dicationic osmium carbyne complexes (*e.g.* **1231**, Scheme 124) were prepared the reaction of chelating *o*-acetophenone osmium complex **1229** with diphenylpropargyl alcohol (**1186**) followed by HBF_4 [903]. Carbyne complex **1231** is in equilibrium with agostically-ligated carbene complex **1232**. Reaction of **1231/1232** with acetonitrile led to the carbene complex **1233**.

1.2.3.2. 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 125.

Several reports using alkyne metathesis for natural product synthesis and for polymer synthesis appeared in 2005;

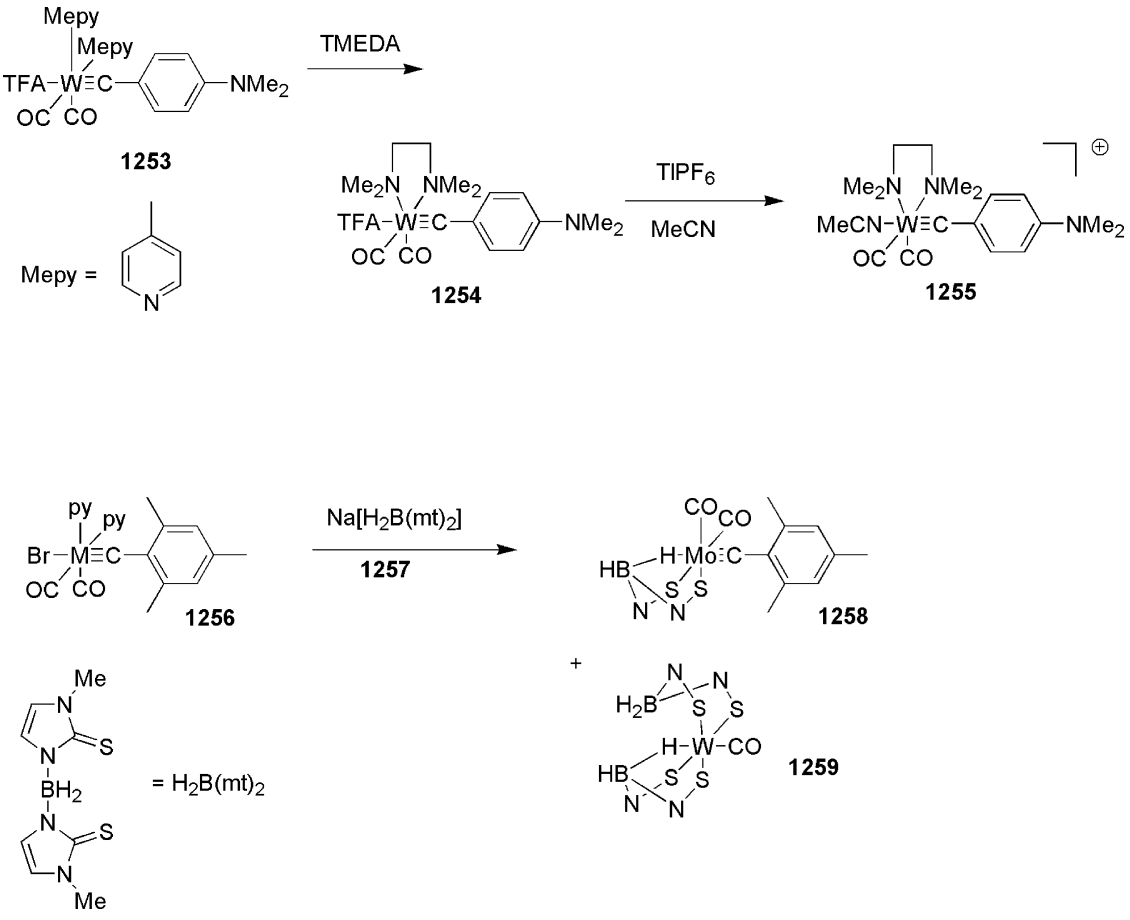


Scheme 127.

representative alkyne metatheses are depicted in Scheme 126. Various molybdenum carbonyl species were tested as catalysts for Adimet polymerization [904]. Carbyne complex **1235** was a catalyst for cyclic hexamerization of bis(alkyne) derivative **1234** leading to hexaalkyne **1236** [905]. Ring closing alkyne metathesis of **1237** was used as a key step in the total synthesis of lantruculin A [906].

1.2.3.3. Other processes involving metal–carbyne complexes. Several examples of all carbon-linked bimetallic carbyne complexes were reported; examples are depicted in Scheme 127. Treatment of bis(alkynyl)mercury compound **1240** with Pt(II) or Rh(I) species induces reductive elimination to afford the bis(carbynyl)ditungsten complex **1243** [907]. Reaction with $Ru(CO)_2(PPh_3)_2$ (**1244**) led to the alkynylruthenium–alkynylmercury complex **1245**, which slowly undergoes reductive elimination to afford the ruthenium complexed carbon-linked bis(tungsten) complex (**1246**) [908]. Thermolysis led to the bis(alkynylruthenium) complex **1247**. Reaction of alkynylcarbyne complex **1248** with fluoride ion in the presence of $(PPh_3)AuCl$ (**1249**) led to carbon-linked bimetallic complex **1250** [909]. A bis(alkynyl) gold complex (**1252**) was obtained from reaction of complex **1248** with gold complex **1251**. Addition of ruthenium hydrides to the C≡C of bis(carbyne)-linked ditungsten complexes ($Tp'(CO)_2W{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}W(CO)_2Tp'$) was also reported [910].

Synthesis and ligand-exchange reactions were reported for tungsten–carbyne complexes (*e.g.* **1253**, **1256**, Scheme 128) [911]. Photoluminescence and fluorescence studies were reported for the complexes. Ligand exchange reactions using the $H_2B(mt)_2^-$ ligand were also reported [912]. The molybdenum complex led to the S- and H-coordinated complex **1258**. The



Scheme 128.

tungsten complex led to the complex **1259** where the carbine ligand has been completely eliminated.

1.2.4. Mechanistic/structural studies

Several mechanistically/structurally-oriented studies of the reactions of metal–carbyne complexes were reported in 2005. The study of phase transitions for tungsten carbyne complexes IR and Raman spectra were reported [913].

Acknowledgements

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