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Review

The chemistry of the carbon–transition metal double and triple bond: Annual survey covering the year 2004☆

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Contents

Abstract

This is a review of papers published in the year 2004 that focus on the synthesis, reactivity, or properties of compounds containing a carbon–transition metal double or triple bond.

Keywords: Multiple bond; Carbene complexes; Carbyne complexes; Metathesis

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 2004 [1–5]. 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 [6–9].[1] This area was reviewed several times in 2004 [10–17]. Another class of stable carbene complexes, amino/phosphine-stabilized or Bertrand carbenes, are less well developed and have been included in this article

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

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[1] Theoretical evidence for π-bonding has been suggested for a silver carbene complex.

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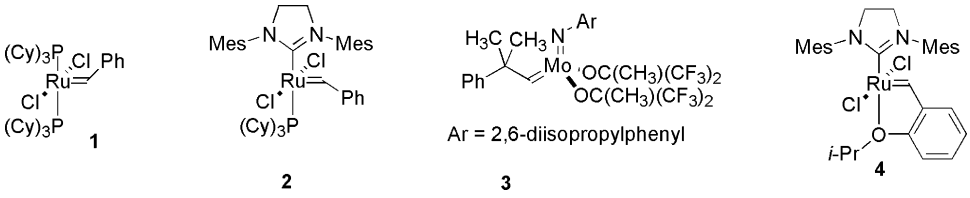


Fig. 1. Structures of alkene metathesis catalysts 1–4.

[18]. A comparison of the electronic properties of several classes of carbene ligands was reported in 2004 [19]. This survey has been divided into two sections, metal carbene (or alkylidene) complexes and metal carbyne (or alkylidyne) complexes; the carbene complex section represents the vast majority of this article. The metal carbene section has been organized according to metal, starting from the left side of the Periodic Table. The Ionic Model [20] 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 [21])

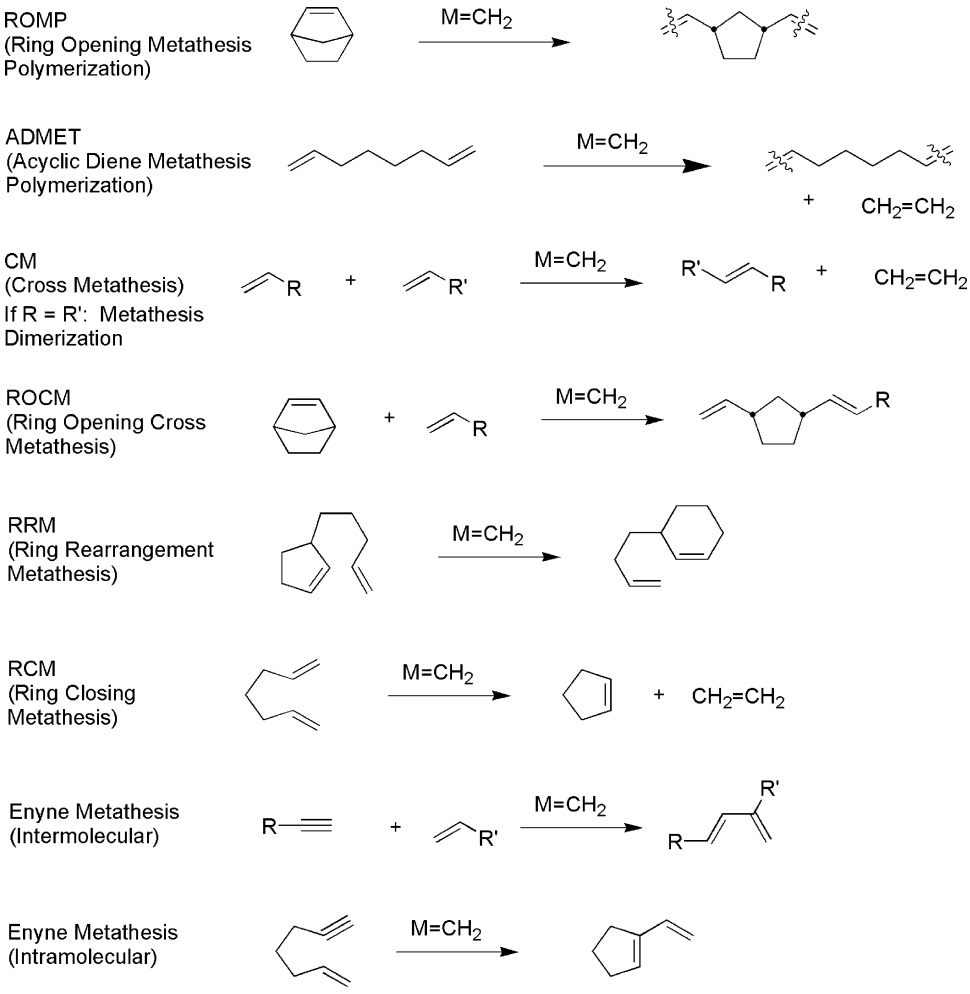
DFT	Density functional theory
Grubbs catalyst I	Structure **1** (Fig. 1)
Grubbs catalyst II	Structure **2** (Fig. 1)
Schrock catalyst	Structure **3** (Fig. 1)
Hoveyda–Grubbs catalyst	Structure **4** (Fig. 1)

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 2004. Many



Scheme 1.

articles focusing on some aspect of carbene complex-initiated olefin metathesis were published, including the following specific subjects: (1) general metathesis [22–24]; (2) alkene metathesis directed toward organic synthesis [25–28]; (3) industrial applications of alkene metathesis [29]; (4) ring-opening cross-metathesis reactions [30]; (5) asymmetric metathesis [31]; (6) ring rearrangement metathesis [32]; (7) enyne metathesis [33,34]; (8) ADMET polymerization [35]; (9) aqueous phase alkene metathesis [36]; (10) synthesis of oxygen and nitrogen heterocycles using RCM [37]; (11) synthesis of phosphorus and sulfur heterocycles using RCM [38]; (12) use of alkene metathesis in combinatorial chemistry [39]; (13) metathesis of unsaturated fatty acids [40]; (14) olefin metathesis using tungsten and molybdenum imido alkylidenes [41]; (15) vinylidene ruthenium complexes in catalysis [42]; (16) allenylidene–ruthenium complexes as metathesis catalyst precursors [43]; (17) bidentate ruthenium carbene complexes for alkene metathesis [44]; (18) heterogeneous catalysts for alkene metathesis [45]; (19) supported catalysts for alkene metathesis [46]; (20) tandem alkene isomerization and metathesis [47]; (21) procedures for enyne metathesis [48]; (22) procedures for RCM using chlorinated alkenes [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) lobelia alkaloids [50]; (2) epothilone derivatives [51]; (3) brevitoxin derivatives [52]; (4) polyfunctional pyrroles [53]; (5) allylsilanes [54]; (6) amino acid analogs [55]; (7) silicon-containing compounds [56]; (8) marine-derived polyethers [57,58]; (9) radicol derivatives [59]; (10) glycolipids bridged by macrocycles [60]; (11) rotaxanes and catenanes built around transition metals [61]; (12) non-rusty catenanes [62]; (13) pheromones [63,64]; (14) welwitindolinones [65]; (15) tetrahydropyridines [66]; (16) nitrogenated organofluorine derivatives [67]; (17) vinyl phosphonates [68]; (18) stilbenes [69]; (19) bridged peptides [70]; (20) propylene (commercial syntheses) [71]; (21) Group IV bent metallocenes [72]. Additional review articles include some metathesis segments. Articles in this category focus on the following subjects: (1) general use of transition metals in organic synthesis [73]; (2) synthetic uses of compounds that contain diastereotopic groups [74]; (3) multifunctional catalysts [75]; (4) tandem catalysis [76]; (5) catalytic polymerization [77,78]; (6) dendritic transition metal catalysts [79]; (7) transition metal catalyst immobilized on mesopourous silica [80]; (8) heterogeneous well-defined catalysts for metathesis of alkenes and other bonds [81]; (9) silsesquioxane coordination chemistry [82]; (10) transition metal catalysts for combinatorial chemistry [83]; (11) aqueous phase polymerization [84]; (12) carbon–carbon bond formation in supercritical fluids [85]. Several reviews on carbene complex chemistry featuring some aspect other that metathesis appeared in 2004. These reviews include the following subjects: (1) cycloaddition reactions of Group VI Fischer carbene complexes [86]; (2) photoinduced reactions of metal carbene complexes [87]; (3) chemistry of α,β-unsaturated carbene complexes [88]; (4) synthesis of heterocycles using Fischer carbene complexes [89]; (5) synthesis and reactivity of metal–vinylidene complexes and higher cumulenes [90–100]; (6) mechanistic aspects of metal vinylidene complex formation [101]; (7) polymerization of 1,6-diynes using molybdenum carbene complex initiators [102] and other initiators [103]; (8) the role of ruthenacyclopentatriene complex in ruthenium-mediated coupling of alkynes [104]; (9) carbonyl olefination using metal carbene complexes [105]; (10) metallocene carbene chemistry [106]; (11) metal cyclopropylcarbenes as intermediates in the coupling of alkynes with alkenes and furans [107]; (12) alkylidene–lanthanide complexes [108]; (13) catalytic additions to fatty compounds [109]. Although not specifically focusing on metal–carbene complexes, some review articles place some emphasis on this subject. Subjects reviewed in this category include: (1) new bonding modes of tertiary phosphines, arsines, and stibines [110]; (2) alkynyl–metal complexes [111]; (3) structure and reactivity of coordinately unsaturated half-sandwich iron, ruthenium, and osmium complexes [112]; (4) *N*-acylhydrazones, which can be accessed through oxidation of Fischer carbene complexes [113]; (5) nonlinear optical properties of metal acetylides and metal vinylidene complexes [114]; (6) nonperfect synchronization in aromatic systems [115]; (7) the versatility of the catalyst RuCl(COD)(C_5Me_5) [116]; (8) ruthenium-promoted radical processes [117]; (9) organic synthesis using methyl trioxorhenium [118]; (10) ruthenium-catalyzed C–C bond formation [119]; (11) metal-supported synthesis methods [120]; (12) nanometric scale catalysis [121]; (13) bis(trimethylsilylacetylene) complexes of titanocenes and zirconacenes [122]; (14) organometallic C–H activation [123,124]; (15) development and use of bulky monodentate ligands [125]; (16) Group V metal complexes [126,127]; (17) complexes of Groups VIII–X [128]; (18) platinum complexes [129]. Article commentaries on carbene complexes were also reported, including: (1) cyclopropanation with Fischer acyloxycarbene complexes [130]; (2) group transfer of nickel imido, phosphinidine and carbene complexes to ethylene [131].

1.1.2. Alkene metathesis

Alkene metathesis was the most common reaction process reported for metal–carbene complexes in 2004, 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 discrete transition metal–carbene complex or metathesis reactions that offer significant discussion of the carbene complex intermediates in this reaction have been included here. Distinct modes of alkene metathesis are depicted in Scheme 1.

1.1.2.1. General studies of alkene metathesis catalysts. Numerous attempts to develop new catalysts for alkene metathesis were reported in 2004; some representative examples are depicted in Fig. 2. Several derivatives of the Grubbs and Schrock catalysts were synthesized and tested in their ability to undergo either ROMP or RCM processes, including: (1) a linear alkyl chain analog of Grubbs catalyst I (**5**) for ROMP in liposomes [132]; (2) an analog of Grubbs catalyst I (**6**) that features

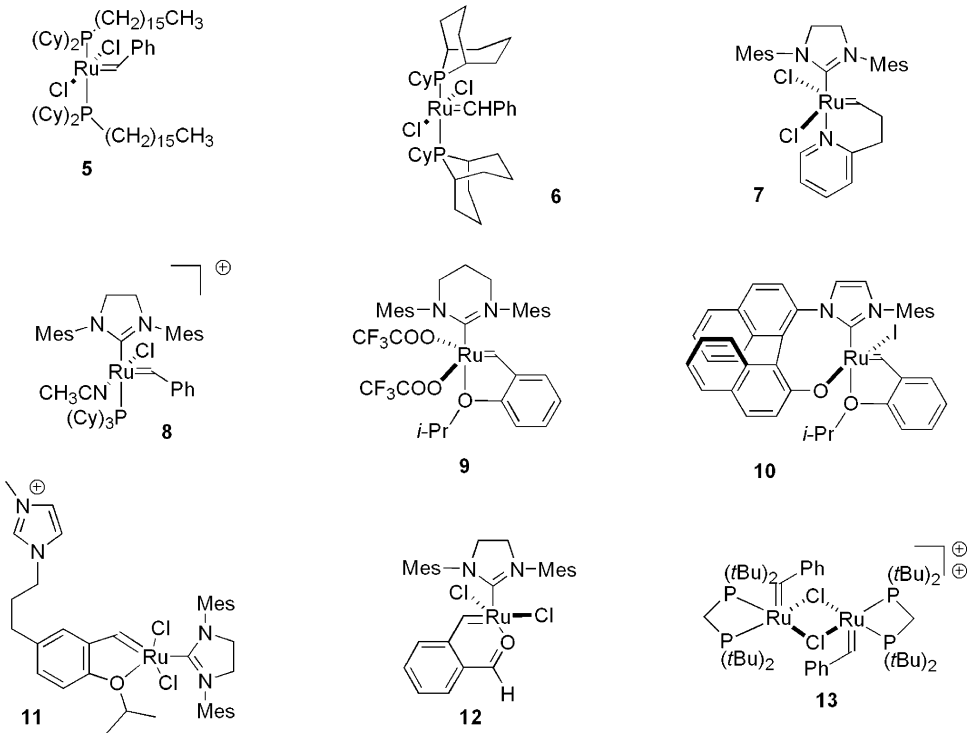
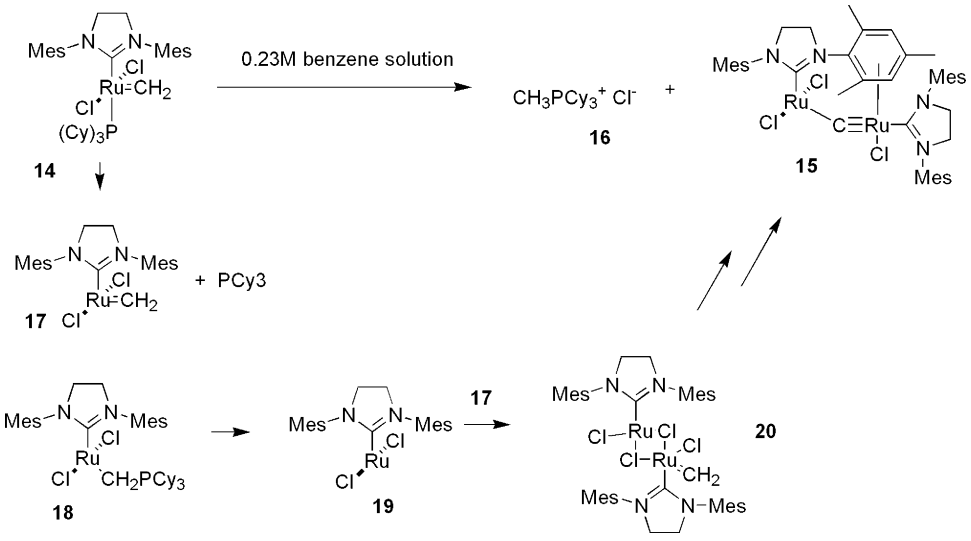


Fig. 2. Representative examples of new catalysts for alkene metathesis.

9-phosphabicyclo[3.3.1]nonane ligands [133]; (3) analogs of Grubbs catalyst II that feature six-membered ring *N*-heterocyclic carbene ligands [134]; (4) hydroxyalkyl derivatives of Grubbs catalyst II and use of the hydroxyl function to immobilize the catalyst [135]; (5) analogs of Grubbs catalyst II (e.g. **7**) that feature chelated pyridine rings [136]; (6) a cationic analog of Grubbs catalyst II (**8**) [137]; (7) aromatic ring substituted analogs of the Hoveyda–Grubbs catalyst [138–140]; (8) trifluoroacetate and/or aromatic ring substituted analogs of the Hoveyda–Grubbs catalyst [141,142]; (9) analogs of the Hoveyda–Grubbs catalyst that feature a six-membered ring heterocyclic carbene ligand (e.g. **9**) [143]; (10) chiral analogs of the Hoveyda–Grubbs catalyst (e.g. **10**) [144]; (11) iminium salt analogs of the Hoveyda–Grubbs catalyst (e.g. **11**) for RCM reactions in ionic liquids [145]; (12) fluorinated analogs of the Hoveyda–Grubbs catalyst for fluorous phase alkene metathesis [146]; (13) ruthenium carbene complexes that feature a carbonyl group chelate (e.g. **12**) [147]; (14) pyrazolylborate-ligated ruthenium carbene complexes [148]; (15) polyethylene glycol-bound analogs of the Hoveyda–Grubbs catalyst [149]; (16) ruthenium carbene complexes bound to single-walled nanotubes [150]; (17) mononuclear and dinuclear ruthenium carbene complexes that feature *cis* chelating phosphine ligands (e.g. **13**) [151,152]; (18) polymer supported asymmetric molybdenum metathesis catalysts [153]. A new synthesis of Grubbs catalyst I was reported [154]. Several patents were issued for the synthesis and development of metal–carbene containing olefin metathesis catalysts [155–158].

The synthesis and reactivity of methylene–ruthenium complexes (e.g. **14**, Scheme 2), hypothetical chain carrying intermediates in catalytic alkene metathesis, was reported [159]. Dilute solutions of **14** in refluxing benzene transform to the bridging carbide–ruthenium complex **15** and phosphonium salt **16**. A mechanism involving phosphine-assisted displacement of the carbene ligand followed by coupling of non-carbene intermediate complex **19** with intermediate carbene complex **17** to afford the binuclear species **20**. Elimination of two moles of HCl from **20** affords complex **15**.

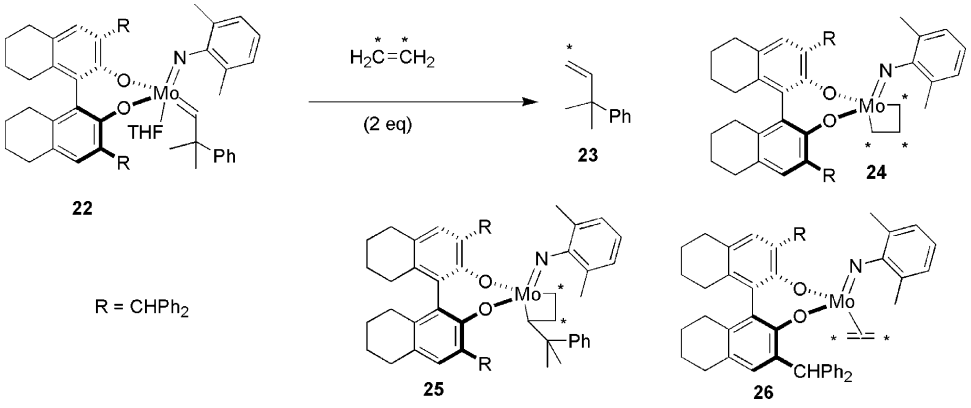
The reaction of asymmetric metathesis catalysts (e.g. **22**, Scheme 3) with C-13 labeled ethylene was reported [160]. Several of the expected compounds from this transformation, including metallacyclobutanes **24** and **25** and π-ethylene complex **26** could be observed by C-13 NMR. Other general studies of alkene metathesis where carbene complexes were discussed include: (1) theoretical mechanistic investigations of ruthenium carbene-catalyzed alkene metathesis [161,162]; (2) theoretical studies of the origins of stereoselectivity in ruthenium-catalyzed asymmetric alkene metathesis (asymmetric induction was attributed to the chiral folding of the N-bonded aromatic groups of the *N*-heterocyclic carbene ligand) [163]; (3) synthesis of polymer-bound phosphines designed to scavenge ruthenium byproducts from alkene metathesis reactions [164]; (4) studies of the beneficial effect of ethyl diazoacetate addition to non-carbene complex initiated ruthenium metathesis reactions [165]; (5) a comparison of methylaluminoxane as a ROMP catalyst with and without transition metal additives [166]; (6) studies of the effect of transition metal additives on ruthenium carbene-catalyzed ROMP reactions [167]; (7) catalysis of ROMP of norbornene by $W(CO)_4py_2$ and isolation of low molecular weight byproducts suggestive of carbene complex intermediates [168]; (8) catalysis of ROMP by norbornene–tungsten complexes in halogenated solvents and correlation of byproducts with intermediate tungsten carbene complexes [169]; (9) discussion of termina-



Scheme 2.

tion/deactivation steps in the metathesis of polyunsaturated fatty acid ester using tetramethyltin and bis(aryloxy)tungsten(VI) complexes [170]; (10) computational evaluation of pathways for decomposition of ruthenium metathesis catalysts [171]; (11) a DFT study of the degradation of ROMP polynorbornenes via cross-metathesis with linear alkenes [172]; (12) use of "no-D NMR" to evaluate the progress of metathesis reactions [173].

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 involving a norbornene derivative and another alkene accounted for a large fraction of all reports of the ROMP reaction in 2004 (Fig. 3). Numerous substituted norbornenes have been subjected to ROMP using metal carbene complexes, including those possessing the following structural features: (1) a *p-t*-butylbenzyloxy-substitutent [174]; (2) sulfonyl chloride-substituents (e.g. **27**) [175]; (3) a bis(diphenylamino)fluorene group (e.g. **28**) [176]; (4) two cinnamyl groups (followed by cross-linking of the polymer through [2 + 2]-cycloaddition) [177]; (5) a 7-alkoxy group [178]; (6) a thiazolium cation group (e.g. **29**) [179]; (7) a carbodiimide group [180]; (8) an *N*-hydroxysuccinimide derived ester group (e.g. **30**) [181]; (9) an *O*-linkage to phosphonate ester groups [182]; (10) a carborane group [183]. Other norbornene derivatives subjected to ROMP include: (1) norbornenes fused to an anthracene ring [184]; (2) benzo-oxanorbornadiene (**31**) [185]; (3) dicyclopentadiene [186]; (4) (bis)norbornenes (e.g. **32**) for the cross-linking of ROMP polymers [187]; (5) 7-alkylidenenorbornene derivatives (e.g. **33**) [188]; (6) norbornenes attached to polymeric phosphazenes [189]; (7) norbornenes attached to a polylactate group [190]; (8) bis(norbornenyl-acac)palladium(II) complexes (e.g. **34**) [191]; (9) norbornenes fused to a ruthenium-complexed phenanthroline ring (**35**) [192]; (10) norbornenes bound to a gold surface through thiol groups [193]. ROMP copolymerizations reported in 2004 include: (1) co-ROMP of alkylnorbornenes and norbornenes featuring chelated zinc–quinoline complexes [194]; (2) block copolymers of indomethacin-linked norbornenes and polyether-linked norbornenes [195], and (3) copolymerization of cyclooctene and diphosphine–ruthenium complexes where the phosphines are part of a norbornene ring (e.g. **36**) [196]. Other ring systems that have been subjected to ROMP reactions include: (1) cyclobutenes [197]; (2)



Scheme 3.

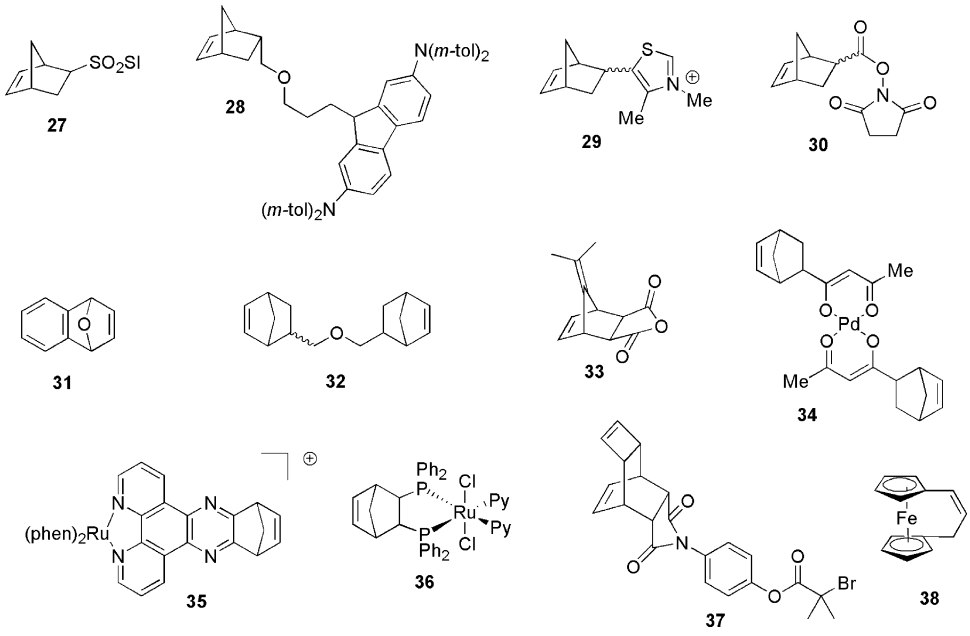


Fig. 3. Representative substrates for the ROMP reaction.

cyclobutenes fused to the bicyclo[2.2.2]octene ring system (e.g. **37**) [198]; (3) cyclopentenes [199]; (4) alkene-bridged ferrocenes (e.g. **38**) [200]; (5) diene-bridged ferrocenes [201]. An examination of the effect of various functionalized additives on the ROMP of norbornene was also reported [202]. Several patents were awarded for various aspects of ROMP reactions [203–209]. A patent was awarded for the synthesis of cyclic polymers using ROMP [210].

Several examples using carbene complexes to initiate acyclic diene metathesis (ADMET, see Scheme 1) polymerization reactions were reported in 2004. Substrates subjected to ADMET polymerization are depicted in Fig. 4, and include: (1) amino acid containing dienes (e.g. **40**) [211]; (2) 1,1-bis(*n*-alkenyl)propene derivatives [212]; (3) 2,6-dialkyl-1,4-divinylbenzene derivatives (e.g. **41**) [213]; (4) bis[4-(4-penten-1-yloxy)]benzoate derivatives (e.g. **42**) [214]. Patents were awarded for the partial retro-ADMET depolymerization of nitrile rubber [215,216].

1.1.2.3. Nonpolymer-forming ring opening metathesis reactions. Several examples of RO-CM (see Scheme 1) were reported in 2004. Representative examples are depicted in Scheme 4. Co metathesis of norbornene derivative **43** and various monosubstituted alkenes proceeded with a high degree of

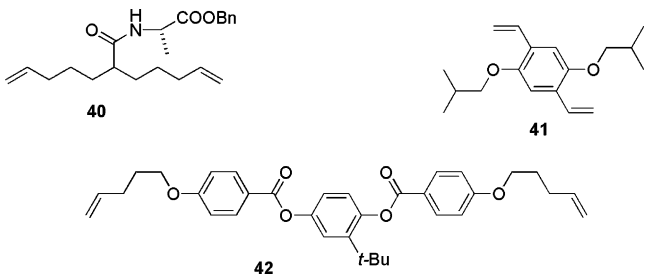
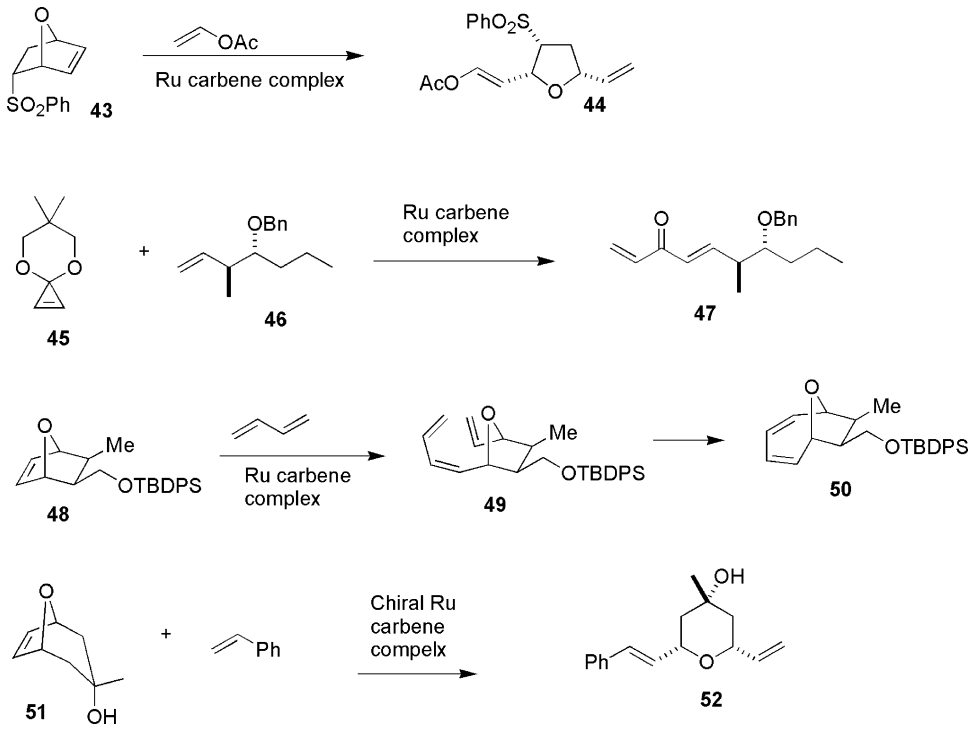


Fig. 4. Representative substrates for ADMET polymerization.

regioselectivity to form the regioisomer depicted by **44** as the major product [217]. A regioselective RO-CM reaction employing 2-azanorbornan-3-ones and allyltrimethylsilane was also reported [218]. Co-metathesis of cyclopropenone ketal **45** and monosubstituted alkene **46** was a critical step in a short total synthesis of bistramide A [219]. A ring expansion was observed in the RO-CM of oxanorbornene **48** and butadiene [220]. This process likely occurs through a RO-CM to afford **49** followed by ring closing metathesis to afford **50**. A high degree of enantioselectivity was observed in the co-metathesis of oxabicyclo[3.2.1]octane derivatives (e.g. **51**) and styrene in the presence of a chiral ruthenium carbene complex [221].

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 2004. Representative examples are depicted in Fig. 5. Specific pairs of compounds subjected to cross-metathesis include: (1) chemoselective cross-metathesis involving acrolein and diene **53**, which features two monosubstituted alkene units [222]; (2) a diene-allylic alcohol and methyl acrylate [223]; (3) vinylcyclopropanes and alkene-containing esters [224]; (4) homoallylic alcohol **54** and acrolein [225]; (5) protected homoallylic alcohols and monosubstituted alkenes for preussin total synthesis [226]; (6) a protected homoallylic alcohol (**55**) and methyl acrylate for RK-397 total synthesis [227]; (7) chiral allylbenzenes and 2-butene-1,4-diacetate [228]; (8) protected homoallylic amines with monosubstituted alkenes [229]; (9) protected 5-hexen-2-ol derivatives and methyl methacrylate [230]; (10) vinylsilanes with allylic sulfides [231]; (11) a diol derivative and methyl acrylate for total synthesis of cocleamycin [232]; (12) *C*-allylcarbohydrate derivatives and monosubstituted alkenes [233]; (13) allylic phosphonates and various allylbenzene derivatives [234,235]; (14) allylic bromides/chlorides and



Scheme 4.

monosubstituted alkenes [236]; (15) allylic fluorides and styrene [237]; (16) 1-chloro-6-hepten-2-one derivatives and monosubstituted alkenes [238]; (17) alkenes **56** and **57** for total synthesis of halichlorine [239]; (18) two highly functionalized monosubstituted alkene partners (**58** and **59**) for amphidinolide W total synthesis [240]; (19) α,β-unsaturated ketone derivative **60** and amino alcohol derivative **61** for carpanic acid total synthesis [241]; (20) two highly functionalized partners for total synthesis of 1-ethylquinolizidine (a later step of the synthesis employs an RCM reaction) [242]; (21) a diol-amide derivative and 1-tetradecene for ceramide total synthesis [243]; (22) steroidal alkene **62** and 10-undecenal (**63**) [244]; (23) a tetrazole-alkene (**64**) and a chiral allylic alcohol derivative (**65**) for total synthesis of brefeldin A [245]; (24) a hydrindene derivative and methyl acrylate [246]; (25) allylamine-phenanthrene **66** and ester **67** for total synthesis of antofine and cryptoleurine (the paper also employs RCM in a later stage of the synthesis) [247]; (26) a highly functionalized 1-hexene derivative and monosubstituted alkenes [248]; (27) carbohydrate derivative **68** and amino-diol derivative **69** [249]; (28) an amino acid-substituted 4-pentenamide derivative and a monosubstituted alkene-ester [250]; (29) highly functionalized allylic alcohols and monosubstituted alkenes [251]; (30) a polyether alkene and a simple monosubstituted alkene for total synthesis of azaspiracid-1 [252]; (31) erythromycin allyl ethers and styrene derivatives [253]; (32) pyran derivative **70** and methacrolein [254]; (33) acrolein and an allylic alcohol for total synthesis of a six-membered ring lactone natural product (a later step of the synthesis employs an RCM reaction) [255]; (34) *cis* selective CM using enynes (e.g. **71**) [256,257]; (35) a vinyl substituted macrocycle and a vinylborate ester for apoptolidinone total synthesis [258]; (36) alkenylboranes and allylsilanes [259]; (37) allylboronic esters and styrene [260]; (38) vinyl-substituted porphyrins and monosubstituted alkenes [261]; (39) octavinylsilsesquioxanes and monosubstituted alkenes [262]; (40) ROMP polymers that contain a vinyl group and alkene-alcohols [263]; (41) naturally occurring unsaturated fatty acid esters and ethylene (ethylenolysis) [264]. Cross-metathesis was frequently employed for the cross-linking of polymers [265]. Patents were awarded for various aspects of cross-metathesis [266,267].

Several examples of dimerization via metathesis (see Scheme 1) were reported in 2004. Compounds subjected to metathesis dimerization are depicted in Fig. 6, and include: (1) *O*-allyl carbohydrate derivatives (e.g. **74**) [268,269]; (2) *O*-allyl carbohydrates (this paper also includes formation of macrocyclic bridges between monosaccharide units via RCM) [270]; (3) allyl and butenyl α,β-unsaturated esters (e.g. **75**) [271]; (4) various *n*-bromo-1-alkenes (e.g. **76**) [272].

Additional examples feature cross-metathesis in tandem with some other metathesis mode. Examples are depicted in Scheme 5. The tandem RCM-CM reaction resulting in **79** was observed upon treatment of triene **77** and 1-decene with Grubbs catalyst II [273]. The RCM of triene **80** led to the α,β-unsaturated lactone **82** [274]. Lactone **82** is the apparent product of a tandem RCM-CM sequence, however no external alkene was added. A tandem metathesis dimerization-RCM was used to prepare hexabenzocoronene cyclophanes (e.g. **84**) [275].

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 2004, including macro-

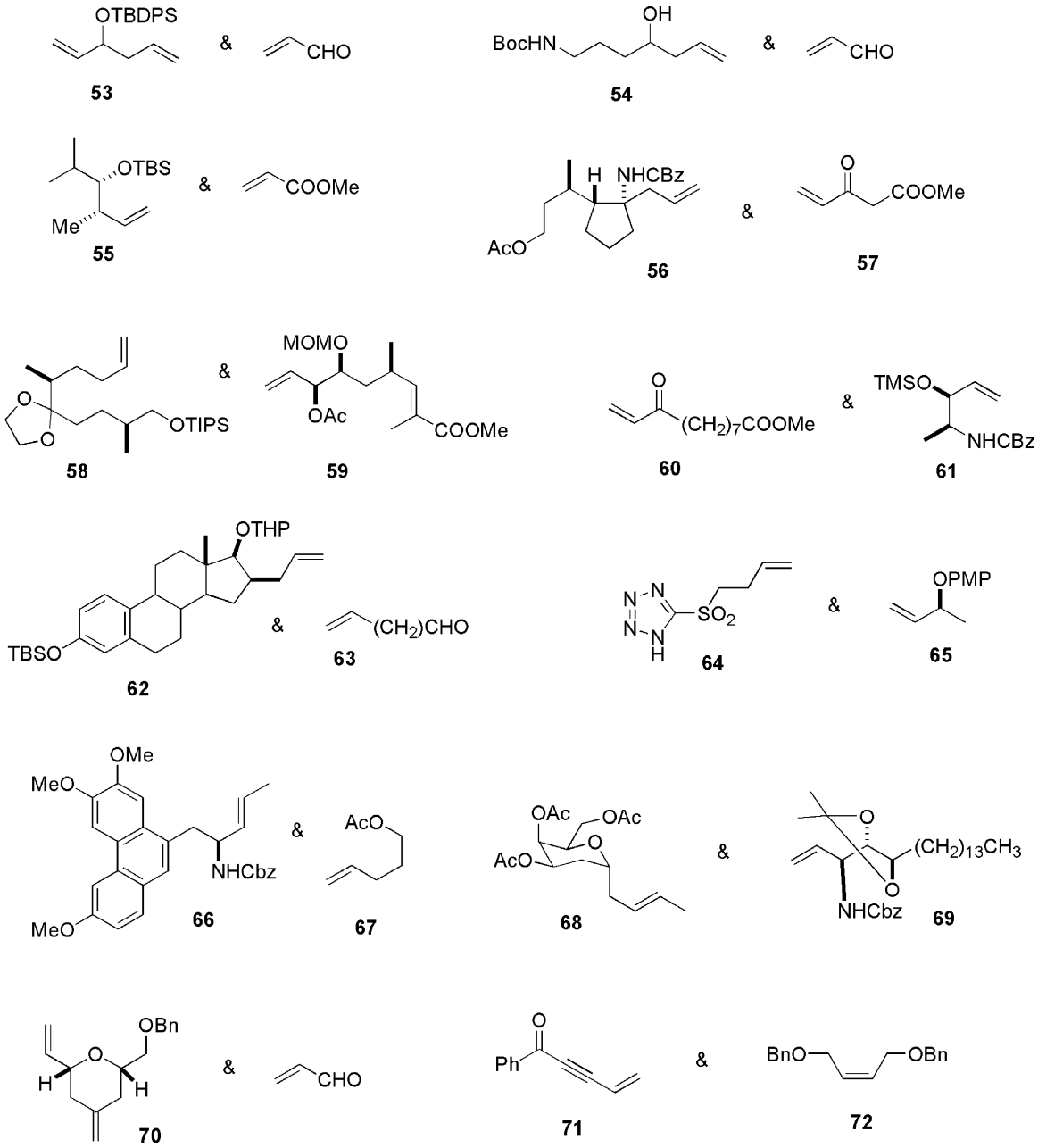


Fig. 5. Represent pairs of alkenes subjected to cross-metathesis.

cycles 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:

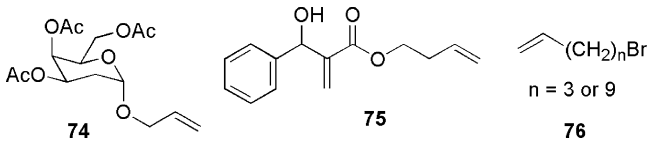
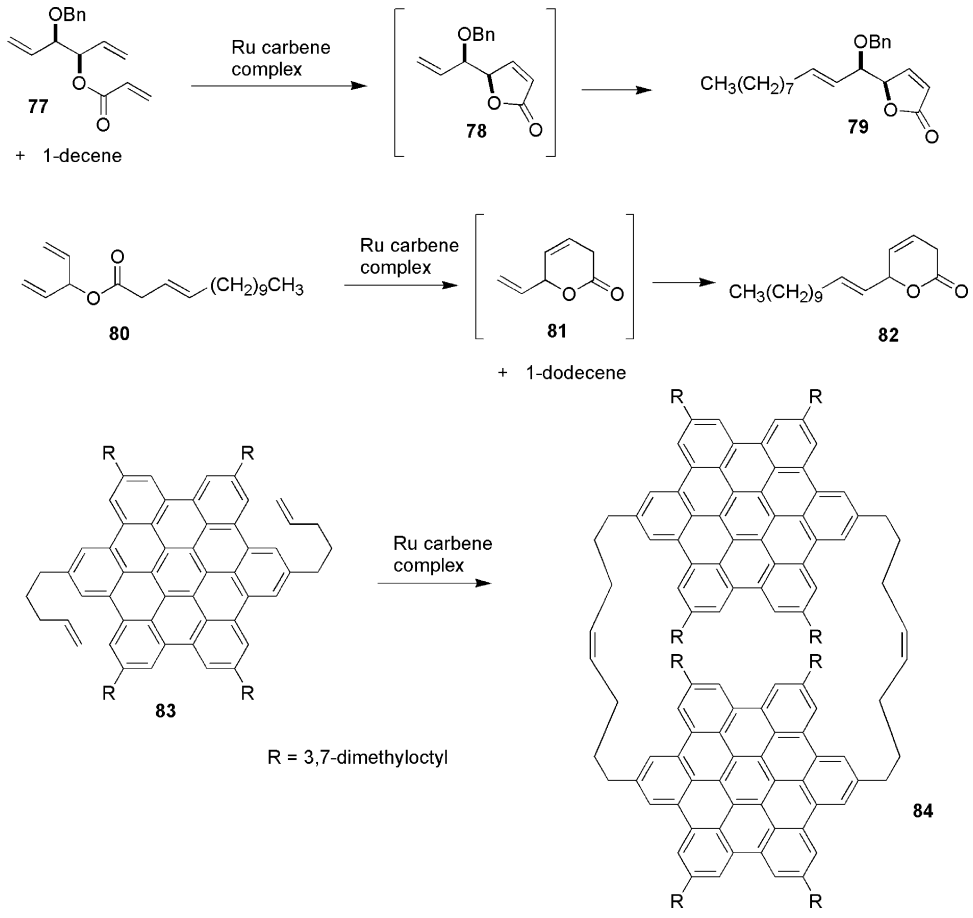


Fig. 6. Representative alkenes subjected to metathesis dimerization.

(1) formation of simple five-membered rings [276]; (2) formation of cyclopentenes for rhizoxin B total synthesis [277] and herbertenediol total synthesis [278]; (3) formation of the five membered ring of the hydroazulene ring system (e.g. **87**) [279]; (4) formation of carbocyclic serine analogs [280]; (5) formation of 1-cyclopentenecarboxylate esters [281]; (6) formation of cyclopentenols [282]; (7) formation of the five-membered ring system of triquinane derivatives (e.g. **88**) [283]; (8) formation of a cyclopentenol derivative for total synthesis of preclavulone B methyl ester [284]; (9) formation of cyclopentenones spiro fused to an oxazolidinone ring [285]; (10) formation of cyclopentenes spiro fused to pyrrolidine rings [286]; (11) formation of spiro-fused cyclopentene derivatives in tandem with the Claisen rearrangement [287]; (12) formation of highly



Scheme 5.

oxygenated cyclopentenones [288]; (13) preparation of oxygenated and aminated five to six-membered rings [289,290]; (14) use of cyanoalkenes for the RCM-based synthesis of various carbocycles and heterocycles [291]; (15) superior formation of cyclopentenones via RCM compared with intramolecular enyne metathesis [292]; (16) formation of cyclopentenones (e.g. **89**) for total synthesis of *C*-nucleoside derivatives [293–296]; (17) one-pot carbonyl-olefination-RCM [297]; (18) formation of cyclopentenone attached to chiral sulfoximine groups [298]; (19) formation of cyclopentenones in a process that releases the new ring from a solid support [299]; (20) formation of indenes (e.g. **90**) for total synthesis of paraquinonic acid [300]; (21) competitive formation of five-membered ring carbocycles and macrocycles in RCM reactions of a triene derivative [301]; (22) formation of five to seven-membered rings spiro fused to a piperidene ring [302]; (23) formation of aminated cyclohexene derivatives (e.g. **91**) [303]; (24) formation of *N*-cyclohexyl derivatives of amino acids [304]; (25) formation of a cyclohexene rings for total synthesis of fumagillol (**92**) [305], cuparenone [306], and isobisabolol [307]; (26) diastereoselective formation of a cyclohexenol derivatives (e.g. **93**) from a precursor containing diastereotopic vinyl groups for a total synthesis of limaspermine [308]; (27) formation of oxygenated α,β-unsaturated cyclohexenone derivatives [309]; (28) formation of six-membered rings for pancratistatin total synthesis [310]; (29) formation of the phenanthrene ring system [311]; (30) formation of hydronaphthalene derivatives (e.g. **94**) [312]; (31) formation of a hydronaphthalene ring for total synthesis of periplanone C [313]; (32) preparation of highly oxygenated six-membered rings for the synthesis of conditurals [314] and inositols [315]; (33) six-membered rings fused to nucleoside rings [316]; (34) formation of a six-membered ring fused to a furan (**95**) for total synthesis of viridin [317]; (35) formation of six-membered rings fused to the anthraquinone ring system [318,319]; (36) six-membered ring allylic silanes (e.g. **96**) [320]; (37) formation of a highly oxygenated cyclohexene rings for synthesis of deoxystreptamine derivatives [321], scyphostatin [322]; (38) formation of bicyclic six-membered rings fused to pyridine rings (e.g. **97**) for huperzine B total synthesis [323]; (39) formation of the six-membered ring of the taxol ring system [324]; (40) preparation of constrained amino acid derivatives [325,326]; (41) formation of one of the carbocyclic rings of the hydroisoquinoline ring system [327]; (42) preparation of cycloheptene derivatives [328]; (43) preparation of a seven-membered ring fused to benzofuran (**98**) for the total synthesis of frondosins [329];(44) formation of a cyclopentene-fused seven-membered ring for total synthesis of thapsigargins [330]; (45) formation of a strained compound featuring an "inside-out" ring (**99**) present in ingenol [331,332]; (46) synthesis of a seven-membered ring containing precursor to the ingenane skeleton [333]; (47) formation of six to eight-membered rings spiro-fused to lactam rings [334]; (48) formation of the bicyclo[4.2.1]nonenone ring system

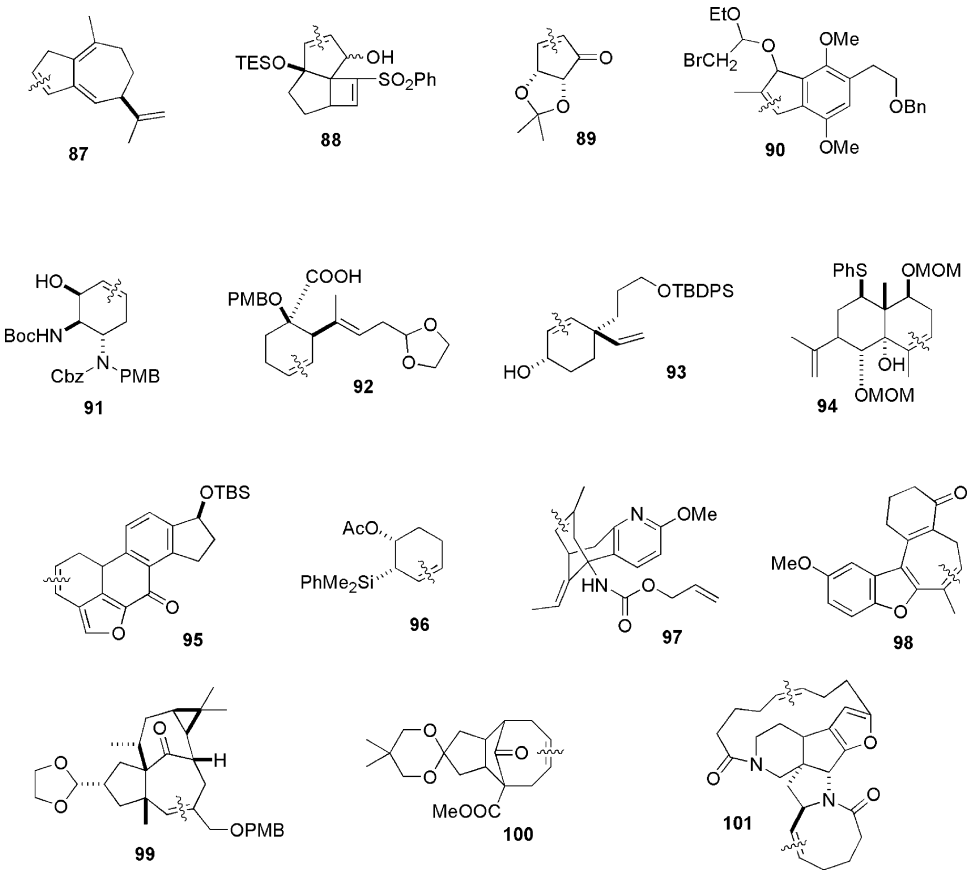


Fig. 7. Representative carbocycles produced through an RCM reaction (bond constructed through RCM indicated).

(e.g. **100**) [335]; (49) formation of six to nine-membered rings fused to the γ-butyrolactone ring system [336]; (50) formation of seven to eight-membered rings fused to the heterocyclic ring of indole [337]; (51) formation of eight-membered rings containing a acetal-protected 1,2-diol group [338]; (52) formation of cyclooctene rings fused to six-membered rings [339]; (53) formation of an eight-membered ring lactam and a macrocyclic lactam in separate steps of a total synthesis of nakadomarin A (see structure **101**) [340].

Numerous examples of the formation of nitrogen heterocycles using the RCM reaction (Fig. 8) were reported in 2004, including: (1) formation of five-membered ring *N*-protected dihydropyrroles [341]; (2) formation of dihydropyrroles for total synthesis of the reported structure of uniflorine A [342] and pyrroloazepine glycosidase inhibitors [343]; (3) formation of dihydropyrroles fused to a five-membered ring cyclic carbamate [344,345]; (4) formation of dihydropyrroles fused to a five-membered ring cyclic carbamate for total synthesis of epiaustraline (see compound **105**) [346] and pseudohellotridane [347]; (5) formation of dihydropyrroles (e.g. **106**) from an enamide precursor [348]; (6) formation of pyrroles through RCM in the presence of the oxidant ruthenium(III) chloride hydrate [349]; (7) formation of dihydropyrroles that can be converted to pyrroles by treatment with base [350]; (8) formation of five-membered ring *N*- and *O*-heterocycles [351]; (9) preparation of five-membered ring cyclic *N*-tosylamides using microwave irradiation [352]; (10) six-membered ring amines where the alkene is conjugated to an ester [353]; (11) tetrahydropyridines where the nitrogen atom features a phosphate protecting group (e.g. **107**) [354]; (12) six-membered rings fused to the indoloazepinone ring system (e.g. **108**) [355]; (13) synthesis of iminosugars [356]; (14) tetrahydropyridines for total synthesis of allosedamine total synthesis [357,358]; (15) tetrahydropyridines attached to carbohydrate ring systems [359]; (16) formation of dihydroquinolines (e.g. **109**) [360]; (17) formation of α,β-unsaturated six-membered ring lactams [361]; (18) formation of α,β-unsaturated six-membered ring lactams for camptothecin total synthesis [362]; (19) formation of α-amido-α,β-unsaturated lactams [363]; (20) formation of cyclic amino acid derivatives [364,365]; (21) cyclic pyridinium salts (e.g. **110**) [366]; (22) formation of β,γ-unsaturated six-membered ring lactams for synthesis of pumilitoxin precursors [367]; (23) formation of six-membered ring amines fused to γ-lactams for total synthesis of a catanospermine derivative [368]; (24) formation of six to eight-membered rings fused to a β-lactam ring [369] and a sulfonamide analog of a β-lactam [370]; (25) formation of a seven-membered ring fused to a five-membered ring lactam for total synthesis of stemoamide [371]; (26) seven-membered ring cyclic amines where the nitrogen is a bound to a diphenylphosphine oxide group [372]; (27) formation of a seven-membered ring lactam (**111**) for FK 565 total synthesis [373]; (28) synthesis of seven-membered ring amines for synthesis of glycosidase inhibitors [374]; (29) formation of eight-membered ring cyclic amides (**112**) for nakadomerin synthesis [375]; (30)

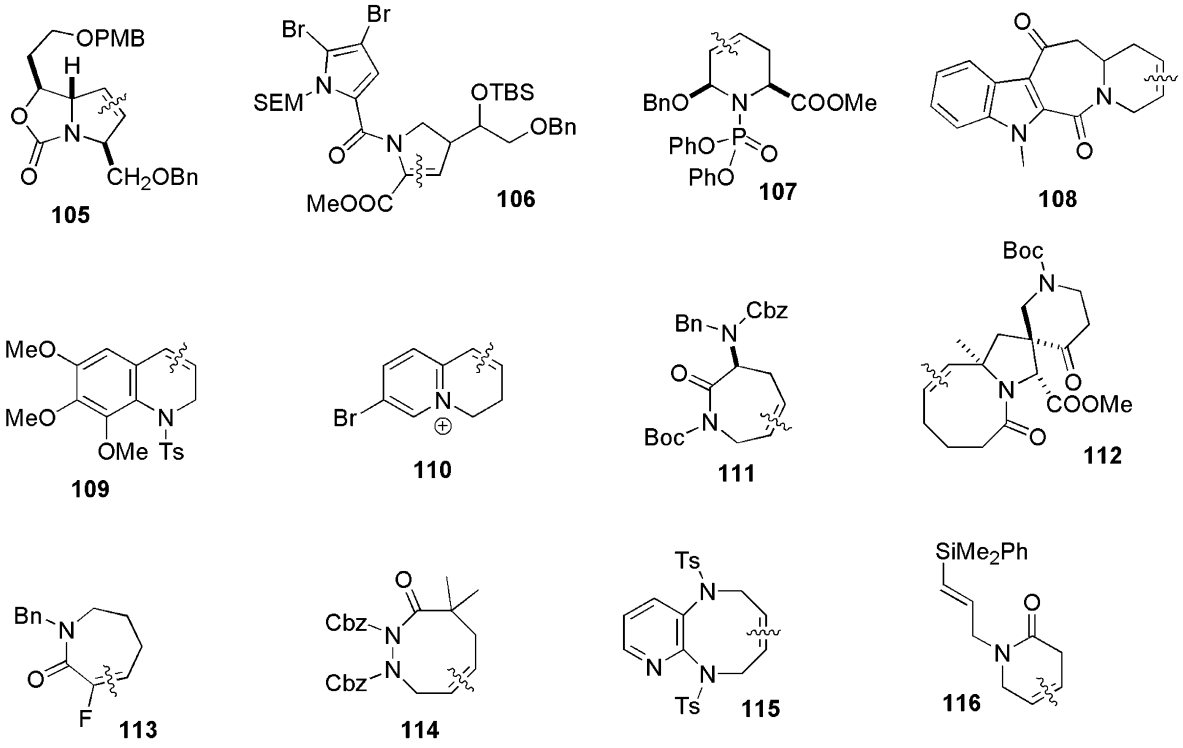


Fig. 8. Representative *N*-heterocycles produced through an RCM reaction (bond constructed through RCM indicated) (includes *N*,*O*-heterocycles).

formation of highly oxygenated eight-membered Cbz-protected cyclic amines [376]; (31) formation fluorinated α,β-unsaturated lactams (e.g. **113**) [377,378]; (32) formation of a six-membered ring cyclic amide and macrocyclic RCM in a later step of the synthesis of taxol analogs [379]; (33) formation of six to nine-membered cyclic amines fused to a six-membered ring through the nitrogen [380]; (34) seven-membered ring aminocyclitols [381]; (35) cyclic hydrazine derivatives where both nitrogens are in the newly formed ring (e.g. **114**) using RCM and/or enyne metathesis [382,383]; (35) preparation of *N*,*N*- and *N*,*O*-heterocycles fused to a benzene ring (e.g. **115**) [384]. A silicon group was employed to direct the RCM reaction for preparation of six-membered ring lactams (e.g. **116**) and macrocyclic lactams from a bis(allylic) amide precursor [385]. A patent was awarded for biologically active RCM-produced benzazepinones [386].

Many examples of oxygen heterocycle synthesis using the RCM reaction were reported in 2004 (Fig. 9), including: (1) formation of dihydrofuran rings for solamin total synthesis [387], guar acid total synthesis [388], and gigantecin total synthesis [389]; (2) formation of a dihydrofuran ring fused to a pyranose ring system [390]; (3) formation of benzofurans [391]; (4) formation of five to six-membered ring cyclic ethers spiro fused to the anomeric carbon of a glucose derivative (e.g. **117**) [392]; (5) formation of a dihydrofuran spiro fused to the β-lactam ring system [393]; (6) formation of α,β-unsaturated γ-lactones for total synthesis of securinine (see compound **118**) [394], syributin [395], and UIC-94017 [396]; (8) formation of six-membered ring α,β-unsaturated lactones [397,398]; (8) diastereoselective formation of bicyclic ethers (e.g. **119**) from C-2 symmetric triene derivatives [399]; (9) formation of six-membered ring lactones for eventual total synthesis of callystatin [400], goniothalamin (see compound **120**) [401,402], massiolactone [403], fluorinated massiolactone [404], passifloricin A [405], hyptolide [406], argentilactone [407], discodermolide segments [408], nucleoside antibiotics (see compound **121**) [409], apratoxin A segments [410], and related natural products [411]; (10) formation of six-membered ring cyclic ethers [412]; (11) formation of fluorinated six-membered ring cyclic ethers [413]; (12) formation of six-membered ring cyclic enol ether segment of laulinamide [414]; (13) formation of multiple glycal rings for oligosaccharide synthesis [415]; (14) tandem RCM and alkene isomerization for the formation of dihypropyran enol ethers (e.g. formation of **122** via RCM followed by isomerization to **123**) using a dual catalyst system [416,417]; (15) formation of a spiro-fused six-membered ring ether for bee pheromone total synthesis [418]; (16) formation of a six-membered ring enol ether for total synthesis of psychorubrin [419]; (17) formation of a seven-membered ring cyclic ether fused to a benzene ring (e.g. **124**) for heliannuol total synthesis [420]; (18) formation of a seven-membered ring cyclic ether for total synthesis of palisadins and related compounds [421]; (19) formation of a seven-membered ring cyclic ether fused to a bicyclic amine derivative (e.g. **125**) [422]; (20) formation of six to nine-membered ring cyclic ethers of brevitoxin, ciguatoxin and related marine toxins (e.g. see compound **126**) [423–428]; (21) formation of eight-membered ring cyclic ethers [429]; (22) formation of eight-membered ring cyclic ether **127** for laurenyne synthesis [430]; (23) formation of eight-membered ring cyclic ethers for lauthisan total synthesis [431]; (24) nine-membered ring lactone **128** for bacillariolide III total synthesis [432]; (25) synthesis of a nine-membered ring cyclic ether for ophirin B total synthesis [433]; (26) formation of 10-membered

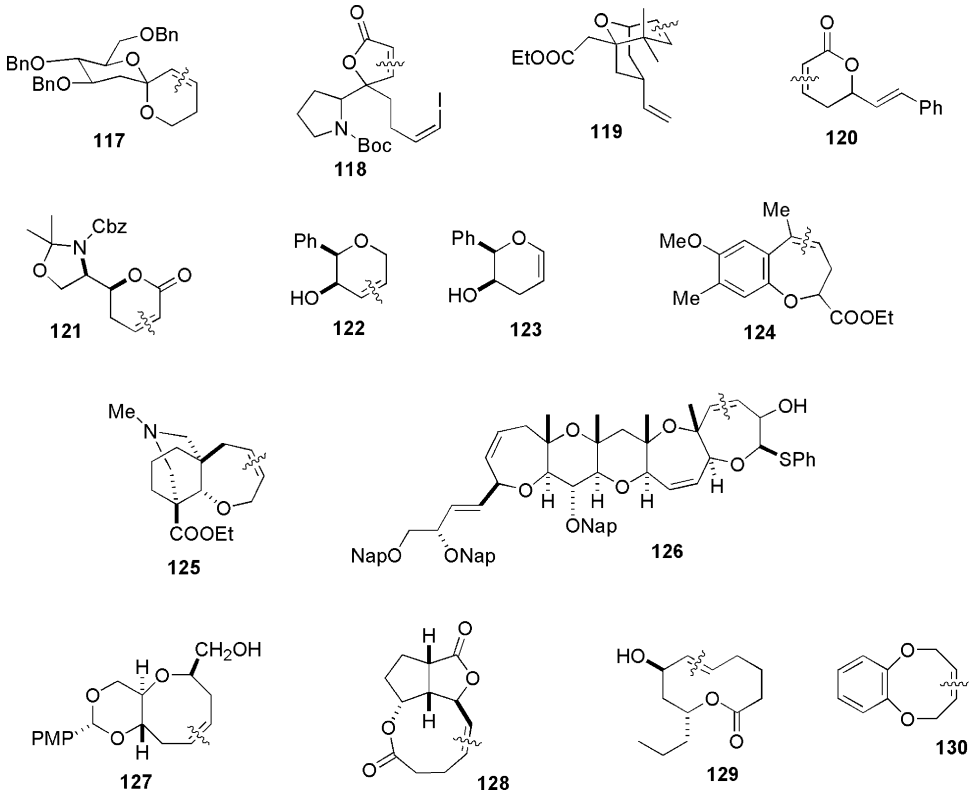


Fig. 9. Representative oxygen-heterocycles produced through an RCM reaction (bond constructed through RCM indicated).

ring lactones for total synthesis of herbarumin (see compound **129**) [434], microcarpalide [435,436], and cladospolide [437]; (27) formation of eight-membered ring cyclic diethers (e.g. **130**) [438]. A patent was awarded for the preparation of cyclic carbonate esters via RCM [439].

Heterocyclic compounds involving elements other than N and O were also constructed via the RCM reaction (Fig. 10). Examples include: (1) enantioselective synthesis of cyclic boronates (e.g. **133**) using a chiral molybdenum carbene complex catalyst [440]; (2) synthesis of cyclic siloxanes (e.g. **134**) [441–443]; (3) synthesis of cyclic siloxanes as an alternative to a moderately efficient cross-metathesis [444]; (4) synthesis of cyclic siloxanes for phaseolinic acid total synthesis [445]; (5) cyclic sulfonamides fused to the β-lactam ring system [446]; (6) cyclic sulfonamides where the nitrogen is part of an α-amino acid residue [447]; (7) solid-phase synthesis of cyclic sulfonamides [448]; (8) synthesis of a cyclic sulfone-*N*-tosylamine (**136**) [449]; (9) synthesis of cyclic sulfones [450]. A "metathesis relay" system has been demonstrated for the activation of a sluggish system through placement of a reactive alkene in a favorable proximity to a less reactive alkene (Scheme 6) [451]. In the RCM reaction of triene **137**, an initial RCM generates methylcyclopentene (**140**) and carbene complex **139**, which then undergoes a second intramolecular metathesis to form the cyclic siloxane **141**.

Numerous examples of successful macrocyclic ring closure (formation of rings with ≥11 atoms) using the RCM reaction were reported in 2004 (Fig. 11), including: (1) formation of macrocyclic compounds containing a gem diester group [452]; (2) synthesis of macrocyclic taxol analogs (e.g. **144**) [453]; (3) formation of a macrocyclic lactone (e.g. **145**) for ansa steroid synthesis [454]; (4) formation of the macrocyclic lactone ring of salicylhalamide (see compound **146**) [455–457]; (5) preparation of macrocyclic lactone that contains an alkyne–cobalt complex (e.g. **147**) within the ring for total synthesis of aigialomycin D [458] and cycloproparadicol [459]; (6) macrocyclic lactones for the total synthesis of epothilone derivatives (e.g. compound **148**) [460–464]; (7) formation of macrocyclic lactones for resorcylide total synthesis [465]; (8) formation of macrocyclic lactones for synthesis of migrastatin analogs in a system where smaller ring sizes can potentially be formed in the metathesis process (e.g. **149**) [466,467]; (9) formation of a macrocyclic epoxide-lactone for oximidine III total synthesis [468]; (10) formation of macrocyclic bis(lactones) [469]; (11) formation of a macrocyclic tris(lactone) for macrosphelide total synthesis [470]; (12) forma-

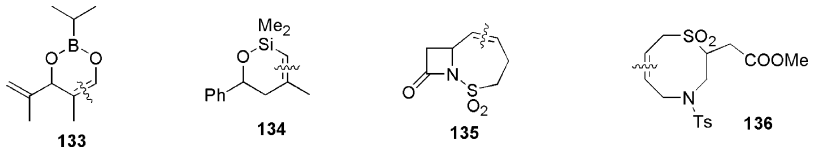
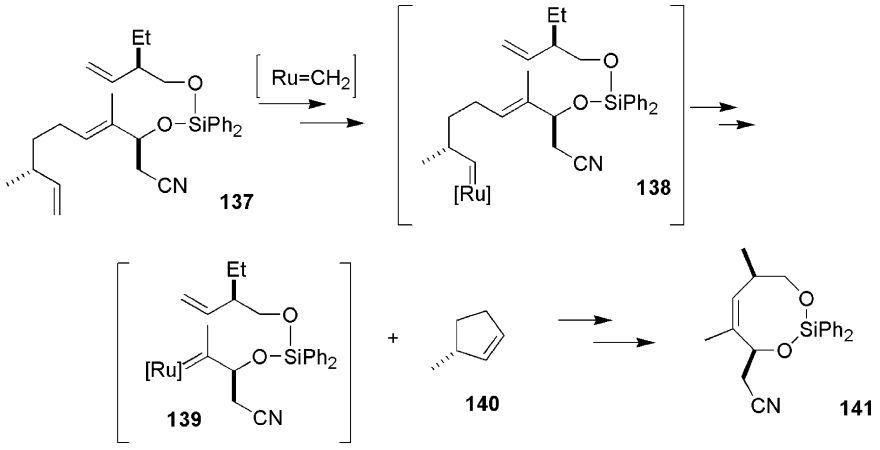


Fig. 10. Representative examples of other heterocycles prepared via the RCM reaction (bond constructed through RCM indicated).



Scheme 6.

tion of a macrocyclic lactone–ketone (**150**) for pochonin C total synthesis [471]; (13) formation of a macrocyclic lactone–lactam for spongistatin total synthesis [472]; (14) formation of macrocyclic carbonates [473]; (15) formation of macrocycle-bridged carbohydrate derivatives [474,475]; (16) formation of macrocyclic amides (e.g. **151**) for oncinotine total synthesis [476]; (17) formation of a macrocyclic amide for spongistatin total synthesis (an early step of the synthesis employs cross-metathesis) [477]; (18) formation of *m*-cyclophane-macrocyclic lactams (e.g. **152**) [478]; (19) formation of lactam-bridged *m*-cyclophane through RCM or intramolecular enyne metathesis [479]; (20) formation of *m*-cyclophanes bridged by a phenanthroline ring [480];

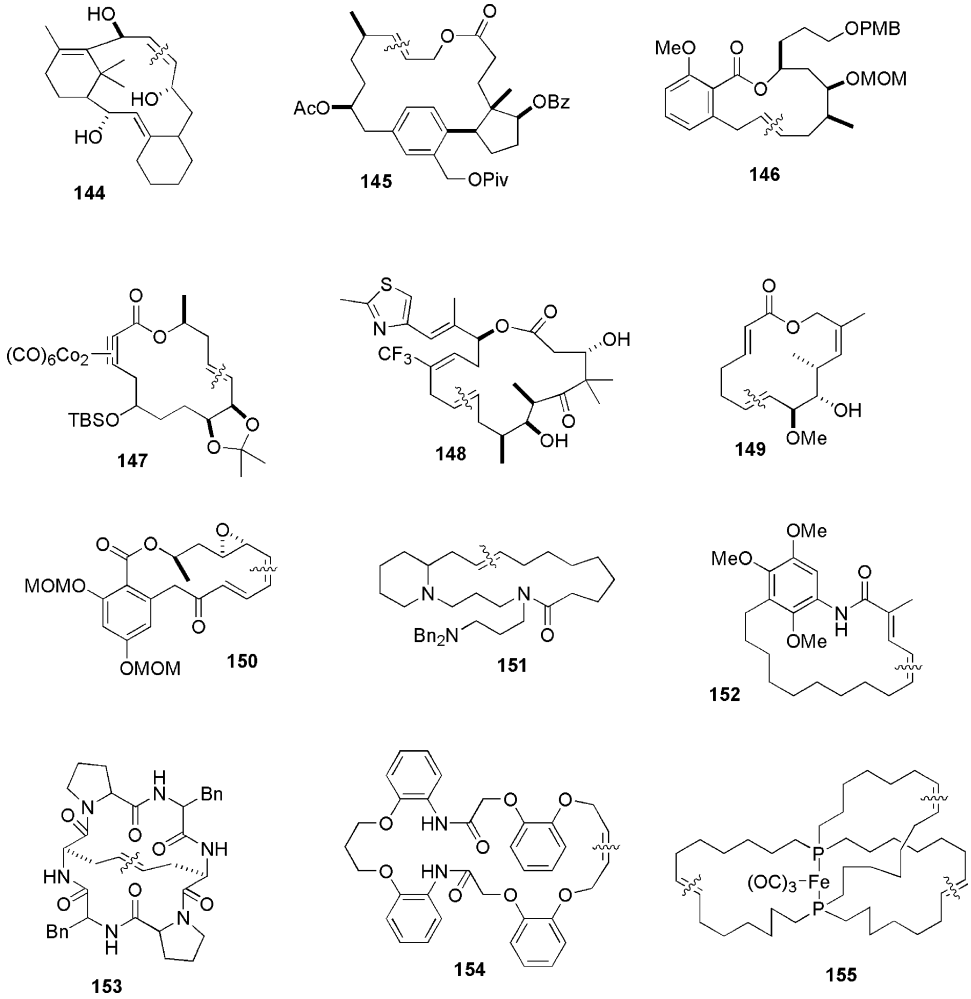
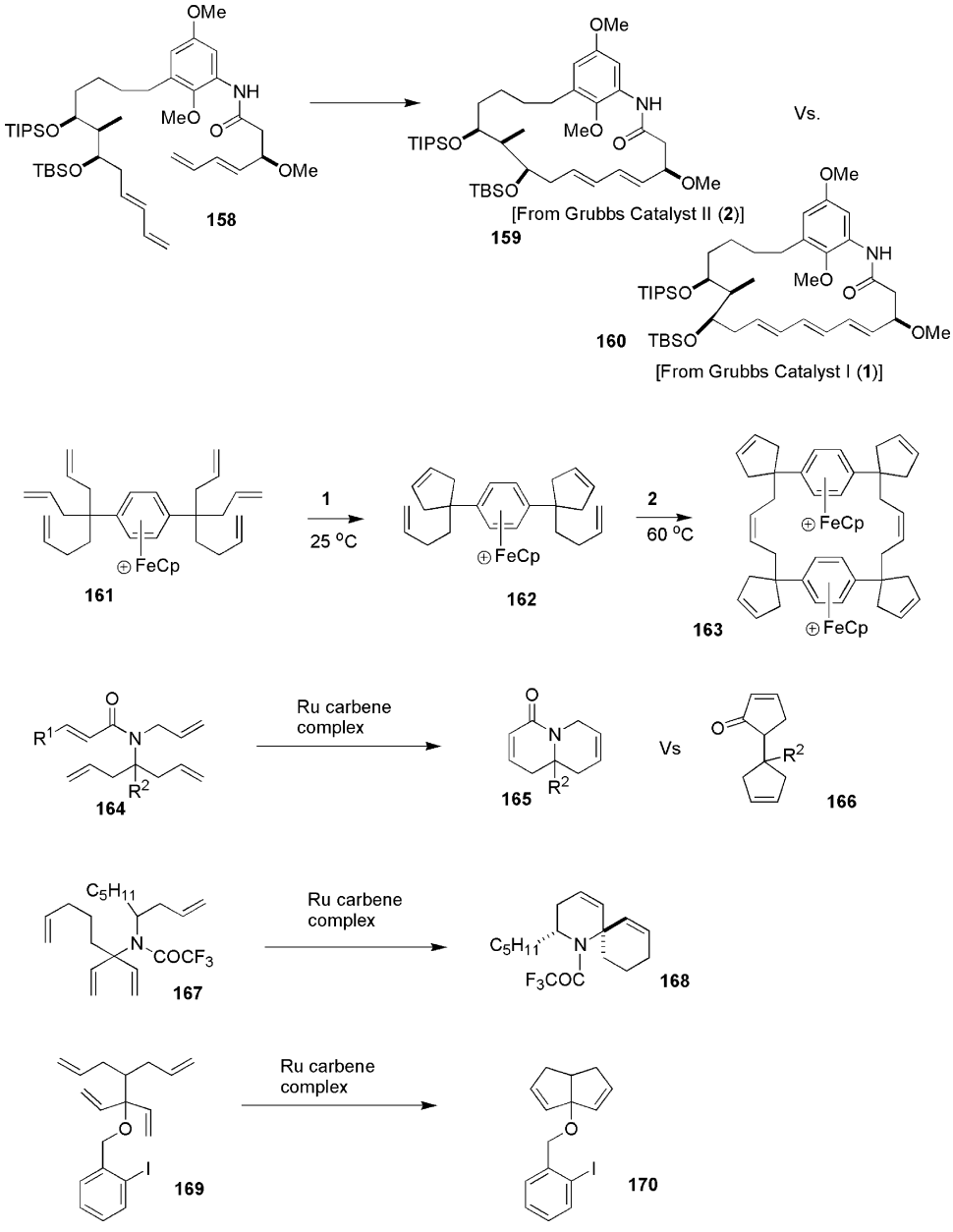


Fig. 11. Representative macrocycles (ring size >10) prepared using the RCM reaction (bond constructed through RCM indicated).

(21) formation of a bis(macrocyclic) *m*-cyclophane [481]; (22) formation of a furanophane derivative [482]; (23) preparation of alkene-bridged macrocyclic peptides (e.g. **153**) [483–488]; (24) formation of a complex macrocycle for pinnatoxin A total synthesis [489]; (25) formation of a complex macrocycle for SCH 351448 total synthesis [490]; (26) failed formation of a macrocycle in a failed synthetic route to diazonamide [491]; (27) formation of a macrocyclic polyether-bis(lactam) (e.g. **154**) [492]; (28) formation of a macrocyclic lactam-bis(lactone) for total synthesis of cryptophycin 24 [493]; (29) formation of a crown ether ring system [494]; (30) formation of macrocyclic peptoidal urea derivatives [495]; (31) formation of cryptands with tetrahedral connectivity [496]; (32) interligand bridged iron phosphine complexes (e.g. **155**) [497]; (33) formation of platinum and tungsten complexes containing bridged phosphine ligands through an "interligand" metathesis process [498]; (34) formation of a mechanically interlocked crown ether derivative [499]; (35) closure of a trefoil knot compound [500]; (36) formation of catenane derivatives [501,502]; (37) formation of rotaxane derivatives [503]; (38) bridging of a dinucleotide through the N-bases [504]; (39) synthesis of macrocycle-bridged calixarene ligands [505]; (40) development of methodology for intramolecular cross-linking of dendrimers [506,507] and star polymers [508]; (41) preparation of slipped cofacial bis(porphyrins) [509]. Patents were awarded for biologically active RCM-produced macrocyclic peptides [510–512].

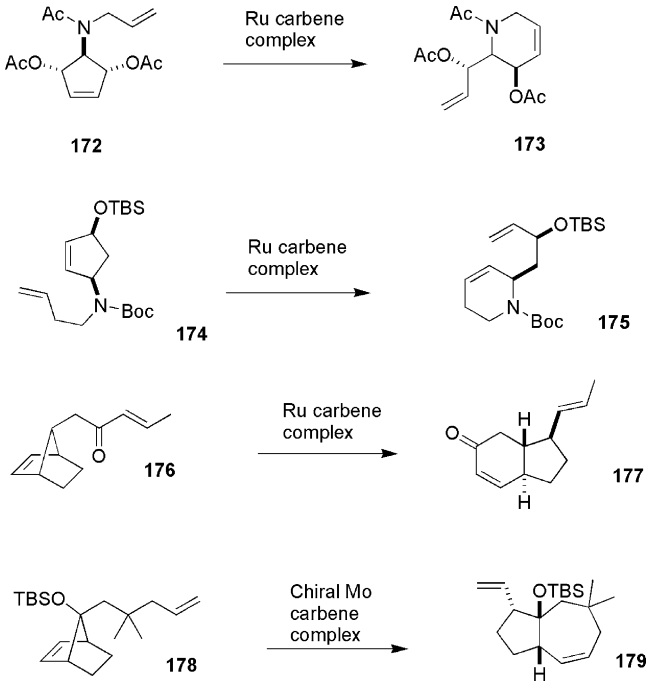
Several examples using tetraenes in RCM reactions were reported in 2004. One example, RCM of tetraene **158** (Scheme 7), involves a selective reaction in the internal alkenes, presumably as a result of ring size thermodynamics—this pro-



Scheme 7.

cess occurs with excision of 1,3-butadiene [513]. The product distribution in this reaction can be controlled by the catalyst. Several examples of to effect double RCM reactions using tetraenes were also reported. Various polyene derivatives of arene–iron complexes (e.g. **161**) were subjected to RCM [514]. Complex **161** initially leads to the bis(cyclopentenyl)arene–iron complex **162**, which undergoes metathesis cyclodimerization at higher temperature to afford **163**. Related reaction processes were reported for Cp–cobalt complexes. RCM of tetraenes of general structure **164** afforded mixtures of fused ring bicyclic amides (**165**) and the "dumbbell" isomer (**166**) [515,516]. The fused ring isomer was predominant when R^2 is H, however a greater proportion of **166** was obtained when R^2 was methyl (**166** is the major product) or an amide group (1:1 ratio of **165**:**166**). The fused ring systems were prepared efficiently from diene substrates where the six-membered ring cyclic amide was already formed. A homologous process resulting in a bis(cyclopentenol) derivative where the rings were spaced by two carbons was also reported [517]. Tetraene **167** afforded the spiro fused compound **168** [518,519]. A high degree of diastereoselectivity was observed using Grubbs catalyst I (**1**) at elevated temperature. An analogous process resulting in spiro-fused five-membered rings was also reported [520]. Use of tetraenes (e.g. **169**) to form bicyclo[3.3.0]octadiene derivatives (e.g. **170**) was reported [521]. Related fused ring forming processes were also reported using trienes featuring two vinyl groups and a cycloalkene substituent.

Several examples of ring rearrangement metathesis (RRM) were reported in 2004 (see Scheme 8). These examples include: (1) the conversion of oxygenated dihydropyrrole derivative **172** to the six-membered ring compound **173** [522]; (2) conversion of the aminocyclopentene derivative **174** to the tetrahydropyridine derivative **175** for lasubine-II total synthesis [523], and analogous processes using 3-aminocyclohexene derivatives [524] and



Scheme 8.

4-aminocycloheptenes (for halosaline total synthesis) [525]; (3) conversion of norbornene derivative **176** to the *trans* hydrindane derivative **177** [526]; (4) conversion of oxanorbornene trienes to tricyclic furans [527]; (5) conversion of acryloylnorbornenes to bicyclco[3.3.0]octene derivatives for total synthesis of indolizidine 251F [528]; (6) enantioselective conversion of meso compound **178** to the hydroazulene derivative **179** for africanol total synthesis [529].

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 2004; representative examples are depicted in Fig. 12. Intermolecular enyne metathesis involving silylated alkene **180** and monosubstituted alkenes (e.g. **181**) provides dienes (e.g. **182**) as nearly exclusively the *Z* stereoisomer [530]. Examples of intramolecular enyne metathesis include: (1) formation of five to seven-membered rings fused to β-lactams [531]; (2) formation of highly oxygenated six-membered rings [532]; (3) formation of vinylcyclohexene derivatives for total synthesis of dysidiolide (conversion of **183**–**184**) [533] and erogorgiane [534]; (4) formation of acetyldecalins through tandem enyne metathesis of involving a silyloxyalkyne (e.g. **185**) followed by hydrolysis of the resulting enol ether (**186**) [535]; (5) formation of vinyldihydropyrroles (e.g. **188** from **187**) (the process can be conducted in tandem with cross-metathesis) [536]; (6) formation of tetrahydropyridine derivatives fused to a piperidine ring for total synthesis of halichlorine [537]; (7) formation of bicyclic amine derivatives (e.g. **190** from **189**) through intramolecular enyne metathesis for anatoxin A total synthesis [538–540] and ferruginine total synthesis [541]; (8) formation of heterocyclic and carbocyclic rings fused to benzene rings [542]; (9) formation of dihydropyran rings (e.g. **192** from **191**) for total synthesis of cacospongionolide [543]; (10) formation of cyclic siloxanedienes [544]; (11) formation of cyclic sulfonamides [545]; (12) preparation of cyclic hydroxylamine derivatives (e.g. **194** from **193**) [546]. The regiochemical preferences for enyne metathesis were studied [547]. A one-pot sequence employing intramolecular enyne metathesis followed by intermolecular Diels–Alder reaction was reported [548]. Treatment of enyne **195** with a Grubbs catalyst I (**1**) followed by dimethyl acetylenedicarboxylate (DMAD) affords the tricyclic compound **197**. This reaction involves generation of enyne metathesis product **196** followed by Diels–Alder reaction with DMAD in the same reaction pot.

Examples of tandem enyne metathesis-alkene metathesis are depicted in Scheme 9. Tandem intramolecular enyne metathesis and cross-metathesis (e.g. conversion of **200** and allyl acetate to **202** in the presence of catalyst **2**) was employed for the synthesis of cyclic ethers [549]. Tandem enyne metathesis–cross-metathesis was also reported for diene-yne derivatives where the cross-metathesis occurs at the alkene not involved in the enyne metathesis event [550]. Tandem enyne metathesis–RCM was observed in the formation of the fused bicyclic compound **205** from dienyne **203** for securinine total synthesis [551,552]. Tandem enyne metathesis–RCM reactions were also employed for the synthesis of: (1) steroid-like molecules [553]; (2) formation

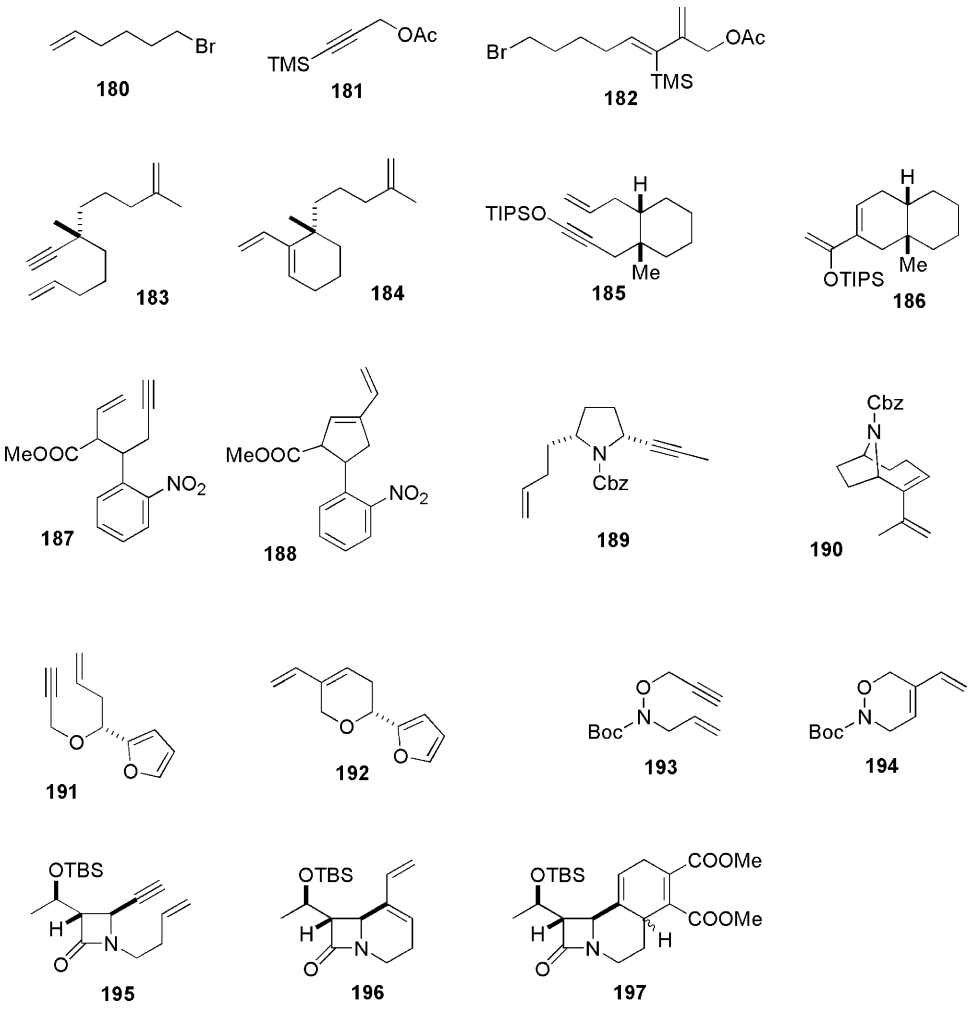


Fig. 12. Representative products and substrates from enyne metathesis reactions.

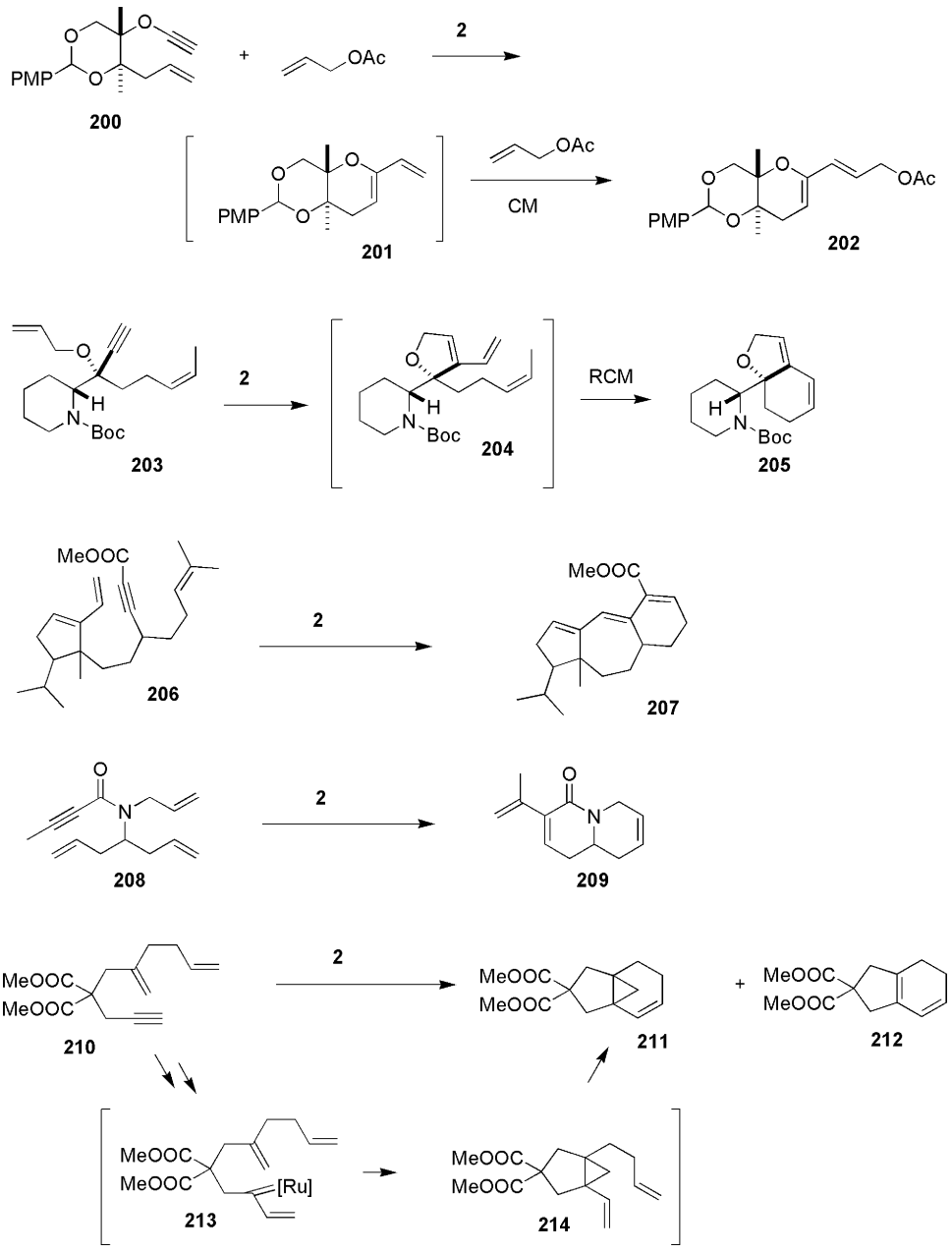
of **207** from **206** in a formal total synthesis of guanacastepene A [554]; (3) bicyclic siloxane derivatives [555]; (4) formation of oxa-triquinane derivatives [556]. An ene-triyne derivative **208** undergoes both RCM and intramolecular enyne metathesis to afford fused bicyclic amide derivative **209** [557]. Cyclopropanation was observed as a side reaction in the tandem enyne metathesis RCM of diene-yne **210** [558]. Competing cyclopropanation and RCM for intermediate **213** was suggested as the source of unexpected cyclopropane product **211**.

Competing ring opening intramolecular enyne metathesis and intermolecular metatheses with ethylene was observed in the treatment of alkynyl-substituted azanorbornenones (e.g. **215**, Scheme 10) and ruthenium carbene complexes [559]. The course of the reaction was highly dependent upon the length of the alkyne-norbornene tether and choice of catalysts. A novel cycloaddition process (formation of **219**) was observed in the co-metathesis of monosubstituted alkynes (e.g. **218**) and 1,5-cyclooctene [560]. Tandem enyne-metathesis RO-RCM was observed upon treatment of bis(propargyloxy)norbornene derivative **220** with ruthenium carbene complexes [561]. A novel tandem enyne metathesis–alkynylcarbene rearrangement–RCM process was observed in the treatment of diene–diyne complex **222** with Grubbs catalyst I [562]. Enyne metathesis of cyclic alkenes (e.g. **224**) was reported [563]. In addition to the expected product **226**, a secondary metathesis dimerization product (**227**) and ethylene enyne metathesis products (**225**) were observed. The reaction course was highly dependent on the ring size of the cycloalkene and length of the alkene–alkyne tether.

1.1.2.7. Non-metathesis reaction processes involving the Grubbs and related catalysts. Several publications in 2004 report on processes unrelated to metathesis that are initiated by ruthenium carbene complex catalysts **1**–**2** and structurally related carbene complexes.

Several examples employing ruthenium–carbene complexes to initiate free-radical reactions were reported in 2004 (Scheme 11). The reaction of dienol **230** with ruthenium carbene complex metathesis catalysts in carbon tetrachloride solvent was studied [564]. The RCM product **231** was obtained from the reaction employing Grubbs catalyst II (**2**), while the free-radical derived product **232** was obtained from reaction with Grubbs catalyst I (**1**). Catalysis of the addition of chloroform or ethyl trichloroacetate to styrene by catalyst **1** was also demonstrated [565].

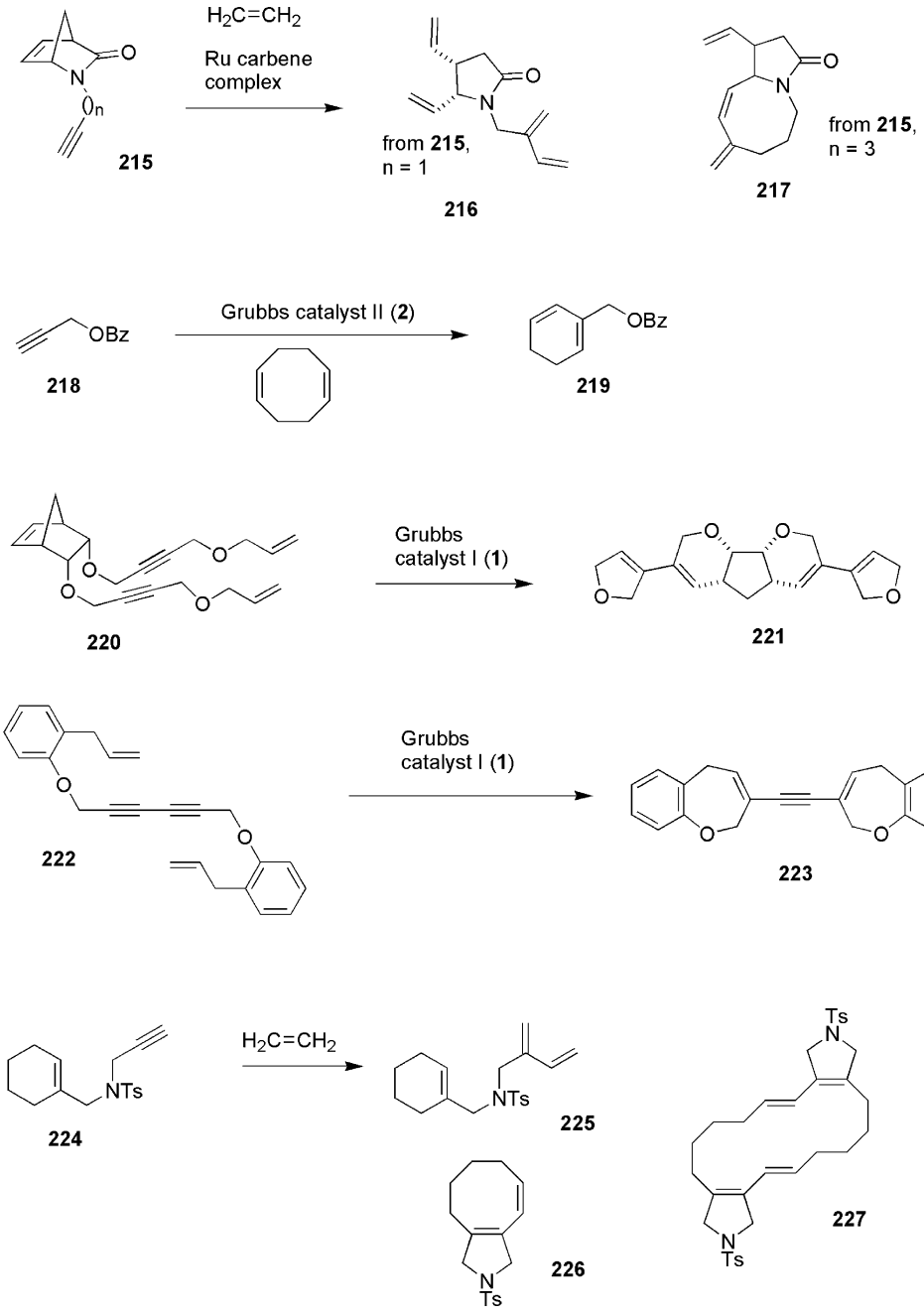
A frequent side reaction during metathesis is alkene isomerization. This side reaction has been attributed to the formation



Scheme 9.

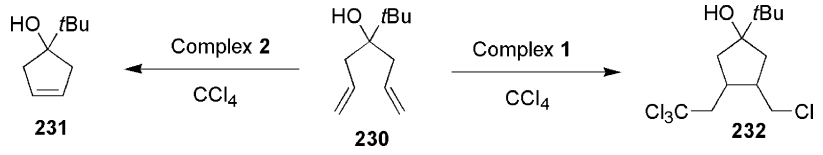
of metal hydride complexes under the conditions necessary for metathesis. Formation of a ruthenium hydride (**233**, Scheme 12) or a ruthenium aryl complex (**234**) from the reaction of Grubbs catalyst II and alcohols and triethylamine was reported [566]. The hydride complex **233** functions as an alkene isomerization catalyst, and may be the source of competing alkene isomerization during alkene metathesis. Attempted RCM of diallyl ethers (e.g. **235**) or homallyl/allyl ethers in the presence of ethyl vinyl ether resulted in Claisen rearrangement products (e.g. **237**) [567]. A mechanism involving isomerization to the allyl vinyl ether (e.g. **236**) followed by Claisen rearrangement was proposed.

Unusual processes occurred if methylene cyclopropanes were allowed to react with carbene complex metathesis catalysts. Stoichiometric cross-metathesis of Grubbs catalyst I or II with methylenecyclopropane derivatives (e.g. **238**, Scheme 13) was reported [568]. The reaction led to the ruthenium complex **239** containing a terminal carbide ligand. Protonation of carbide complex **239** afforded the highly active metathesis catalyst **240**, which affords the Hoveyda–Grubbs catalyst (**4**) upon treatment with *o*-isopropoxystyrene. Reaction of methylenecyclopropane-containing enyne **242** with Grubbs catalyst I (**1**) resulted in intramolecular cycloaddition product **243** [569]. An analog of **242** lacking the alkyne (**244**) undergoes stoichiometric cross-metathesis with Grubbs catalyst I to afford cyclopropylideneruthenium complex **245**. Ruthenium carbene complex **245** was an even more effective catalyst for the cycloaddition reaction.

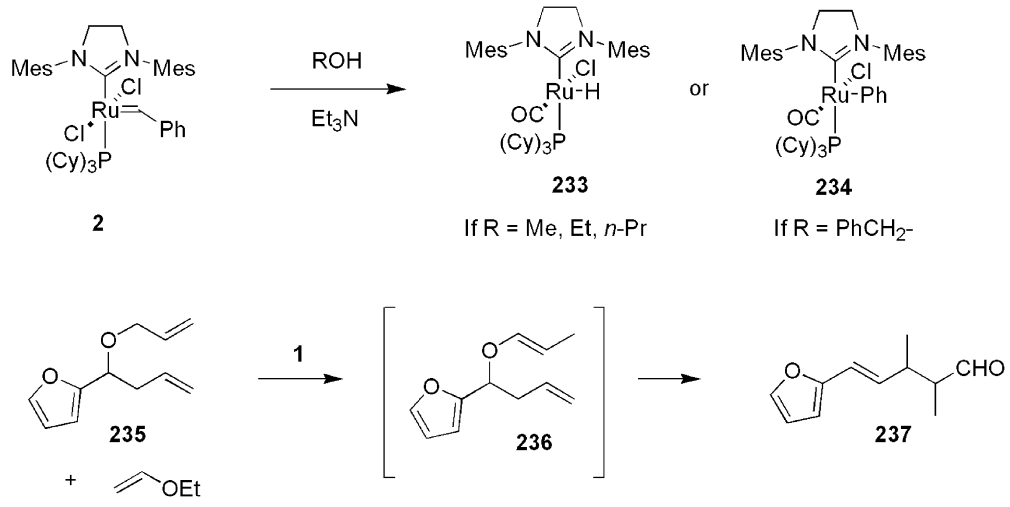


Scheme 10.

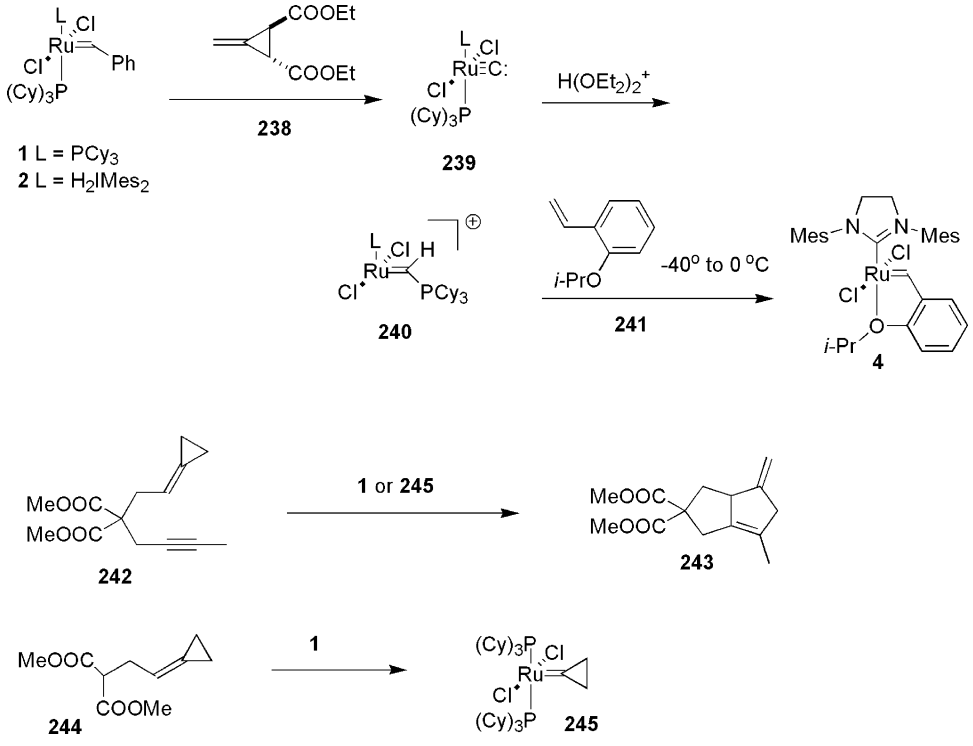
Additional non-metathesis reactions exhibited by the Grubbs catalysts and related complexes reported in 2004 include: (1) catalysis of the conversion of 3-acylazirenes to the corresponding isoxazoles [570]; (2) catalysis of acetylene polymerization [571]; (3) catalysis of alkyne hydrosilylation by catalyst **1** [572]; (4) catalysis of cycloisomerization and not RCM in the reaction of diene **246** (Scheme 14) with Grubbs catalyst II (**2**) in the presence of vinyl trimethylsilyl ether [573]. In this latter reaction, a reaction mechanism employing the hypothetical stoichiometric cross-metathesis product **248** was considered. However the electronically similar compound **249** functioned as an RCM catalyst and not a cycloisomerization catalyst.



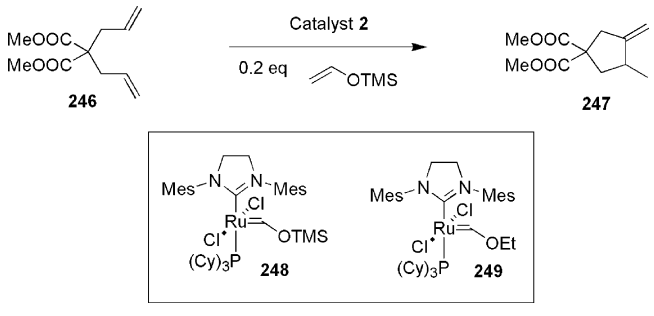
Scheme 11.



Scheme 12.



Scheme 13.

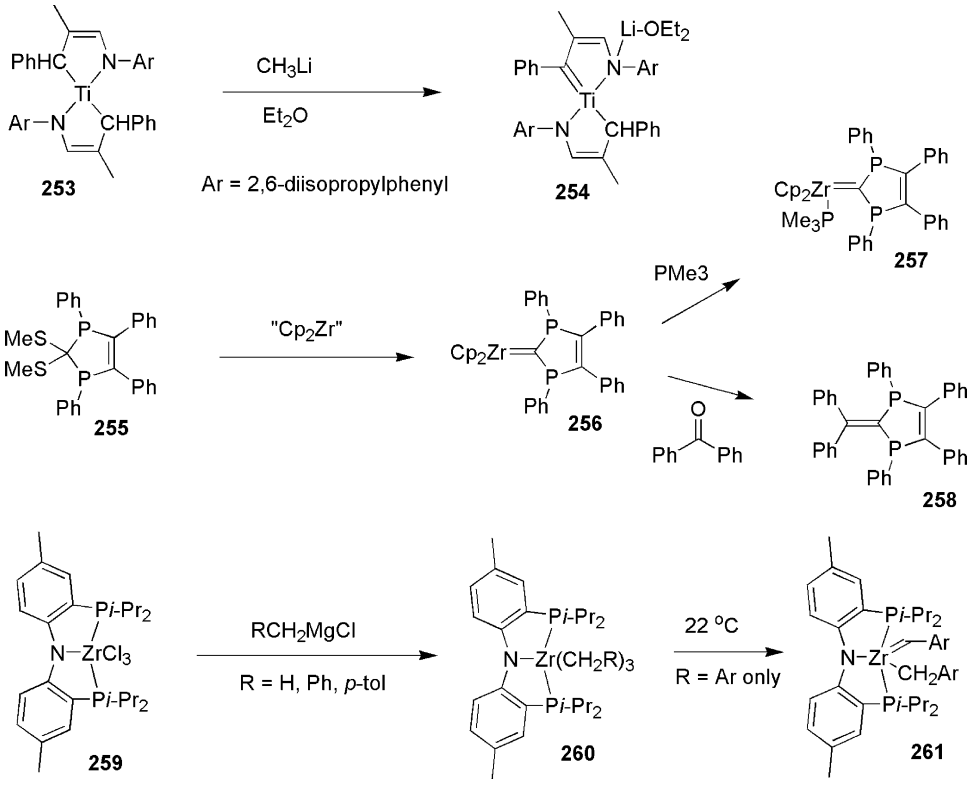


Scheme 14.

1.1.3. Individual carbene or alkylidene complexes classified according to metal

One manuscript discusses many different metals bound to the carbene ligand. A computational study of the bonding of a diverse array of metal fragments to the vinylidene ligand was reported [574]. An increase in the electron density of the metal fragment causes a slight decrease in the M=C bonding energy. Bond energies for $d^{2–4}$ and d^8 complexes were higher than for d^6 complexes. Fragments examined include $Cp_2Ti(PH_3)$, $CpMo(PH_3)_2^+$, $ClRh(PH_3)_2$, and $ClIr(PH_3)_2$.

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



Scheme 15.

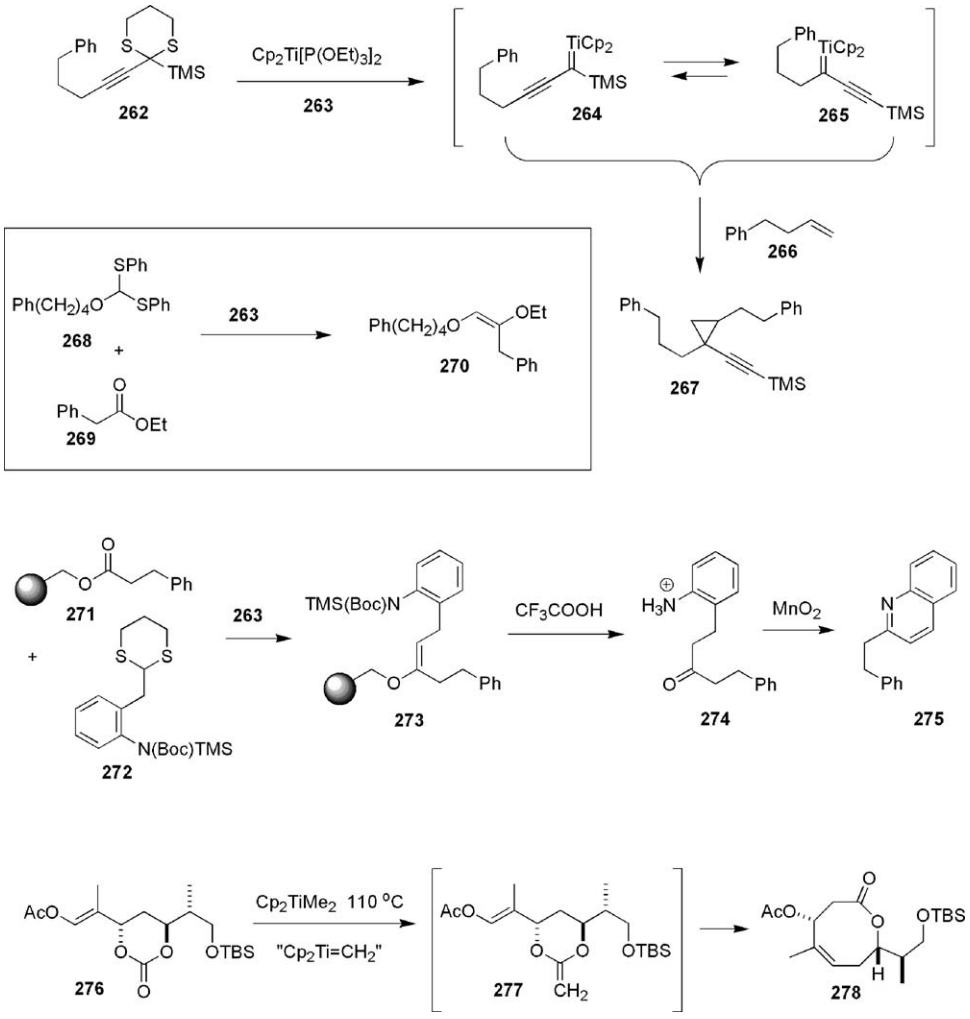
Examples of stable titanium carbene complexes are depicted in Scheme 15. Titanium carbene complex **254** was generated by deprotonation of chelated bis(σ-allyl) complex **253** [575]. The stable zirconium carbene complex **256** was prepared through reaction of diphosphine-thioacetal **255** with in situ-generated zirconacene [576]. Reaction of complex **256** with trimethylphosphine led to complex **257**. Reaction with ketones led to carbonyl olefination products (e.g. **258**). Zirconium carbene complexes (**261**) were produced in the coupling of tridentate zirconium complex **259** with Grignard reagents [577]. The complex initially produces the trialkylzirconium complex **260**, which converts to the carbene complex **261** at room temperature. The trimethylzirconium complex is stable and does not convert the carbene complex.

Several examples employing in situ-generated titanium–carbene complexes in synthetic organic chemistry were demonstrated in 2004; representative examples are depicted in Scheme 16. Treatment of alkynyldithiane derivatives (e.g. **262**) with titanium complex **263** in the presence of various alkenes led to alkyne-shifted cyclopropane derivatives (e.g. **267**) [578]. The proposed mechanism involves formation of a titanium carbene complex (e.g. **264**) followed by a 1,3-shift of the carbene functionality to afford alkynylcarbene complex **265**, followed by cyclopropanation. A variety of alkenes substituted by 1-2 alkoxy groups (e.g.**270**) were prepared through the coupling of 1-alkoxy-1,1-bis(thiophenyl) derivatives (e.g. **268**) with various carbonyl compounds in the presence of titanium complex **263** [579]. A solid phase pyridine synthesis that involves titanium carbene intermediates was reported [580]. Treatment of dithiane **272** with titanium complex **263** in the presence of solid-phase bound esters (e.g. **271**) led to the corresponding enol ethers (e.g. **273**). Hydrolysis of the enol ether followed by heating in the presence of an oxidizing agent afforded the pyridine derivative (e.g. **275**). A mechanistically similar process was employed for the synthesis of thiophene derivatives [581]. Six-membered ring forming intramolecular carbonyl olefination using a dithioacetal and titanium complex **263** was a key step in the synthesis of marine-derived polyethers [582]. Reaction of the Petassis reagent (Cp_2TiMe_2 at elevated temperature) with carbonate derivative **276** led to cyclic ether **278** in a process involving carbonyl methylenation followed by Claisen rearrangement [583]. Sequential Petassis olefination-RCM was demonstrated as a general method for the preparation of six-membered rings fused to pyranose derivatives [584]. Tebbe olefination was part of a failed synthetic route to diazonamide [491]. A new procedure for carbonyl group methylenation was reported using dichloromethane, magnesium, and titanium tetrachloride [585]. Titanium carbene intermediates were suggested.

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 [586,587]. The hypothetical carbene complex was studied by DFT and the calculated IR spectrum compared with the observed IR spectrum.

Possible but unlikely involvement of Group IV metal carbene complexes in alkene addition polymerization using bridged bis(Cp) complexes was evaluated by DFT [588].

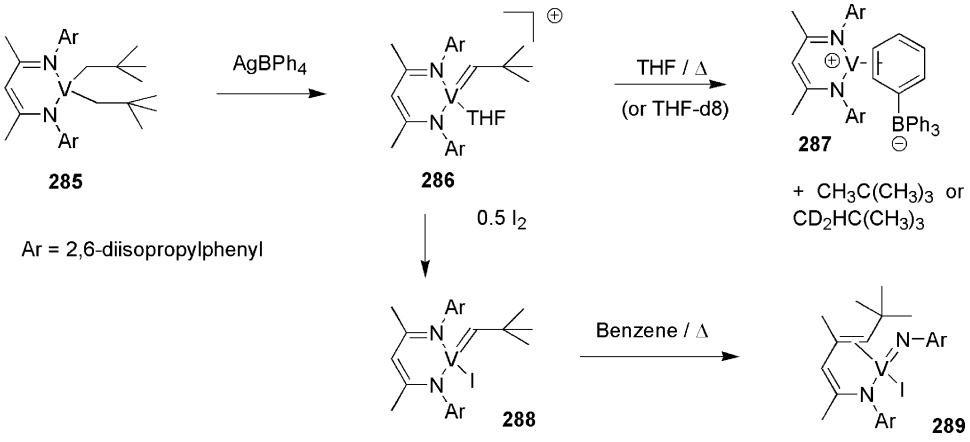
1.1.3.2. Group V metal–carbene complexes. Vanadium carbene complexes (e.g. **286**, Scheme 17) were generated through



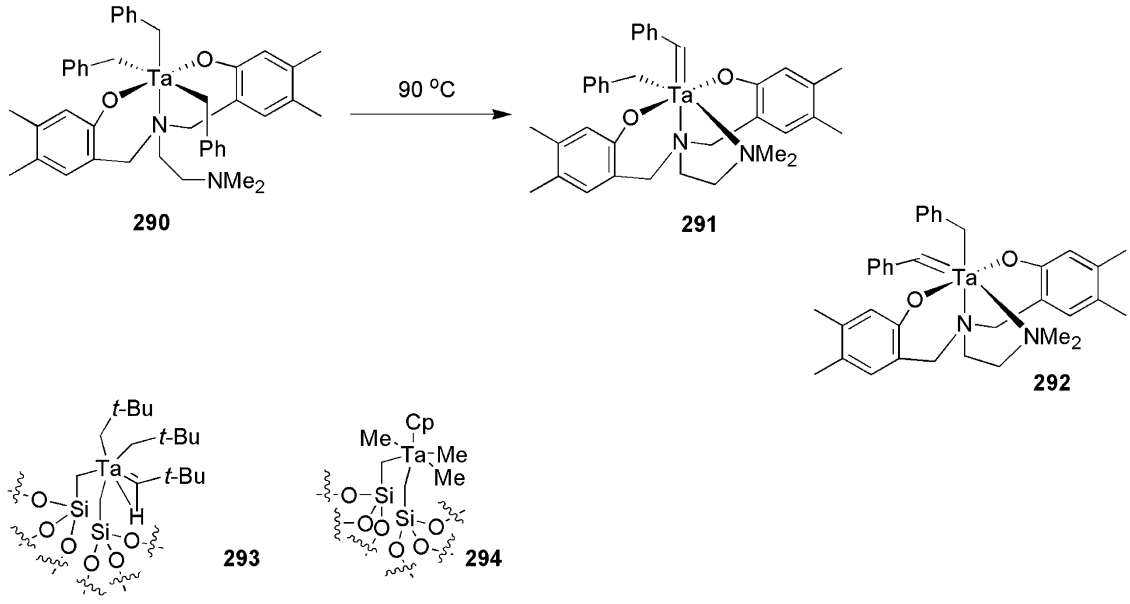
Scheme 16.

oxidation of bis(alkyl)vanadium complex **285** [589]. The complex is stable in the solid state but decomposes in solution to afford the η^6-arene complex with the tetraphenylborate anion. Neopentane is a byproduct, and the extra hydrogen atoms arise from THF. This was verified by a deuterium labeling study. Reaction with 0.5 equiv. of iodine led to the iodide compound **288**. Thermolysis of this complex in benzene led to the intramolecular metathesis product **289**.

The synthesis of tantalum–carbene complexes **291** and **292** (Scheme 18) was reported [590]. Thermolysis of benzyl complex **290** at 90 °C resulted in a 3:1 ratio of isomeric tantalum carbene complexes **291** and **292**. The reaction followed first order kinet-



Scheme 17.



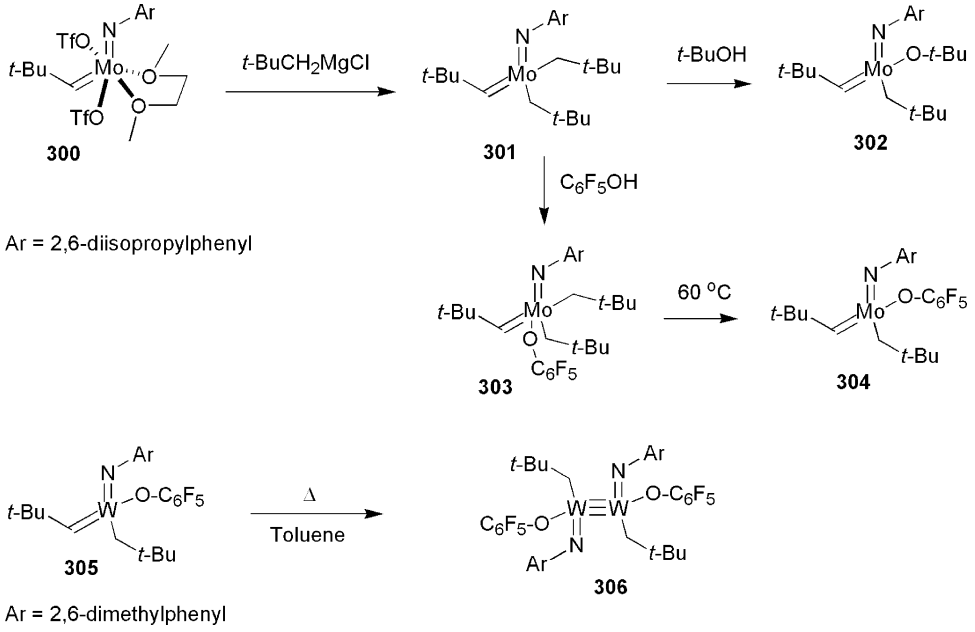
Scheme 18.

ics. The synthesis of silica-bound tantalum carbene complexes (e.g. **293**) was reported [591]. The agnostically bound tantalum carbene complex **293** was active in propane metathesis. An analogous dialkyltantalum complex **294** was inactive.

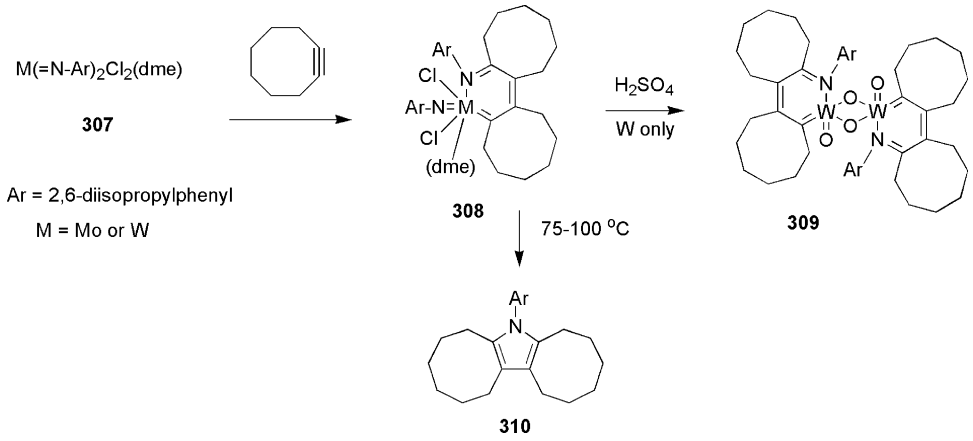
1.1.3.3. Group VI metal–carbene complexes (further classified according to structure and reaction type).

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 (**3**) belongs to this class of compounds.

The reaction of molybdenum carbene complex **300** (Scheme 19) with neopentyl Grignard resulted in molybdenum carbene complex **301** [592]. The addition product **303** was formed upon treatment with pentafluorophenol, which transformed to carbene complex **304** upon heating to 60 °C. Reaction with bulky aliphatic alcohols led to the complex **302** directly. The complexes were capable of initiating alkene metathesis but were short-lived. Similar studies were reported for tungsten carbene complex analogs. The synthesis and reactivity of tungsten carbene imido complexes was reported [593]. Thermolysis of carbene complex **305** in toluene d_8 led to carbene



Scheme 19.



Scheme 20.

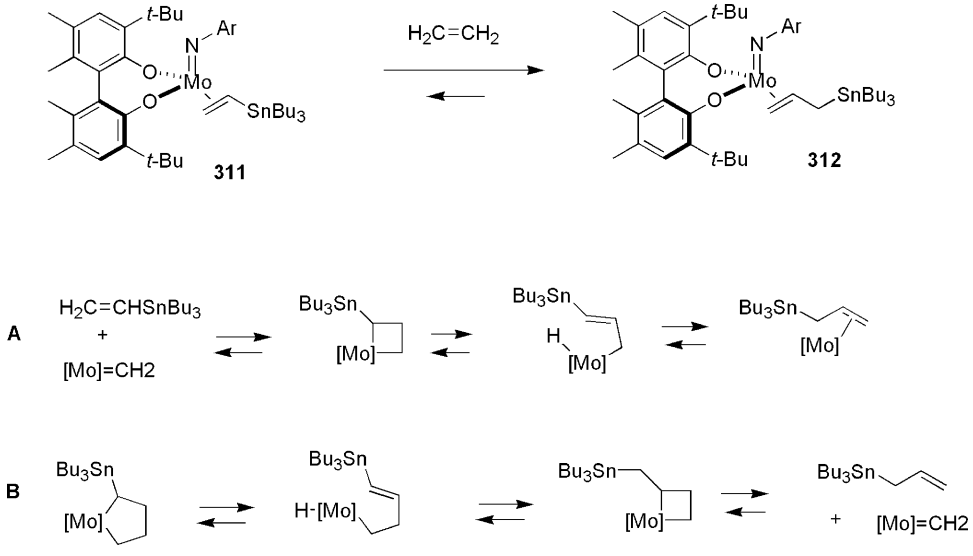
dimer 1,2-*t*-butylethylene and dimeric tungsten compound **306**. The 2,6-bis(isopropyl)phenylimido analog of complex **305** was more thermally robust. Similar carbene complexes of molybdenum and tungsten featuring a Cp^* ligand were also reported [594].

A novel alkyne dimerization of cyclooctyne to cyclic molybdenum (or tungsten) carbene complex **308** (Scheme 20) was reported [595]. The proposed mechanism involves [2 + 2]-cycloaddition of the alkyne and metal imido functionality followed by ring opening, followed by a [2 + 2]-cycloaddition between the alkyne and metal carbene functionality. Thermolysis afforded pyrrole derivative **310**. The dimeric complex **309** was formed upon protonation of tungsten complex **308**.

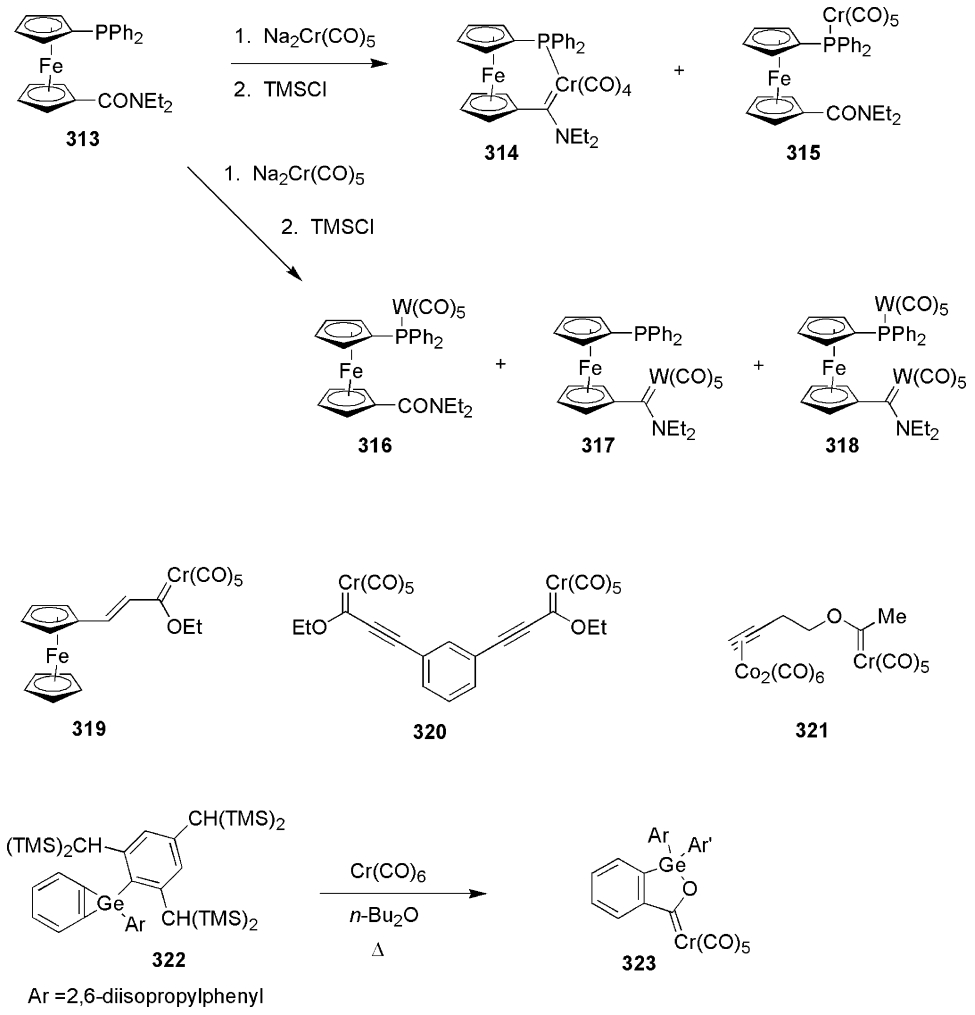
Molybdenum–carbene complexes were proposed as intermediates in the conversion of vinylstannane complex **311** (Scheme 21) and ethylene to the corresponding allylstannane complex **312** [596]. The complex can also serve as a catalyst for conversion of vinyltributyltin and ethylene to allyltributyltin. Two mechanistic scenarios (**A** and **B**) were considered. In mechanism **A** [2 + 2]-cycloaddition of a carbene complex and the vinylstannane occurs, followed by β-hydride elimination and reductive elimination to afford the allylstannanes. Mechanism **B** involves oxidative ligand coupling to afford the metallacyclopentane, followed by β-hydride elimination and insertion with regiochemistry opposite to the reductive elimination to afford the metallacyclobutane. The allylstannane forms by retro[2 + 2]-cycloaddition. The latter mechanism was favored.

A computational study of ring opening reactions of molybdacyclobutenes was reported [597]. A molybdenum–carbene complex oxide was observed by IR from the reaction of acetaldehyde with a molybdenum carbide [598]. An X-ray structure of isocyanide complex tris[*N*-(3,5-dimethylphenyl)-*N*-*t*-butylamido]Mo–C≡N-*t*-Bu revealed that the cumulene structure is a more accurate description of the complex [599].

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



Scheme 21.



Scheme 22.

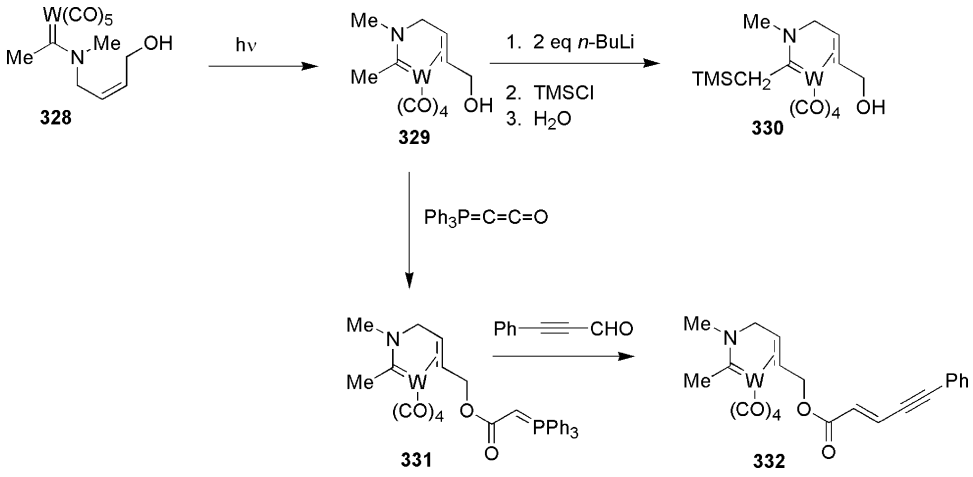
Synthesis of chelated ferrocenylcarbene complexes (e.g. **314**, **317–318**, Scheme 22) was reported [600]. Reaction of ferrocenylamide derivatives (e.g. **313**) with metal carbonyl anions and chlorotrimethylsilane led to the chelated carbene complexes (e.g. **314**) and the phosphine-ligated metal carbonyl derivatives (e.g. **315–316**). Analogous iron complexes were also reported. The electrochemistry of the carbene complex products was studied. Various bimetallic carbene complexes were generated from reaction of Group VI acylate carbene complexes with various transition metal halides [601]. Electrochemical studies were also reported for these complexes. Various bimetallic carbene complexes (e.g. **319–321**) were prepared and their behavior in electrospray mass spectrometry tested [602]. The bis(carbene) complex could not be ionized unless hydroquinone was an additive. The ferrocenylcarbene complexes were ionizable due to the presence the ferrocenyl group. No ionization was observed with the cobalt complex due to reduction in the ESI source. Treatment of the germanium species **322** with chromium hexacarbonyl led to cyclic chromium carbene complex **323** [603].

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

The intramolecular coupling of alkenes and carbene complexes was reported (Scheme 23) [604]. Allylaminocarbene complexes (e.g. **328**) afforded the internally coordinated complexes (e.g. **329**) upon irradiation. Both *O*- and *C*-silylation reactions were reported for the internally coordinated complexes. Conversion of the free alcohol group of complex **329** to the stabilized Wittig reagent **331** and subsequent carbonyl olefination reactions were reported [605].

Chromium-pentacarbonyl catalyzed cyclopropanation reactions were reported [606]. Treatment of diazo compounds (e.g. **333**, Scheme 24) with alkoxybutadiene derivatives in the presence of (cyclooctene)-$Cr(CO)_5$ led to the alkenylcyclopropane derivatives (e.g. **337**). Preferential cyclopropanation at the less substituted double bond was observed. Chromium carbene complexes were proposed as intermediates in the opening of furan rings using diazo compounds and (cyclooctene)$Cr(CO)_5$ [607].

1.1.3.3.4. Reaction of Group VI metal–carbene complexes with alkynes—benzannulation. Many examples of benzannulation using α,β-unsaturated chromium–carbene complexes



Scheme 23.

(Scheme 25) and alkynes (commonly known as the Dötz reaction) were reported in 2004. Examples are depicted in Scheme 25 and include: (1) synthesis of highly oxygenated naphthalenes (e.g. **342**) through coupling of carbene complex **340** and alkyne-protected diol-alkyne **341** [608] and (2) synthesis of quinones fused to benzofurans using benzofuranylcarbene complexes [609]. A more complex example employing multiple benzannulation reactions for the synthesis of tris(quinones) was reported [610]. Reaction of triyne **344** and cyclohexenylcarbene complex **343** led to the *o*-dialkyne-substituted naphthol derivative **346**. Acetylation of the alcohol and desilylation of the bis(alkyne), followed by a double benzannulation using two equivalents of the carbene complex **343** led to tris(quinone) precursor **346**. This synthetic sequence was not successful for alkyl analogs of **344** due to preferential benzannulation of one of the outer triple bonds. A complex benzannulation reaction was observed when bis(carbene complex) derivative **347** couples with bis(alkyne) derivatives (e.g. **348**). This coupling resulted in the formation of calixarenes (e.g. **349**) in moderate yields [611].

1.1.3.3.5. Nonbenzannulation reactions of Group VI metal–carbene complexes with alkynes. Other processes involving the capture of vinylcarbene complexes generated from the coupling of carbene complexes and functionalized alkynes were reported in 2004.

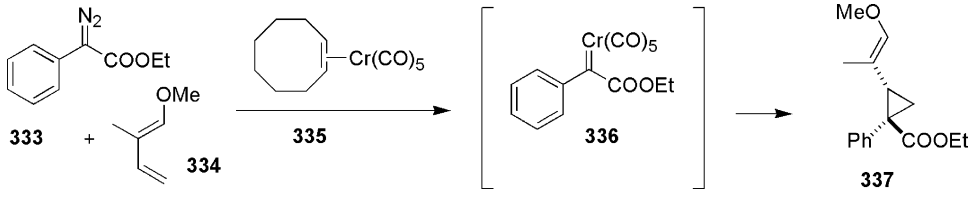
The coupling of 2-alkynylstyrene derivatives (e.g. **350**, Scheme 26) with carbene complexes (e.g. **351**) was reported [612]. This reaction results predominantly in the formation of indene derivatives (e.g. **355**–**356**). The proposed mechanism involves nucleophilic attack of the alkene at the carbene complex (conversion of **352**–**353**). The efficiency of the reaction could be correlated directly with the nucleophilicity of the alkene and the electrophilicity of the carbene complex.

The coupling of Fischer carbene complexes with propargylsilanes (e.g. **358**, Scheme 27) was reported [613]. If the R^1 group is not H, this reaction resulted in the formation of silicon-shifted diene derivatives (e.g. **361**). The reaction employing the simple propargylsilane (**358**, R^1 = H) and phenylcarbene complex **359** led to the benzannulation product **364**. The key mechanistic event in the formation of dienes is the 1,2-migration of silicon in intermediate vinylcarbene complex **359**, which requires the presence of a carbocation-stabilizing group at the propargyl position. In the absence of this stabilization the Dötz benzannulation (see Scheme 25) product **364** was obtained.

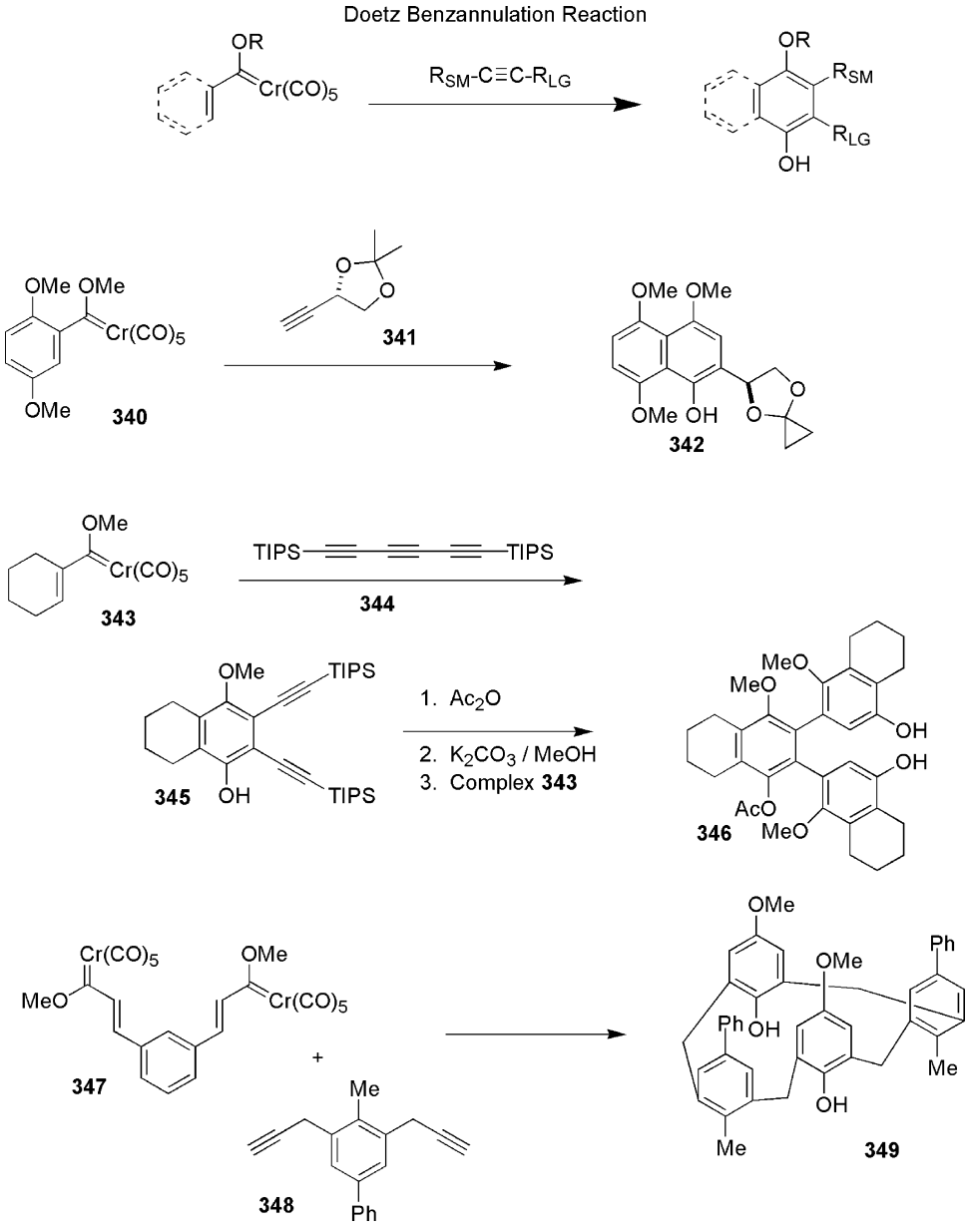
The coupling of β-aminoalkenylcarbene complexes (e.g. **365**, Scheme 28) with alkynes was reported [614,615]. In general this coupling leads to aminocyclopentadiene derivatives, which undergo Diels–Alder reactions with the alkynes to afford the ring-fused norbornadiene derivatives. The overall conversion was also successful using diynes and tetraynes.

1.1.3.3.6. Photolytic generation of ketenes from Group VI metal–carbene complexes. The formation of chromium ketene complexes (e.g. **372**, **375**, Scheme 29) through photolysis of Fischer carbene–chromium complexes (e.g. **370**, **374**) was reported [616]. The cyclobutenone products (e.g. **373**) were subjected to ring expansion reactions for the preparation of cyclopentenones. Benzannulation resulting in carbazole derivative **376** was reported. This process occurs via tandem photolytic ketene generation and electrocyclic ring closure [617].

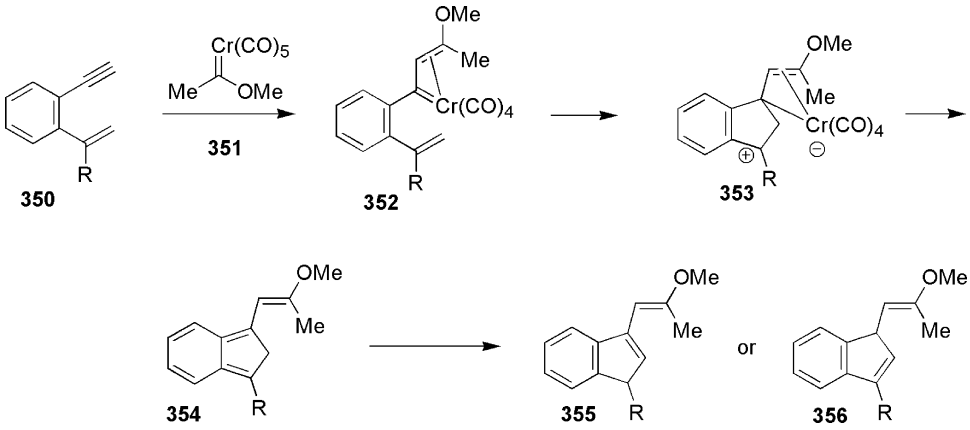
1.1.3.3.7. Reactions occurring at the conjugated C–C π-bond of α,β-unsaturated Group VI metal–carbene complexes. Numerous reaction processes were reported in 2004 where a carbene complex activates a π-bond for nucleophilic addition or cycloaddition reactions (i.e. the carbene complex is a surrogate for an "activated ester").



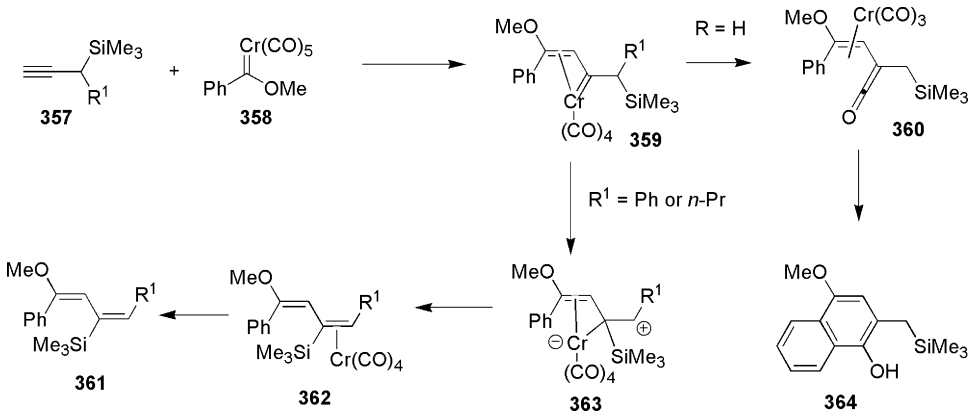
Scheme 24.



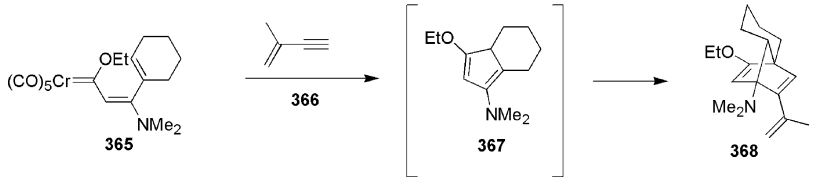
Scheme 25.



Scheme 26.



Scheme 27.

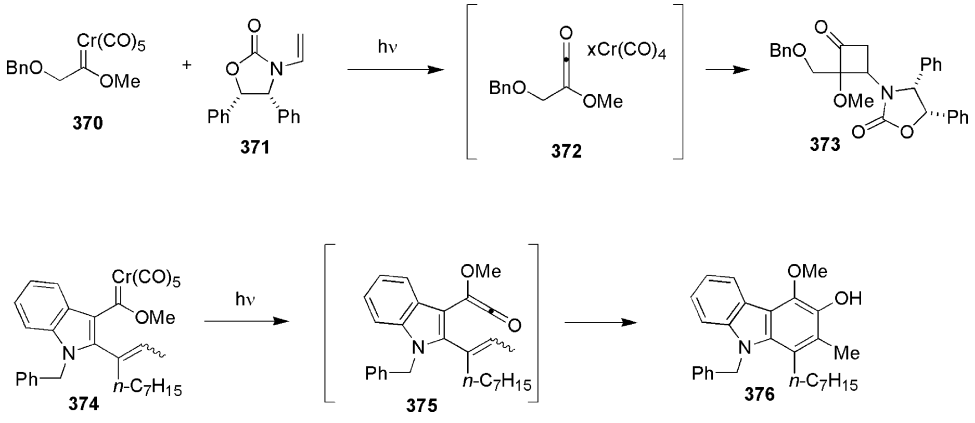


Scheme 28.

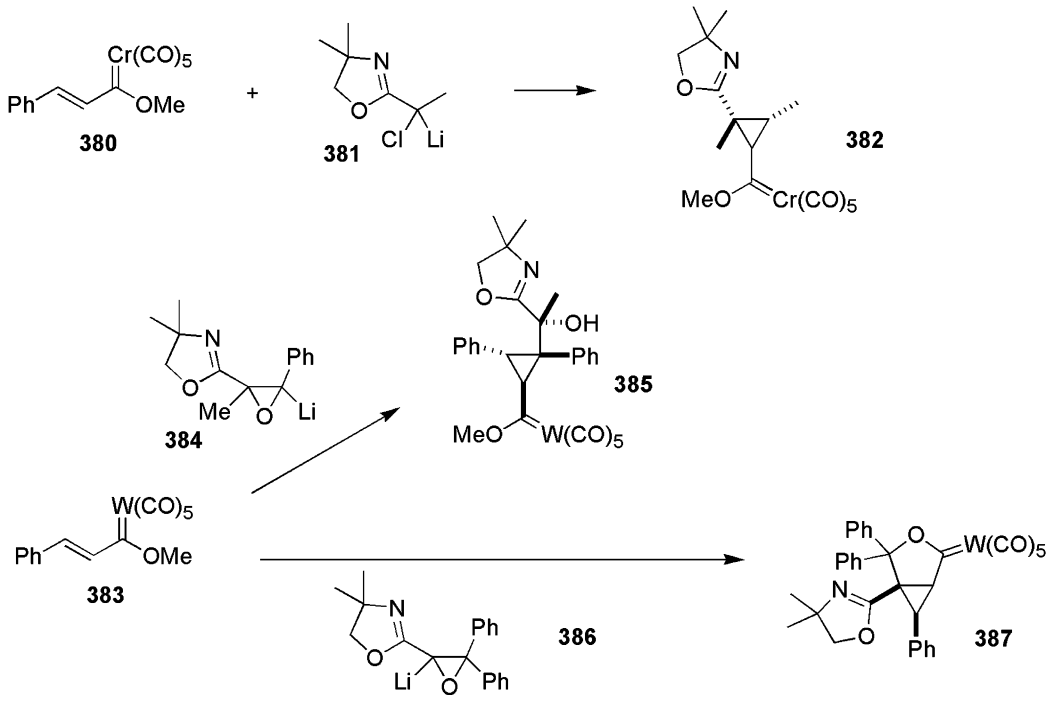
A new synthesis of cyclopropylcarbene–chromium complexes (e.g. **382**, Scheme 30) from α,β-unsaturated chromium carbene complexes (e.g. **380**) and lithiated α-chloroiminoesters (e.g. **381**) was reported [618]. The reaction involves the Michael addition to the carbene complex followed by intramolecular S_N2 reaction. Cyclopropylcarbene tungsten complexes were similarly prepared by Michael addition of lithiated epoxide-iminothers (e.g. **384**, **386**) to α,β-unsaturated tungsten complexes (e.g. **383**) [619]. Cyclopropanes fused to cyclic carbene complexes (e.g. **387**) were prepared from coupling of α-lithio epoxide-iminoesters (e.g. **386**) with alkenylcarbene–tungsten complexes. This process involves Michael addition, followed by attack of the resulting anion at the epoxide, followed by alkoxy group exchange. The β-lithio epoxide-iminoesters (e.g. **384**) afforded simple cyclopropanes. Since the opposite stereochemistry was obtained for the cyclopropane ring the alkoxy group exchange process does not occur.

Michael addition of thiols to alkynylcarbene complexes (e.g. **388**, Scheme 31) was reported [620]. A reductive benzannulation reaction was reported for the resulting thioethenylcarbene complex **391** and phenylacetylene. Conversion of the alkoxycarbene complexes to aminocarbene complexes (e.g. **393**) was also reported. Michael addition of stannyl anions to alkynylcarbene complexes was also reported [621]. In addition to the Michael addition product **395**, the cyclopentadienylcarbene complex **396** was also obtained. A free radical mechanism was suggested for the formation of **396**. Formation of the radical anion **397** through electron transfer followed by dimerization and protonation afforded dimeric complex **399**, which then undergoes a base-induced cyclization.

Diels–Alder reactions were reported for α-alkoxy-α,β-unsaturated carbene complexes (e.g. **400**, Scheme 32) [622]. Reactions with cyclopentadiene led to predominantly the endo adduct **402** accompanied by the oxidation product **403**. The



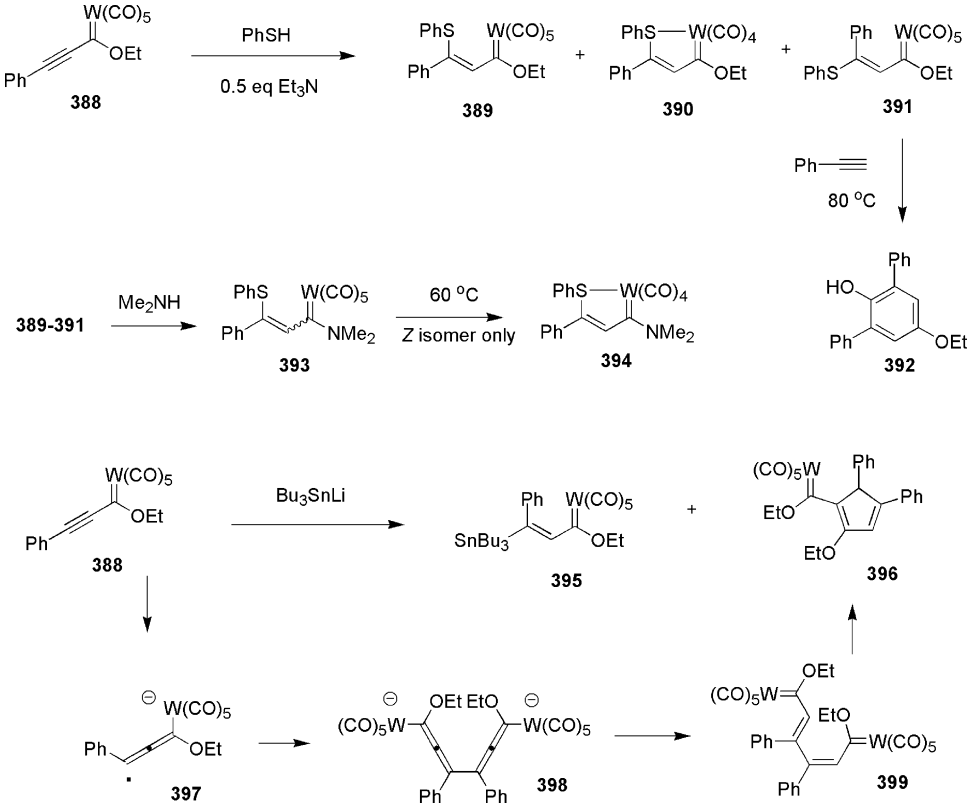
Scheme 29.



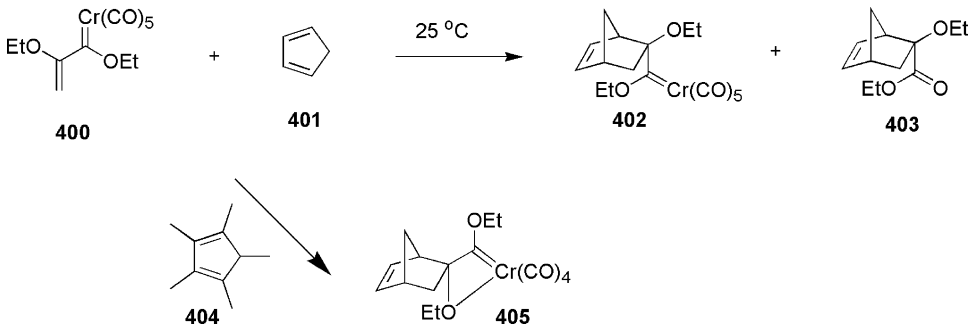
Scheme 30.

oxygen coordinated exo isomer (**405**) was obtained from the reaction employing pentamethylcyclopentadiene.

1.1.3.3.8. Physical organic chemistry of Group VI Fischer carbene complexes. The effect of arene complexation on the rate of aminolysis of aryl(alkoxy)carbene chromium complexes (e.g. **408** and the uncomplexed analog, Scheme 33) was reported [623]. Arene complexation has a minor effect on the electrophilicity of the carbene complexes, however the presence of arene complexation alters the rate determining step of aminolysis from leaving group departure (uncom-

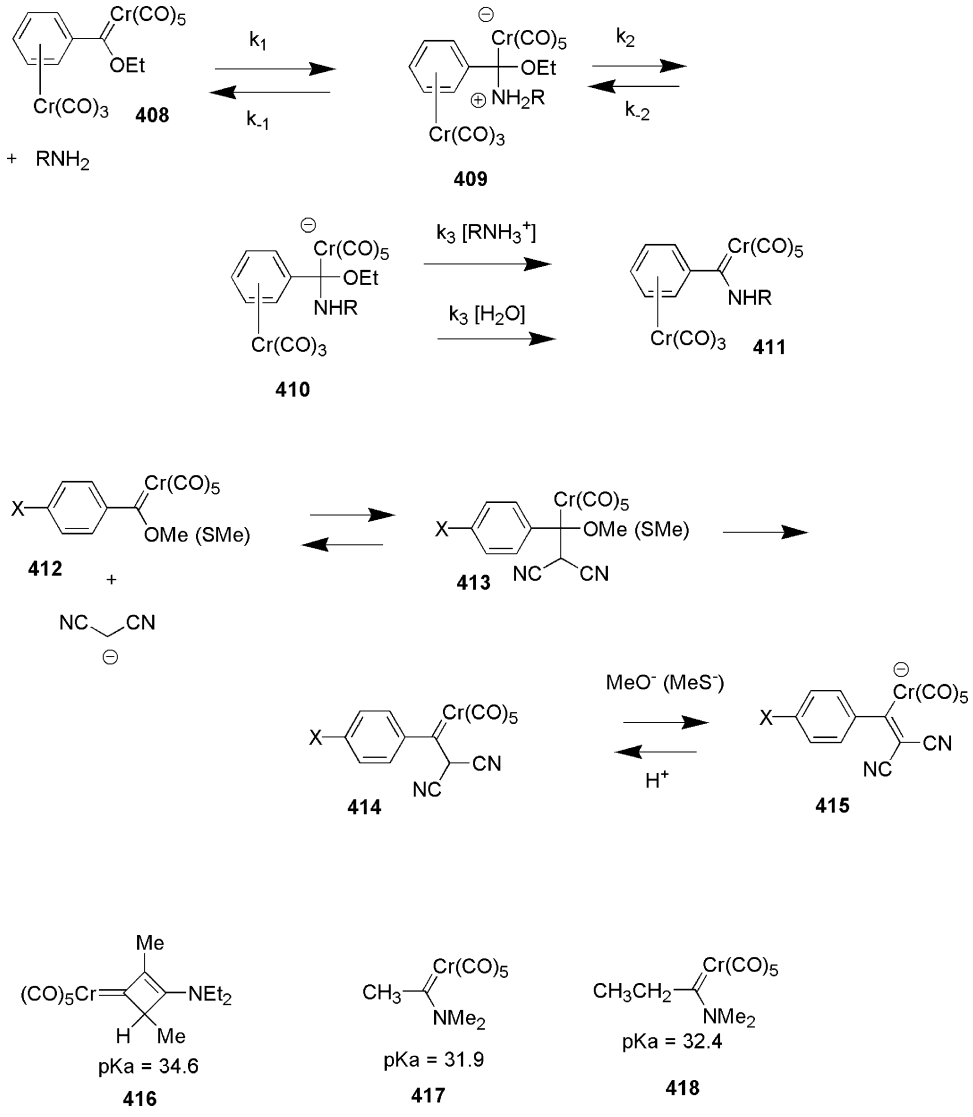


Scheme 31.

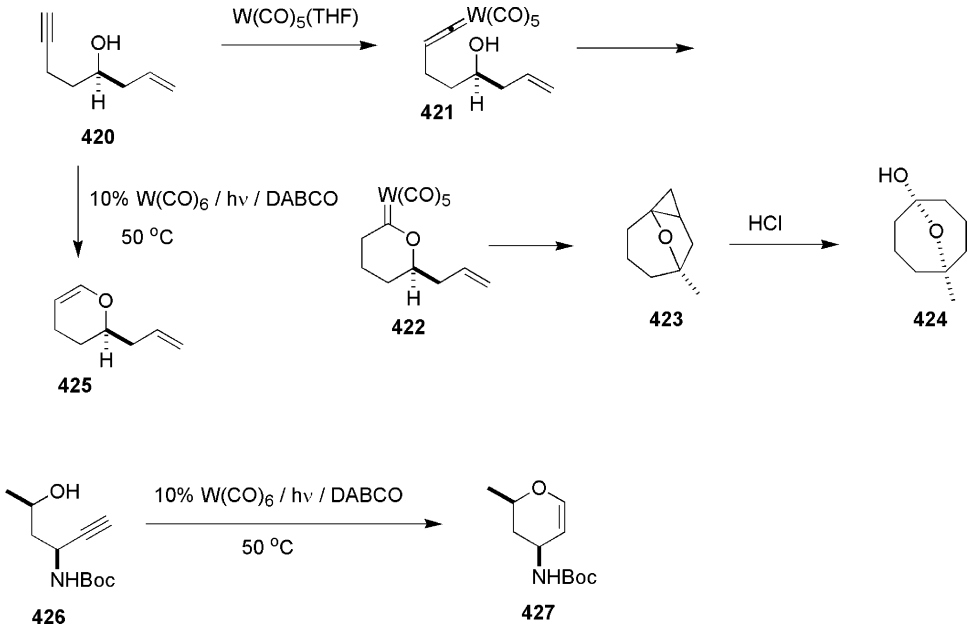


Scheme 32.

plexed) to rate limiting proton transfer (complexed). Detailed rate studies for the aminolysis of thiocarbene complexes were also reported [624]. The kinetic parameters for reaction of Group VI metal–carbene complexes (e.g. general structure **412**, Scheme 33) with dicyanomethyl anion were evaluated in aqueous acetonitrile [625]. The dicyanomethyl anion was more reactive than hydroxide or amines but less reactive than thiolates. Reactions employing alkoxycarbene complexes were faster than analogous reactions involving thiocarbene complexes. A comparison of the acidity of complex **416** and simple aminocarbene



Scheme 33.



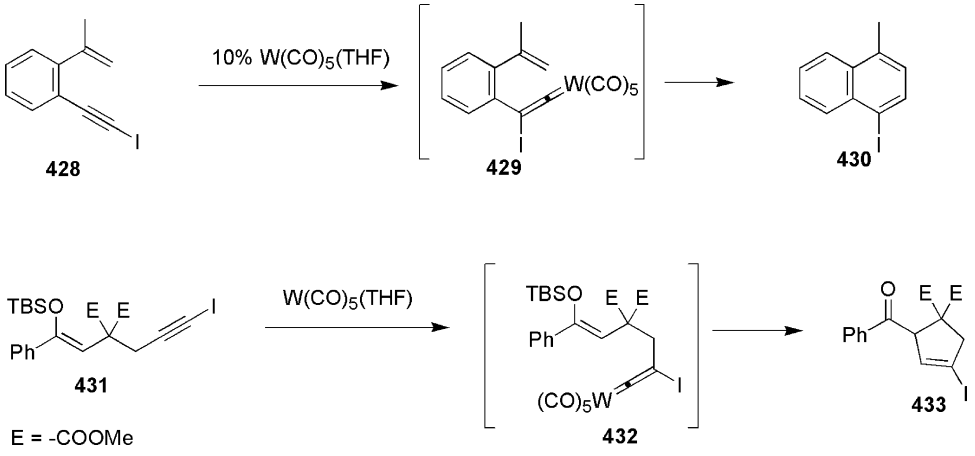
Scheme 34.

complexes (e.g. **417**–**418**) was reported [626]. The lesser acidity of complex **416** was attributed to the antiaromatic character of the resulting anion.

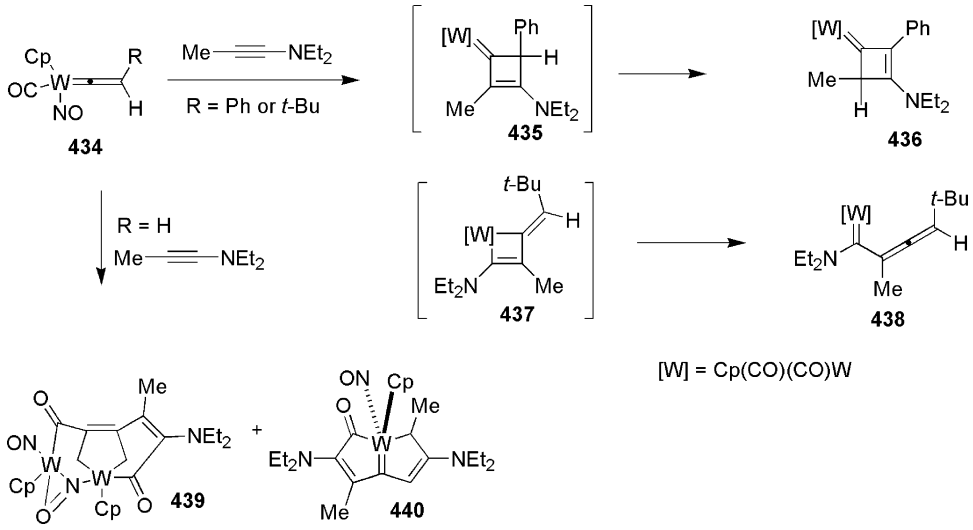
1.1.3.3.9. Synthesis and reactivity of Group VI metal–vinylidene complexes, and reactions that involve vinylidene–metal complexes as intermediates; also includes other process that involve the formation of a carbene complex from an alkyne and a non-carbene metal complex. The synthesis of eight-membered rings (e.g. **424**, Scheme 34) from enynols (e.g. **420**) and tungsten pentacarbonyl sources was reported [627]. The mechanism for this process involves formation of a vinylidene (e.g. **421**) followed by formation of the cyclic carbene complex (e.g. **422**), followed by an intramolecular cyclopropanation to afford a tricyclic compound (e.g. **423**). Acid-induced opening of the cyclopropane ring of **423** affords the eight-membered ring compound. If the reaction was performed at elevated temperature the enol ether derivative **425** was obtained, presumably through base-induced decomposition of carbene complex intermediate **422**. Formation of amide-substituted dihydropyran derivatives (e.g. **427**) was reported using alkynols and photochemically generated tungsten pentacarbonyl [628]. Similar conditions were employed for the preparation of seven-membered ring glycals from alkyne-diol derivatives [629].

The reaction of *o*-alkynylstyrene iodides (e.g. **428**, Scheme 35) with tungsten pentacarbonyl sources was reported [630]. The reaction afforded naphthalenes (e.g. **430**) through formation of a vinylidene complex (e.g. **429**) followed by electrocyclic ring closure. A mechanistically similar reaction occurred upon treatment of the enol ether–iodoalkyne **431** with tungsten pentacarbonyl sources. Vinylidene formation followed by intramolecular nucleophilic attack on the vinylidene complex led to the iodocyclopentene derivative **433**.

The reaction of tungsten vinylidene complex **434** (Scheme 36) with ynamines was reported [631]. Cyclobutenylidene complexes (e.g. **436**) were obtained using the



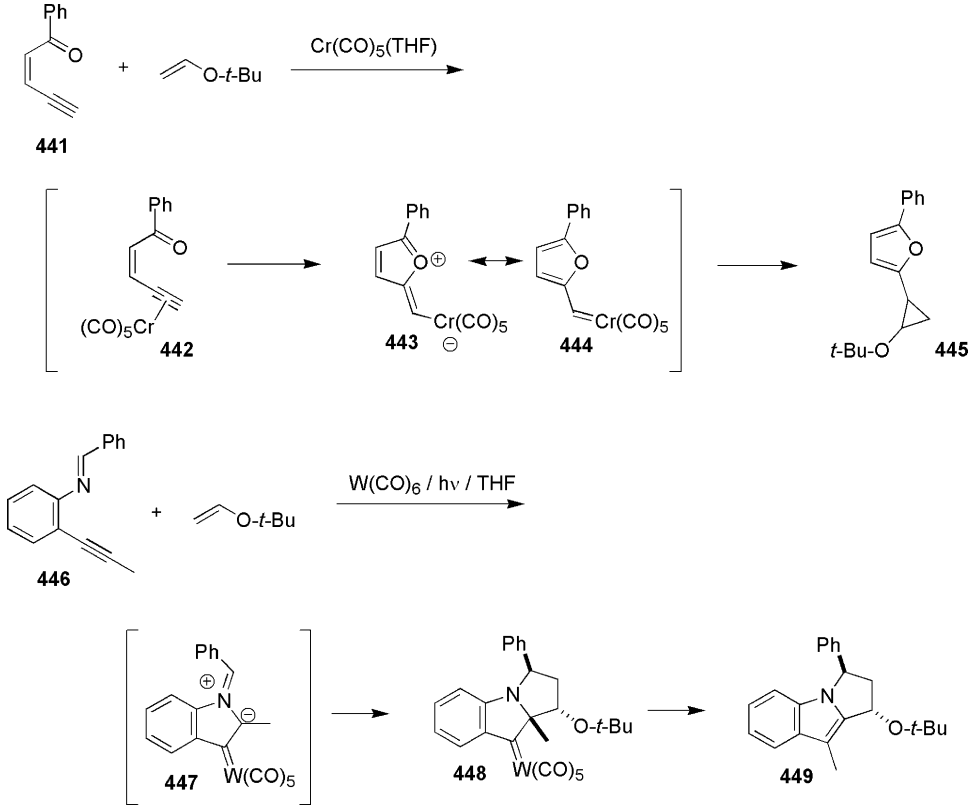
Scheme 35.



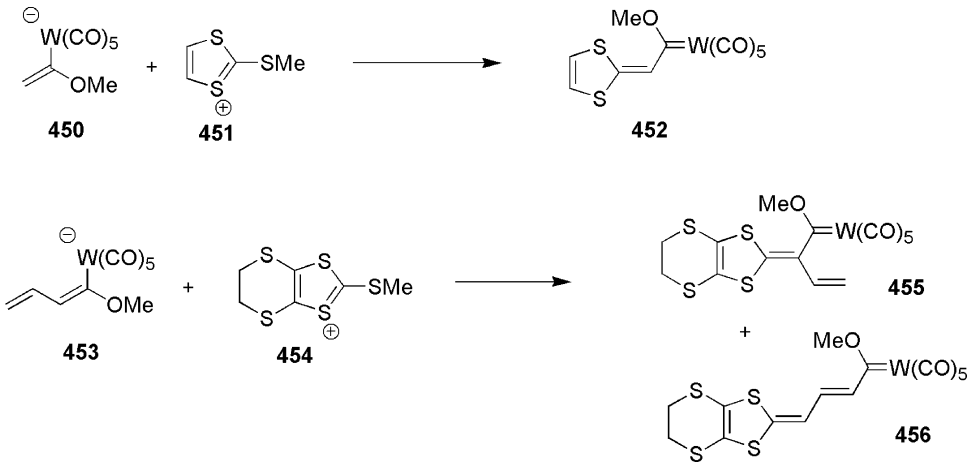
Scheme 36.

phenylvinylidene complex via rearrangement of the [2 + 2]-cycloaddition product **435**. The allenylcarbene complex **438** was obtained from the *t*-butylvinylidene complex, likely through ring opening of the initially formed metallacyclobutene complex **437**. A complex reaction pathway resulting in binuclear complex **439** and bicyclic carbene complex **440** was observed using the terminal vinylidene complex. A complex mechanistic scheme initiated by nucleophilic attack of the β-ynamine carbon at the carbene carbon was proposed.

The formation of furanylcyclopropanes (e.g. **445**, Scheme 37) through coupling of enyne-ketones (e.g. **441**) with monosubstituted alkenes in the presence of chromium pentacarbonyl sources was reported [632]. The reactions proceed via initial formation of a π-alkyne complex (**442**), which undergoes nucleophilic attack by the carbonyl oxygen to afford the furanylcarbene complex (**444**), which then undergoes cyclopropanation with the alkene. In the absence of an alkene additive carbene dimers were observed. A mechanistically similar process was



Scheme 37.



Scheme 38.

observed in the reaction of *N*-2-alkynylphenylimines (e.g. **446**) with tungsten pentacarbonyl sources in the presence of enol ethers, which leads to fused indoles (e.g. **449**) [633]. A mechanism involving alkyne complexation and nucleophilic attack to generate the 1,3-dipole–carbene complex (**447**) followed by 1,3-dipolar cycloaddition with the enol ether was proposed. The initially formed carbene complex **448** can be isolated however in most cases an alkyl shift occurred to afford the indole derivative **449**.

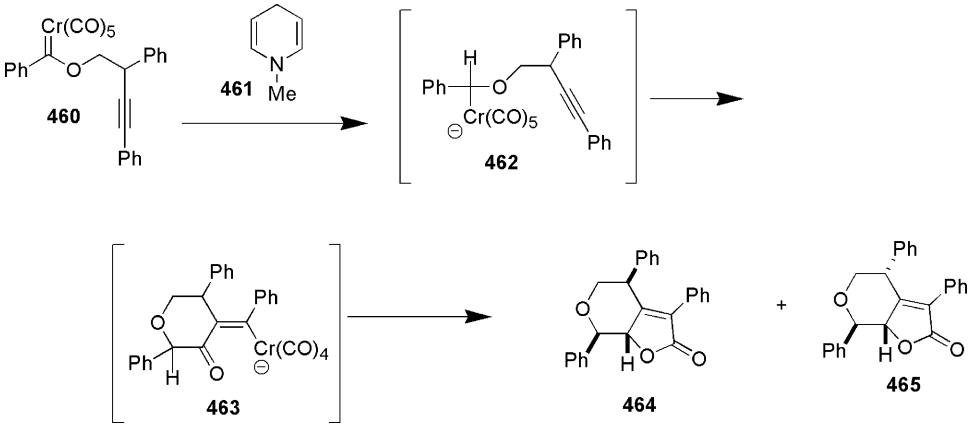
Ligand substitution reactions were reported for allenylidene–$Cr(CO)_5$ complexes [e.g. $Me_2N(Ph)C{=}C{=}C{=}Cr(CO)_5$] [634]. Irradiation in the presence of phosphines in an argon stream led to the *cis* phosphine-substituted allenylidene complexes, which isomerize to *cis–trans* mixtures in solution at room temperature. In some cases a bis(phosphine) complex could be formed.

1.1.3.3.10. Reactions involving carbanions derived from deprotonation of Group VI metal–carbene complexes. The coupling of carbene complex-derived anions (e.g. **450**, **453**, Scheme 38) with dithiolium cations (e.g. **451**, **454**) was reported [635]. The reaction afforded the condensation products **452** and **455–456**. Reaction employing the extended anion **453** afforded predominantly the product of γ-attack, **456**. These products were subjected to dimerization using palladium(II) salts.

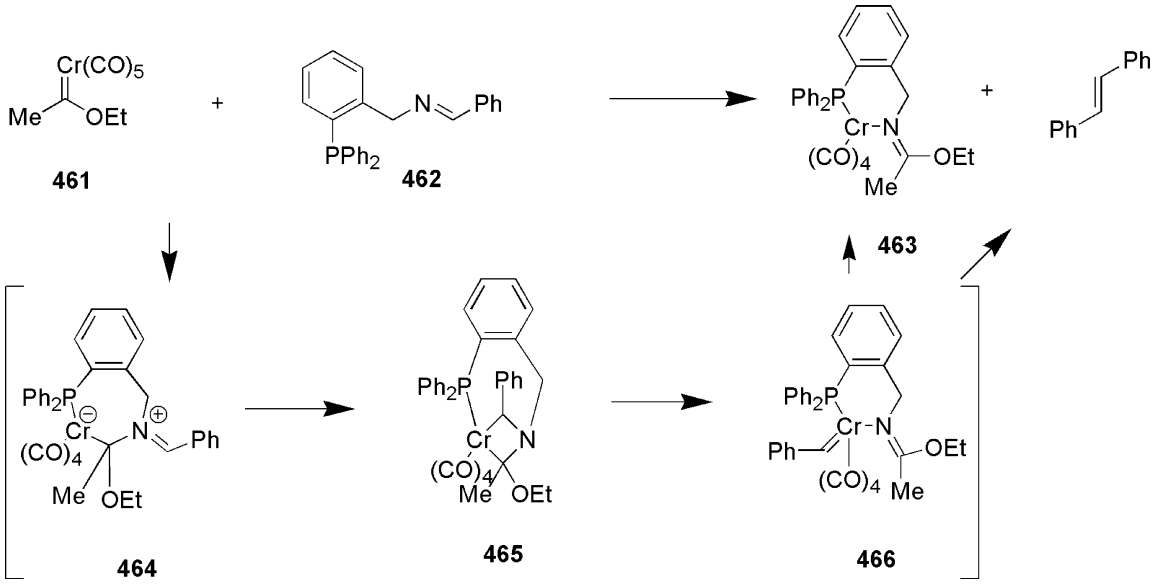
1.1.3.3.11. Reactions involving the addition of nucleophiles to the carbene carbon. The coupling of alkyne-containing chromium–carbene complexes (e.g. **460**, Scheme 39) with dihydropyridine derivatives (**461**) and with carbon nucleophiles was reported [636]. A variety of annulated furanones can be produced from this reaction, depending upon the type of alkyne–carbene complex tether employed. In general this reaction proceeds via nucleophilic addition to the carbene carbon (e.g. hydride addition leading to **462**), followed by CO insertion and alkyne insertion, followed by a second CO insertion and coupling of the carbonyl oxygen and acylmetal complex.

An imine metathesis reaction was observed upon treatment of methylcarbene complex **461** (Scheme 40) with imino esters (e.g. **462**) where the *N*-substituent is connected to a phosphine group [637]. The proposed mechanism involves phosphine coordination followed by nucleophilic addition of nitrogen to the carbene carbon to afford **464**. Formation of the metallaazacyclobutane (**465**), followed by retrocycloaddition affords carbene complex intermediate **466**, which undergoes carbene dimerization to afford the observed products **463** and stilbene.

A novel allylation reaction was reported involving the reaction of allylic alkoxides and cinnamylcarbene complexes (e.g. **467**, Scheme 41) where the arene ring is complexed to the chromium tricarbonyl unit [638]. A mechanism involving addi-



Scheme 39.



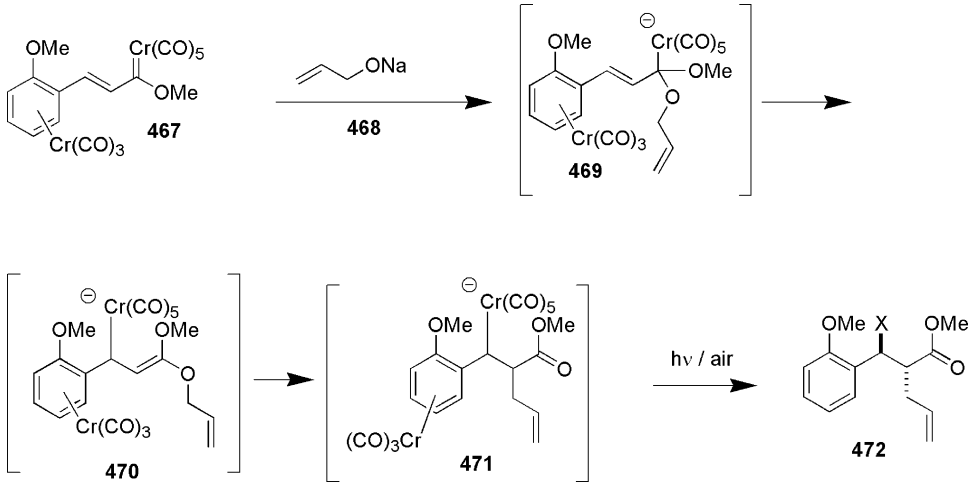
Scheme 40.

tion of the alkoxide to the carbene carbon, followed by 1,3-shift of the resulting allylmetal complex resulting in allyl vinyl ether **470**, followed by Claisen rearrangement and demetallation was proposed. Chromium carbenes led to the reduced derivatives (**472**, X = H), while tungsten carbenes led to the alcohol derivatives (**472**, R = OH). High de's relative to the chiral chromium arene functionality were observed.

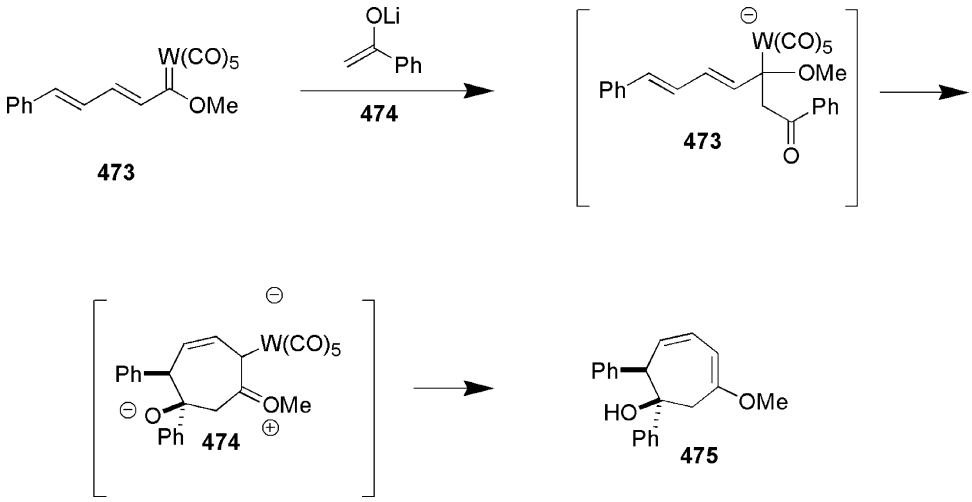
A new cycloheptadiene synthesis that utilizes the coupling of dienylcarbene–tungsten complexes (e.g. **473**, Scheme 42) and enolates was reported [639]. A mechanism involving addition of the enolate to the carbene carbon followed by nucleophilic addition of the resulting pentadienoyl–tungsten complex to the carbonyl group was proposed.

1.1.3.3.12. Reactions that involve transfer of a Fischer carbene ligand to another metal. The coupling of alkenylcarbene chromium complexes (e.g. **380**, Scheme 43) with electron-deficient alkynes in the presence of rhodium catalysts (e.g. **476**) was reported [640]. This reaction results in cyclopentenone derivatives (e.g. **479**–**480**). A mechanism involving carbene transfer to afford rhodium carbene complex **477**, followed by [4 + 2]-cycloaddition of the metalladiene unit followed by reductive elimination was proposed. The rhodium carbene complex could be isolated.

The coupling of alkenylcarbene complexes (e.g. **380**, Scheme 44) with allenes in the presence of a nickel catalyst was reported [641]. The reaction affords alkylidenecyclopentenes (e.g. **484**). A mechanism involving transfer of the carbene ligand to nickel, followed by [2 + 2]-cycloaddition, followed by σ- to π-allyl isomerization and reduction elimination was proposed. An isomeric compound was obtained using a rhodium catalyst. A mechanism involving [4 + 2]-cycloaddition followed by reductive elimination was proposed. Cyclic allenes were also



Scheme 41.



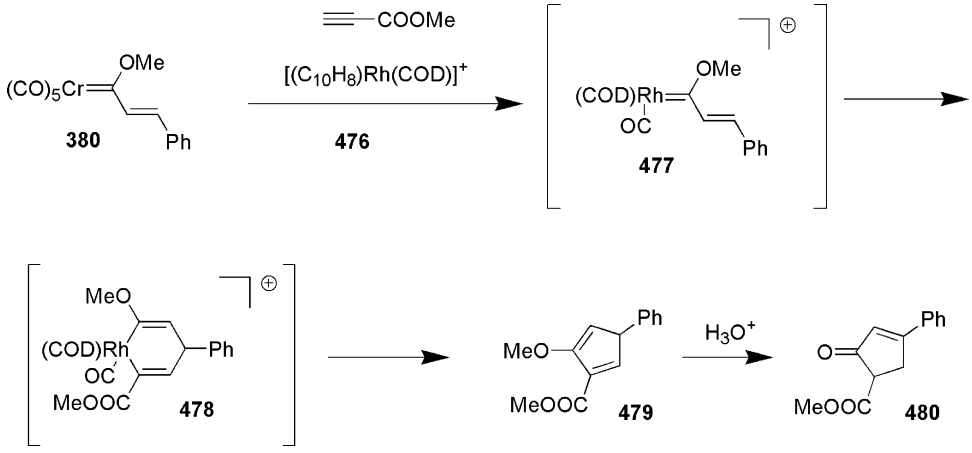
Scheme 42.

employed in the reaction. A similar reaction employing an excess of 1,1-dimethylallene led to cycloheptanone derivatives (e.g. **488**) [642]. A mechanism similar to that leading to **484** was proposed. However prior to the reductive elimination step insertion of a second mole of allene occurred.

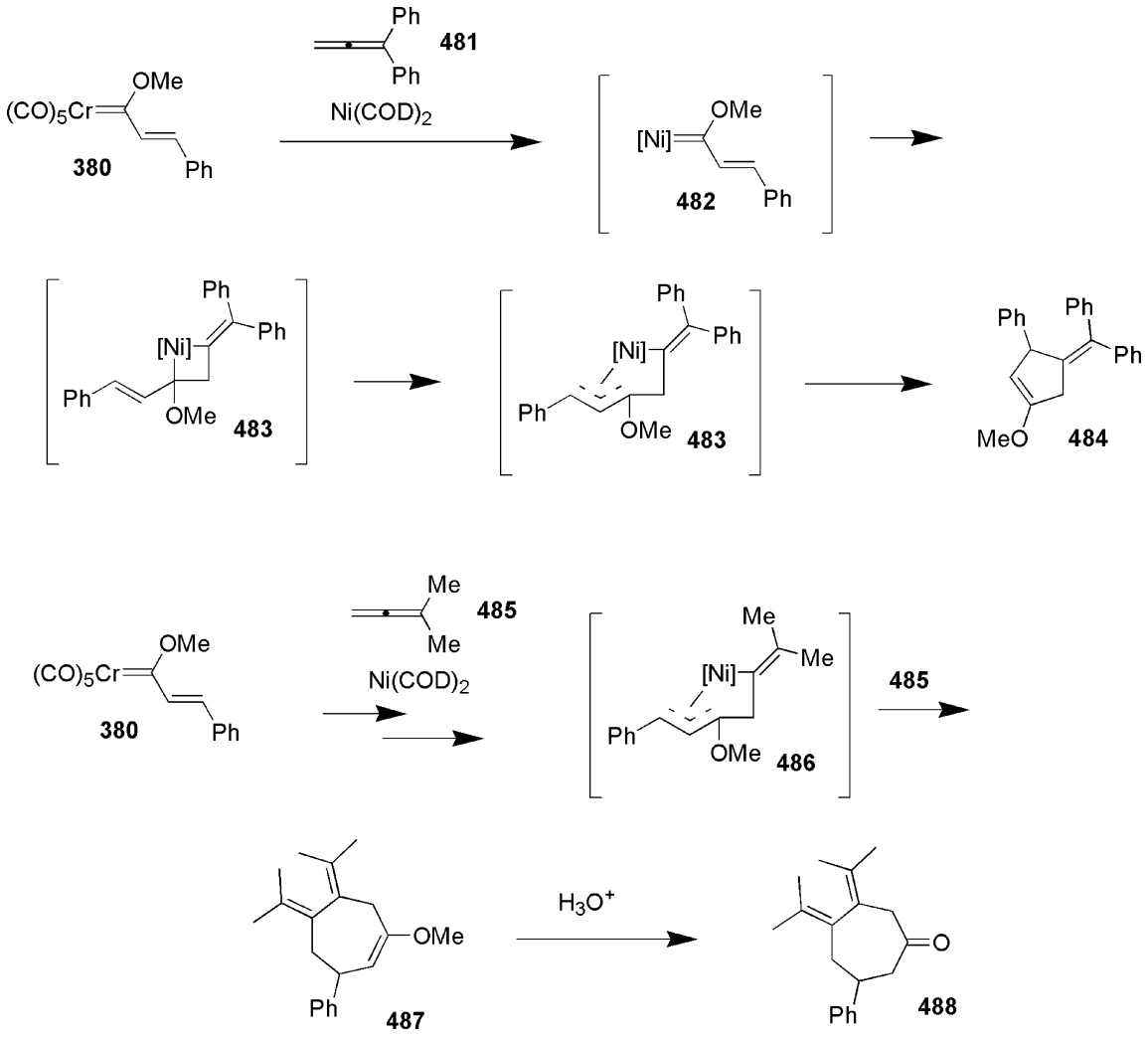
Catalysis of carbene dimerization by copper and nickel salts was reported (Scheme 45). Reaction of phenylcarbene complex **358** with nickel and copper salts led to the dimerization product **489** [643]. Reaction with $Ni(COD)_2$ in the presence of methyl acrylate led to the cyclopropanation product **490**. Reaction with Raney nickel as the catalyst led to the β-oxo ester **491**. These reactions were proposed to proceed through transfer of the carbene ligand to the other metal, followed by reaction with the added alkene. Copper-catalyzed dimerization of α,β-unsaturated carbene complexes (e.g. **492**) afforded conjugated trienes (e.g. **493**), which cyclized to cyclopentenones (e.g. **494**) upon treatment with trifluoroacetic acid [644]. The products from dimerization of aminocarbene complexes (e.g. **496**) underwent electrocyclic ring closure and oxidation to afford 1,2-diaminobenzene derivatives.

1.1.3.3.13. Other reactions of Group VI metal–carbene complexes. The reaction of anionic tungsten carbene complex **500** (Scheme 46) with proton sources in the presence of ligand additives was reported [645]. Protonation in the presence of phenylacetylene led to acyl(alkyne) complex **502**. A mechanism involving protonation at tungsten, followed by a 1,2-shift of H, followed by CO insertion and alkyne complexation was proposed. Protonation in the presence of phenyl(dimethyl)phosphine led to the η^2-acyl complex **504** in equilibrium with the methyl(dicarbonyl) complex **503**. Increasing the cone angle of the phosphine led to a greater proportion of the η^2-acyl complex at equilibrium.

Bimetallic carbene complexes (e.g. **508**, Scheme 47) were prepared from alkynylcarbene complexes (e.g. **505**) [646]. Reaction of the aminocarbene complex with one mole of *n*-butyllithium followed by either an iron or platinum halide complex led to mixtures of the *N*-metallated and *C*-metallated complexes. Bis(metallated) complexes were produced if two equivalents of base and two equivalents of metal halide were used.



Scheme 43.



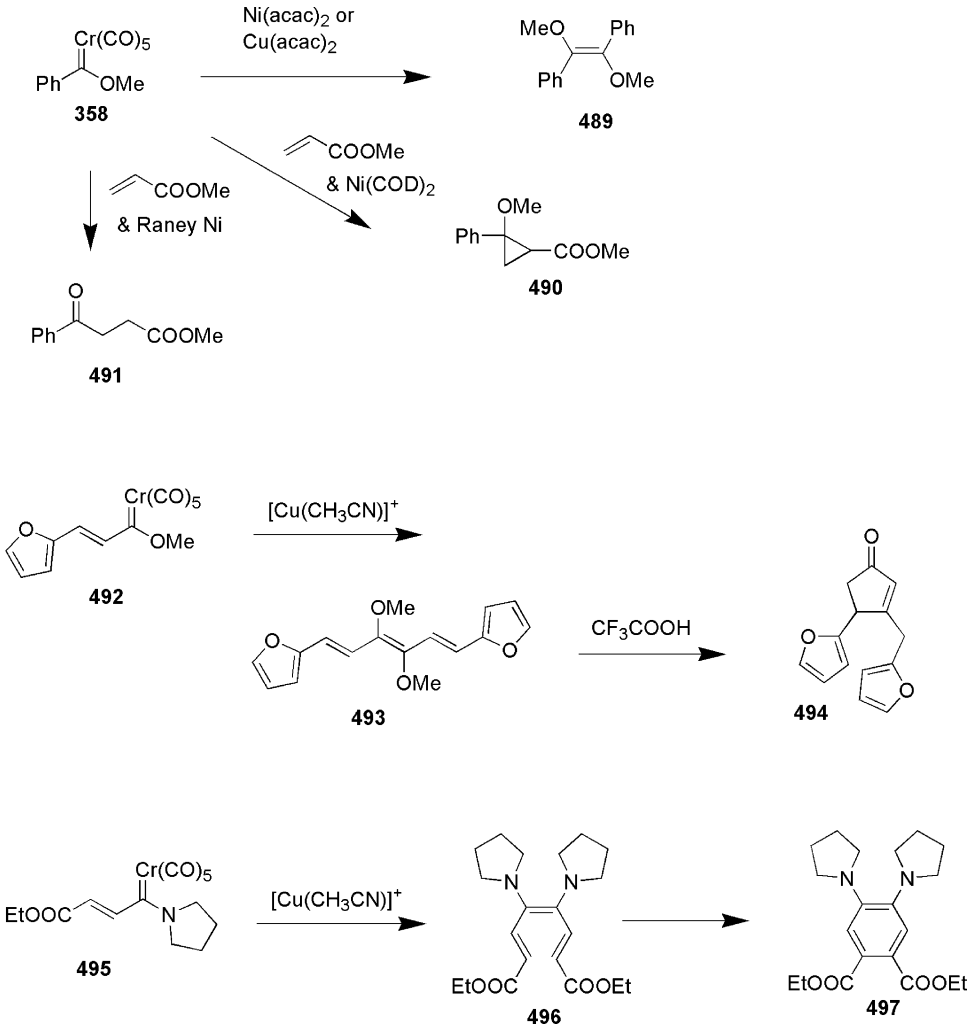
Scheme 44.

Other experimental studies of Group VI metal–carbene complexes are depicted in Scheme 48 and include: (1) preparation of *N*-heterocyclic carbene complexes (e.g. **509**–**510**) through reduction of *o*-nitrophenylisocyanide–Group VI metal complexes [647]; (2) diastereoselective preparation of chiral propargylstannanes (e.g. **512**) by reaction of chiral carbene complexes (e.g. **511**) with tributyltin hydride [648]; (3) a new procedure for the oxidation of Fischer carbene complexes to corresponding esters using fluoride ion in air [649]; (4) implication of chromium carbene complexes as intermediates in the formation of alkylideneallyl complexes from metal carbonyl anions and 1,4-dichloro-2-butyne [650]; (5) gas phase studies of molybdenum carbene complexes [651].

A computationally based comparison of the structure of Fischer carbene complexes (**514**, Scheme 49) and the analogous free carbenes (**513**) was reported [652]. In both cases the anti conformation is favored for every case except where R is alkynyl. The primary reason for this conformational preference in the free carbenes is electronic. A favorable electronic interaction was noted in the anti conformation of the carbene complex involving the π^* orbital of a CO ligand and σ orbital of the methyl C–H bond, and the complementary interaction between the π orbital of the CO ligand and a σ^* orbital of the C–H bond. The energy differences are more severe in the free carbenes than in the carbene complexes.

1.1.3.4. Group VII metal–carbene complexes. Generation of isobenzofuranylcarbene complexes (e.g. **523**, Scheme 50) through reaction of *o*-alkynylacetophenones (**520**) with rhenium complex **521** and light was reported [653]. The isobenzofuran complexes (**523**) are fluxional molecules in equilibrium with π-alkyne complex **522**. The proportion of isobenzofuranylcarbene complex at equilibrium was highest when the arene group is electron withdrawing. The isobenzofuran nucleus would undergo Diels–Alder reactions resulting in carbene complex **524**. Reaction with oxygen led to the η^2-ketone complex **525**.

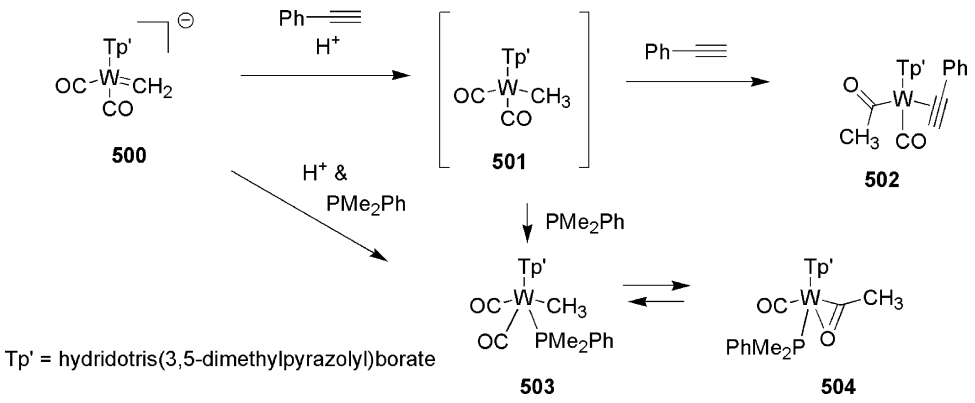
Rhenium carbene hydride complex **528** (Scheme 51) was prepared through protonation of dimethylrhenium complex **526** [654]. A cationic hydride (**527**) was initially formed and could be observed spectroscopically at −90 °C. Upon warming to −60 °C elimination of methane and formation of carbene complex **528** was observed. Treatment of carbene



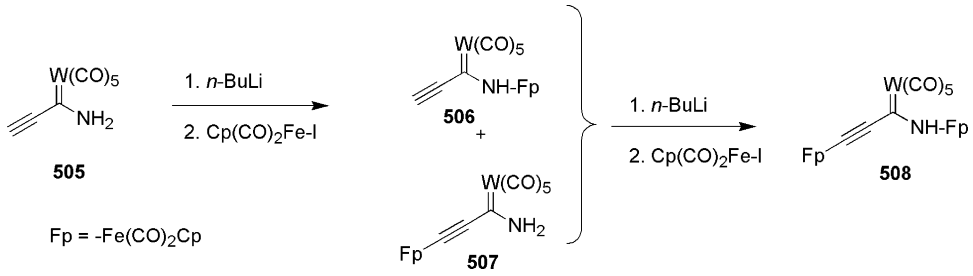
Scheme 45.

complex **528** with trimethylphosphine led to the methylrhenium complex **529**. Exchange of hydride for chloride occurred upon treatment with PPN^+Cl^-. Protonation of **526** in the presence of a nonnucleophilic counterion led to the methyl methylene complex **531**. These processes were also evaluated computationally.

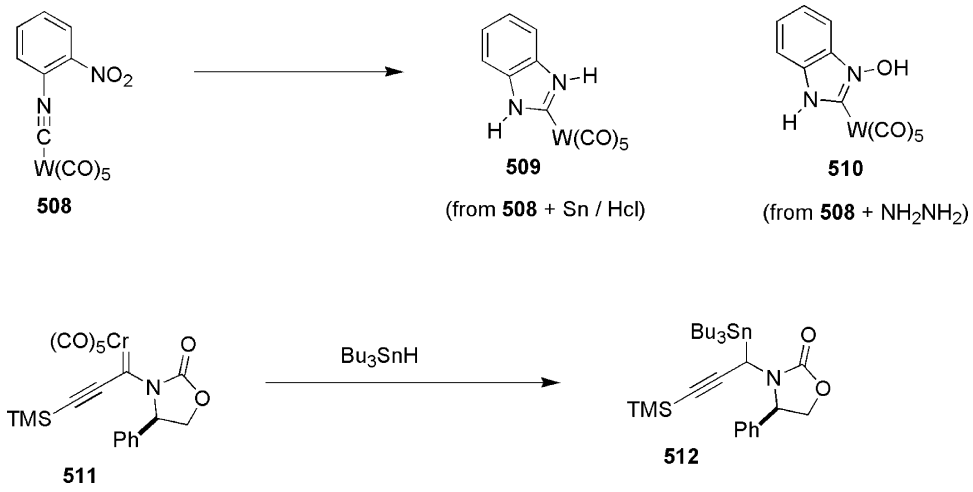
Carbene-like reactions were reported for rhenacyclobutadienes (e.g. **533**, Scheme 52) [655,656]. Alkylation of the rhenacyclobutenone **532** afforded the rhenacyclobutadienes (e.g. **533** and **539**), which feature a Fischer carbene complex functionality. The myriad of reactions featured in Scheme 52 is merely a sample of the numerous carbene-like reactions reported for these



Scheme 46.



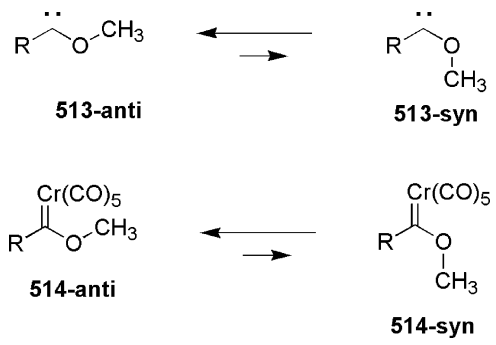
Scheme 47.



Scheme 48.

complexes. Alkyne coupling reactions led to highly substituted ruthenium Cp-complexes (e.g. **540**).

Several examples of Group VII metal–cumulene complexes were reported in 2004 (see Scheme 53). See Scheme 64 for the general reactivity profile of metal vinylidene complexes. Oxidatively induced dimerization of rhenium vinylidene complexes **542** led to bis(vinylidene)–dirhenium complex **544** [657]. Formation of **542** involves initial formation of the radical cation vinylidene complex (**543**), which was observable in solution. The binuclear alkynylvinylidene complex **545** was a minor product in the reaction. The manganese alkynylvinylidene complex **548** was prepared through reaction of dialkyne **547** with complex **546** and bis(diphenylphosphino)ethane [658]. A dimeric complex (**549**) was obtained upon thermolysis in the presence of methanol. The reaction of **546** and dialkyne **550** led to alkynylvinylidene complex **551**, which afforded butatrienylidene complex **552** via fluoride induced destannylation. Similar reaction processes were reported for other stannylated dialkyne derivatives. The reaction processes were also evaluated computationally. Rhenium carbene complexes (e.g. **556**) were prepared from the reaction the reaction of rhenium complex **553** with alkynols [659]. The mechanism likely involves a manganese vinylidene complex (e.g. **555**) as an intermediate.



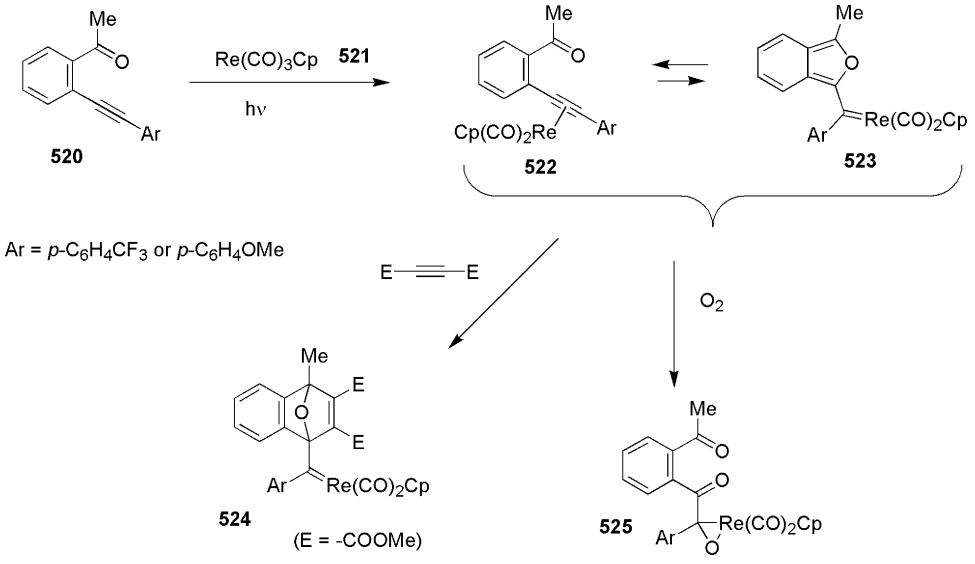
Scheme 49.

Carbene complexes were detected in the electrospray ionization mass spectra of (bipy)Cl(OCH_2CH_2O)Re=O and related complexes [660]. Fragmentation of these complexes was also studied computationally.

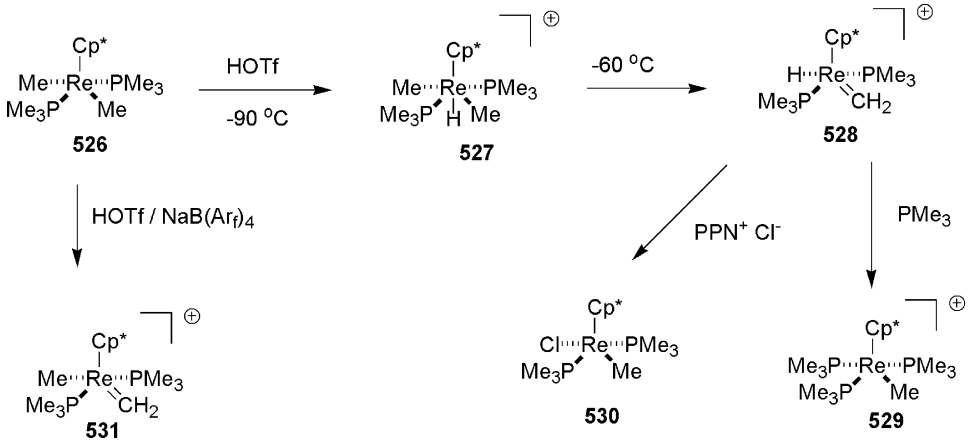
Manganese carbene complexes have been produced as part of a study of platinum and palladium carbene complexes; see Scheme 88.

1.1.3.5. Group VIII metal–carbene complexes.

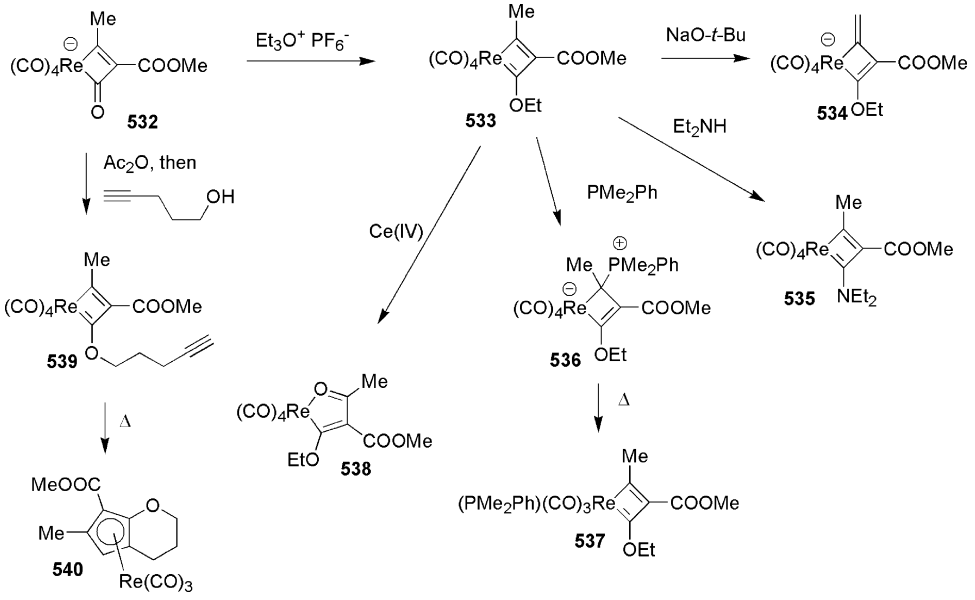
1.1.3.5.1. Cationic metal–carbene complexes that are not cumulenes. The coupling of ruthenium hydride complexes (e.g. **560**, Scheme 54) with terminal alkynes followed by protonation led to cationic ruthenium carbene complexes (e.g. **562**) [661]. Reaction with the alkyne initially affords the ruthenium alkenylmetal complex (e.g. **561**). Protonation affords the cationic carbene complex, which can be converted back to the alkenylmetal complex by treatment with trimethylphosphine.



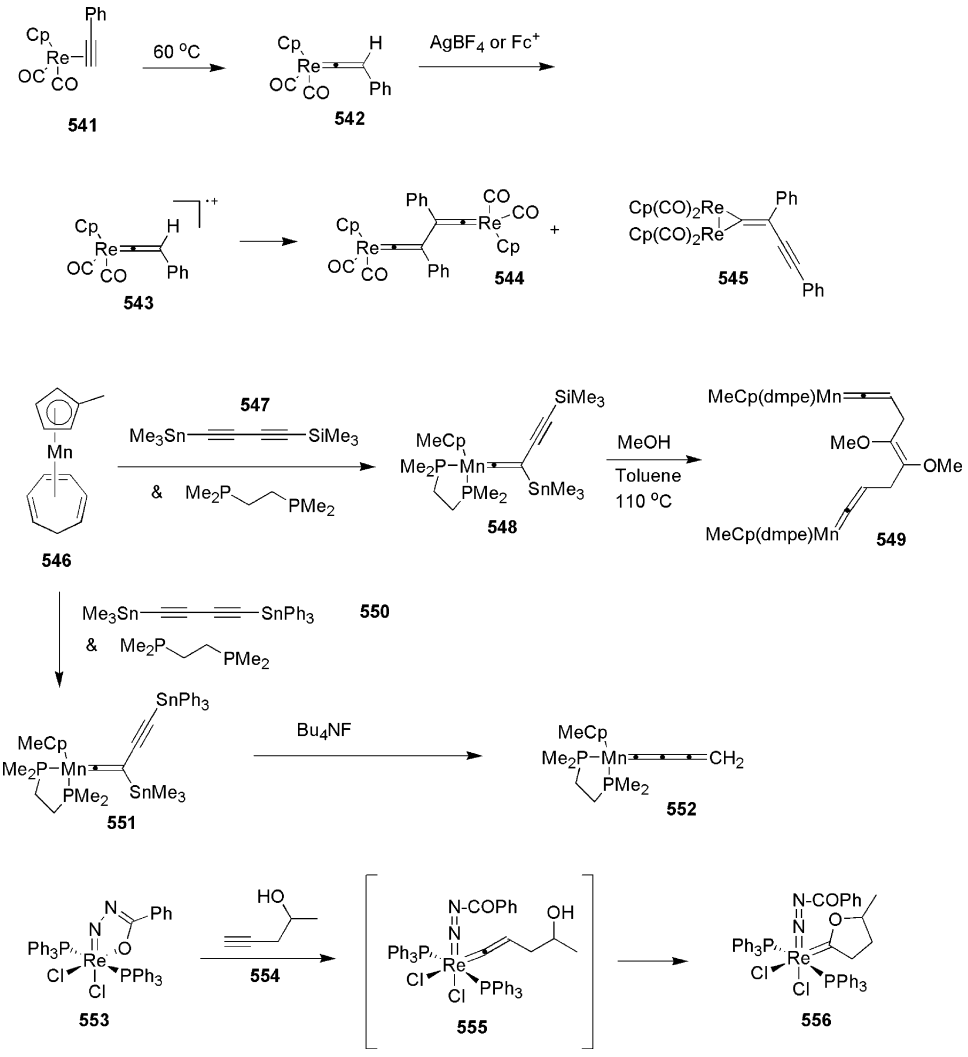
Scheme 50.



Scheme 51.



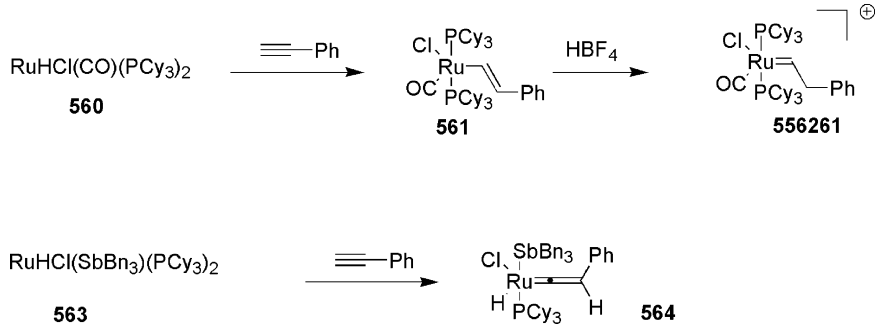
Scheme 52.



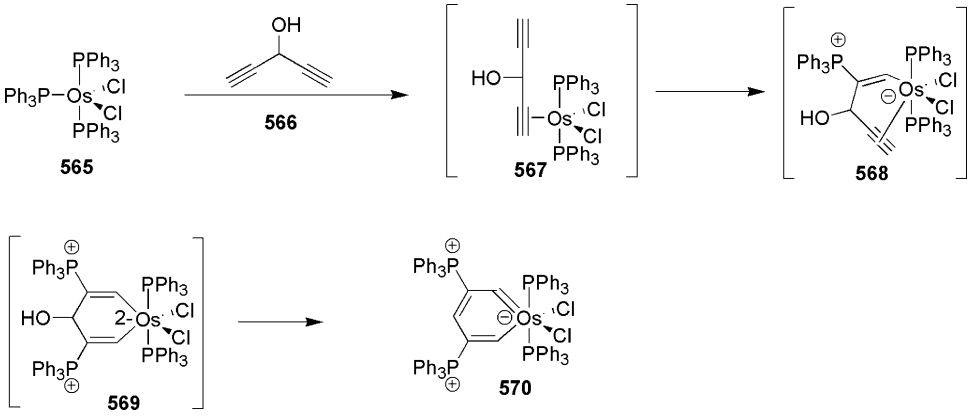
Scheme 53.

Exchange of the phosphine ligands was reported. Similar studies were reported using RuH(η^2-OAc)(CO)(PCy_3) as the starting material. The neutral vinylidene(hydride) complex **564** was obtained by treatment of ruthenium complex **563** with phenylacetylene.

The formation of osmabenzene derivatives (e.g. **570**, Scheme 55) from 1,4-pentadiyn-3-ol derivatives and osmium (II) complex **565** was reported [662]. The proposed mechanism involves generation of a π-alkyne complex (**567**), followed by nucleophilic addition of phosphine to afford the internally coordinated vinylosmium intermediate (**568**), which can be isolated under some conditions. Addition of a second mole of phosphine followed by elimination of hydroxide yields the osmabenzene. Ligand exchange reactions were also reported for the osmabenzene. Related osmabenzene derivatives were studied computationally [663]. Studies emphasize determination of the degree of aromaticity, their mechanism of formation, and side reactions encountered in their synthesis.



Scheme 54.



Scheme 55.

Additional studies of cationic Group VIII carbene complexes include: (1) formation of ruthenium carbene complexes (e.g. **573**) (Scheme 56) as transient intermediates in the synthesis of hydroxymethylpyrroles from enyne imines [664]; (2) a computational study of the cyclopropanation of alkenes by cationic iron carbene complexes [665]; (3) comparison of the bonding and electronic properties of cationic iron carbene complexes with those of borylene–iron complexes [666].

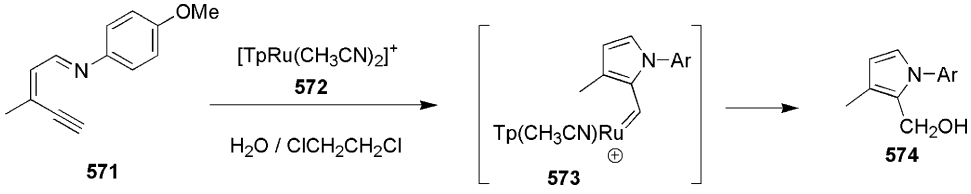
1.1.3.5.2. Bis(carbene)ruthenium complexes from coupling of two alkynes and a ruthenium complex. Neutral bis(carbene) chlororuthenium complex **579** (Scheme 57) was generated from bis(alkynylacyl) derivative **577** and ruthenium complex **578** [667]. Longer reaction times at room temperature resulted in the conversion of bis(carbene) complex **579** to the ruthenium–cyclobutadiene complex **580**. Ruthenium bis(carbene) complexes were suggested as intermediates in: (1) ruthenium catalyzed formation of bicyclic ether derivatives (e.g. **584**) from diyne-alcohols (e.g. **581**) and ruthenium catalyst **582** [668]; (2) alkyne trimerization involving co-cyclization of (bis)alkynes (e.g. **585**) with another alkyne using ruthenium catalyst **578** [669]; (3) alkyne trimerization involving the co-cyclization of a 2-ethynyl-3,4-dihydropyan and a bis(alkyne) derivative [670]; (4) tandem alkyne trimerization—Suzuki coupling using an alkynylborane, a propargyl alcohol, and a third alkyne, followed by palladium-catalyzed reaction of the resulting arylborane with an aryl iodide [671].

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.

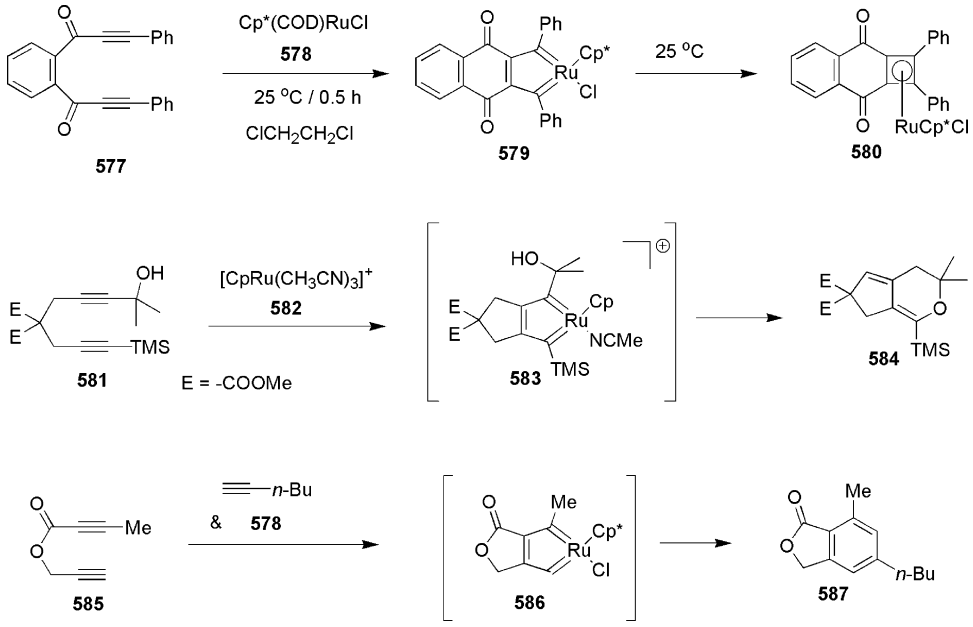
Ruthenium carbene complexes featuring a pincer ligand (e.g. **594**, Scheme 58) were reported [672]. Deprotonation of the cationic complex **593** afforded the neutral carbene complex **594**. Protonation of the carbene complex affords either complex **593** or **592**. DFT calculations suggest that the carbene carbon of these complexes is nucleophilic, consistent with the observed reactivity.

The use of carbene(porphyrin) complex **596** (Scheme 59) as a catalyst for aziridination of imines by diazo compounds was reported [673]. The carbene complexes were found to be inferior catalyst relative to the non-carbene complexes studied (e.g. the analog of **596** featuring a CO ligand in place of the carbene ligand). A mechanism involving ruthenium complexation to the imine nitrogen followed by nucleophilic addition of the diazo compound and intramolecular displacement of nitrogen was proposed. Several tetrakis(pentafluorophenyl)porphyrin-ligated ruthenium carbene complexes (e.g. **599**) were prepared through the reaction of carbonyl complex **598** with diazo compounds [674]. Cyclic voltammetry, spectroelectrochemical studies, and ligation reactions were reported for these complexes. Computational studies of the structure of ruthenium, iron, and cobalt porphyrin complexes were reported [675]. A metal–carbon double bond was present if the complex was a singlet, while a single bond was present if the complex contains unpaired electrons.

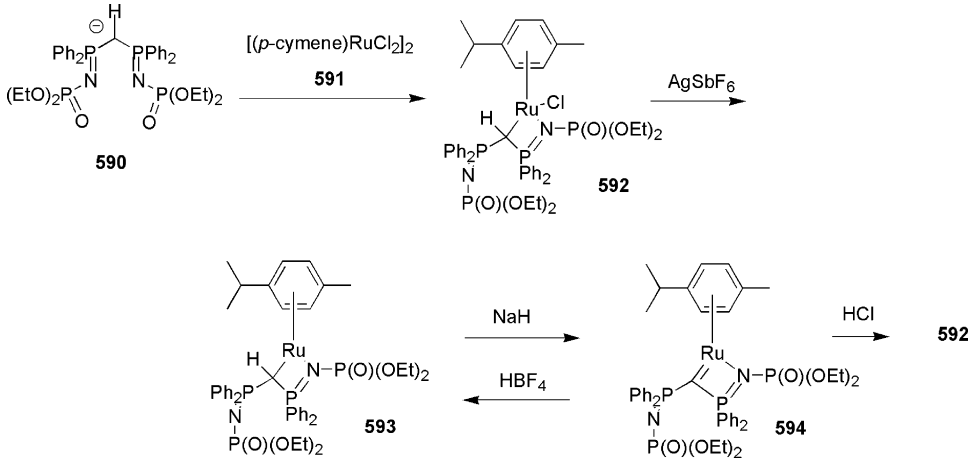
The synthesis and reactivity of osmium carbene complexes that contain vinylphosphine ligands (e.g. **602**, Scheme 60) was reported [676]. The complex was prepared through reaction of chelated phosphine–osmium complex **601** with phenyldiazomethane. Thermolysis at 70 °C led to metallacyclobutane derivative **603**. Reaction with methyllithium afforded styrene(hydride) complex **604**. Halide abstraction from carbene complex **602** led to cationic carbyne(hydride) complex **605**. The hydride could be removed by treatment with sodium methoxide. The hydrogen removal process was reversible. Treatment of the



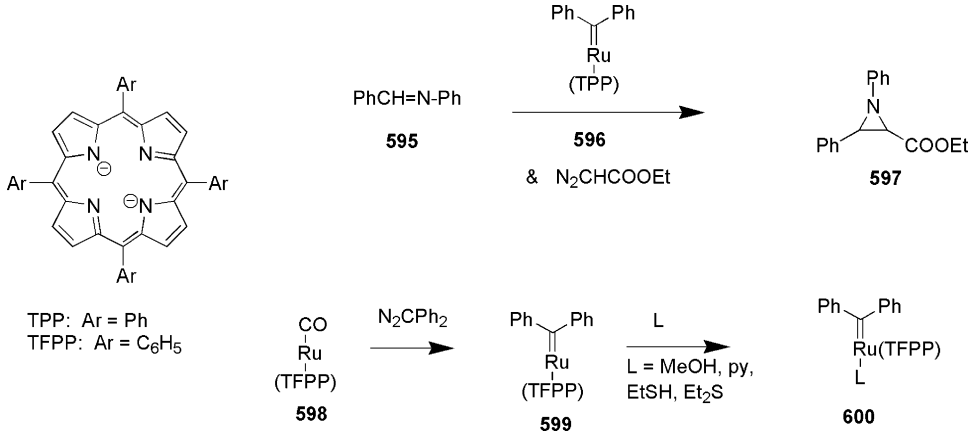
Scheme 56.



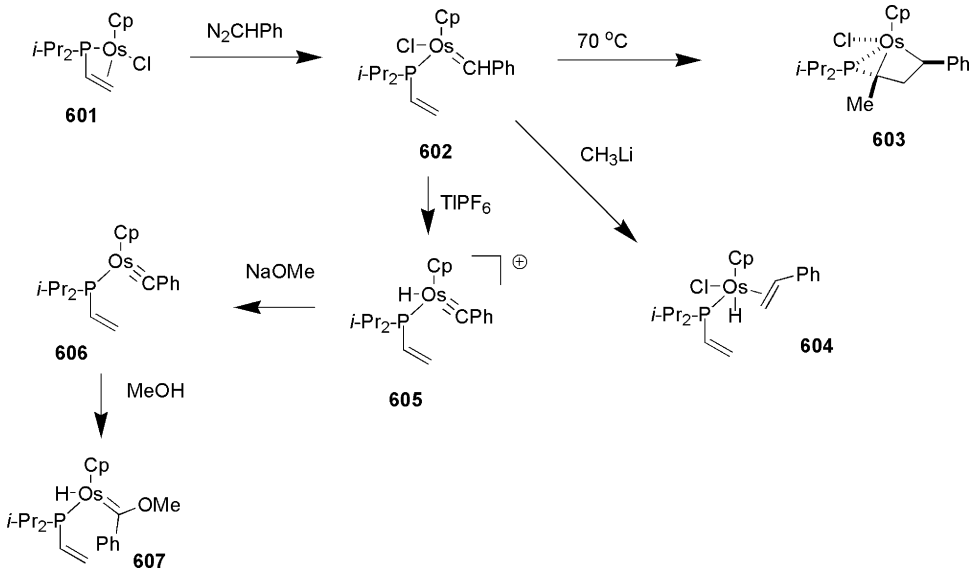
Scheme 57.



Scheme 58.



Scheme 59.



Scheme 60.

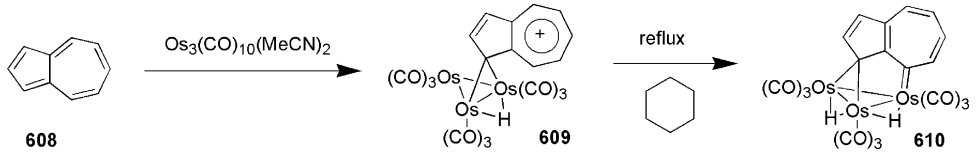
neutral carbyne complex **606** with methanol led to the alkoxycarbene complex **607**.

Other studies of carbene complexes in this category are depicted in Scheme 61, and include: (1) formation of osmium carbene complex **610** through thermolysis of bridging carbene–triosmium complex **609** [677]; (2) a computational study of species in the gas-phase reaction of osmium oxo cations and methane [678]; (3) computational based studies of the vibrational spectra of chiral osmium carbene complexes [679]; (4) resonance contribution of the cumulene structure for ruthenium isocyanide complexes [680].

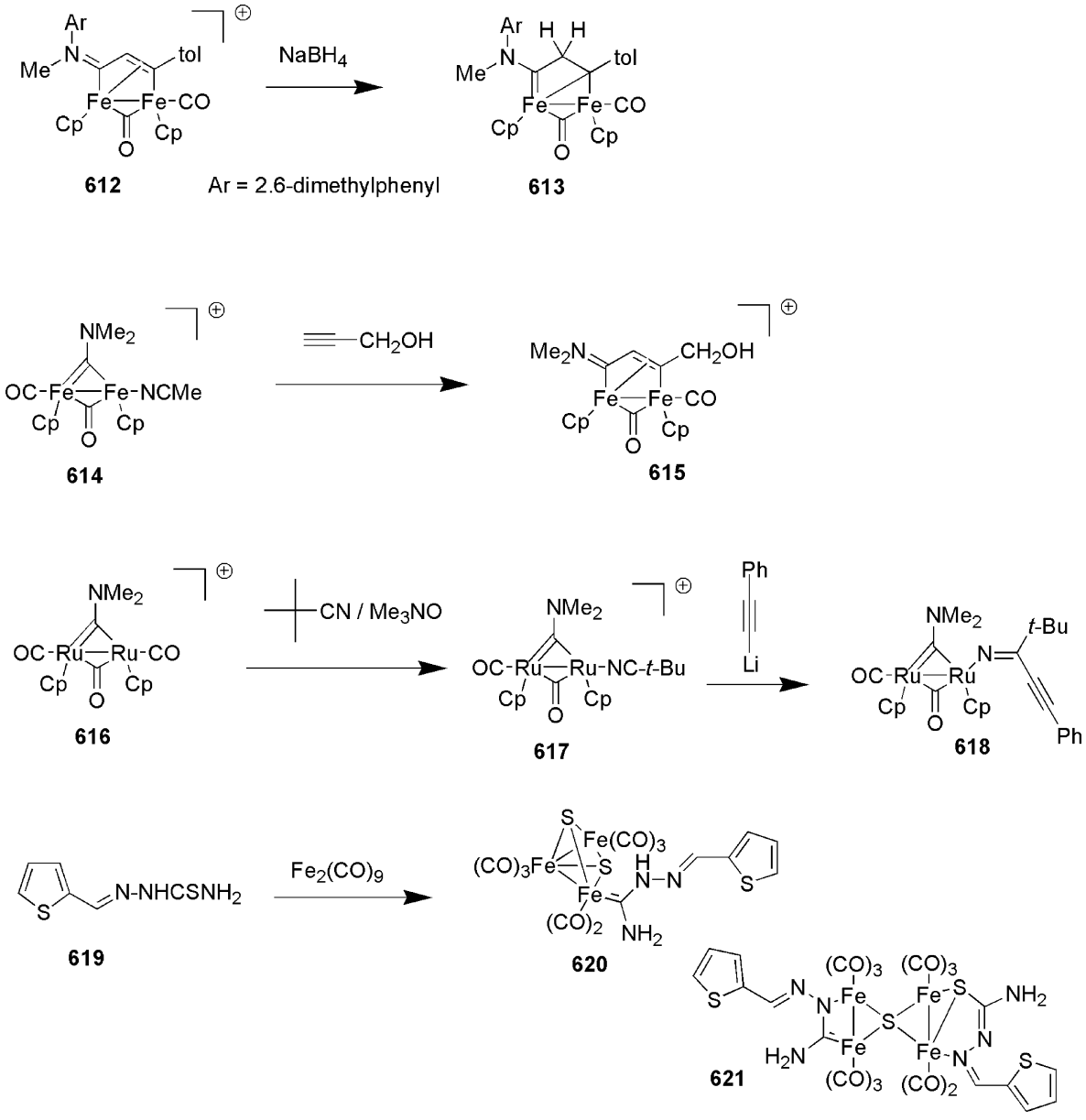
1.1.3.5.4. Heteroatom-substituted Group VIII-metal carbene complexes. Bridging aminocarbene–iron complexes (e.g. **613**, Scheme 62) were prepared through sodium borohydride reduction of binuclear iron complex **612** [681]. This reaction was restricted to cases where the bulky 2,6-dimethylphenyl group was used. An enamine complex was obtained using the benzyl or methyl analogs. The reaction of bridging aminocarbyne–diiron complexes (e.g. **614**) with phenylacetylene was reported [682]. This reaction led to the alkyne inserted complexes (e.g. **615**). Conversion of bridging aminocarbyne–diruthenium complexes (e.g. **616**) to the corresponding nitrile complexes (e.g. **617**) was reported [683]. Nucleophilic addition reactions to the coordinated nitrile led to the neutral imine complexes (e.g. **618**). Polynuclear iron complexes featuring a carbene ligand to one of the irons (**620–621**) were formed in the reaction of thienylhydrazone derivative **619** with diiron nonacarbonyl, along with other polynuclear iron complexes [684].

Additional examples of heteroatom-stabilized carbene complexes are depicted in Scheme 63. An alkoxycarbene–iron complex (**625**) was prepared by room temperature thermolysis of iron carbonyl derivative **624** [685]. A mechanism involving nucleophilic addition of an aromatic carbon to a carbonyl ligand followed by a 1,3-shift of silicon was proposed. Osmium-carbene complex **629/630** was a product of the coupling of osmium hydride derivative **626** with iminopyridine derivative **627** [686]. Trinuclear cationic alkoxycarbene complex **632** was prepared by methylation of the corresponding triiron acylate **631** [687]. A resonance contribution of a carbene complex structure to the overall structure *O*-chelated β-osma-α,β-unsaturated aldehyde complexes (osmafurans) was noted [688].

1.1.3.5.5. Group VIII metal–vinylidene complexes. Many examples of the formation of metal vinylidene complexes (**635**, Scheme 64) via coupling of coordinatively unsaturated Group VIII metal complexes with terminal or silylated alkynes were reported in 2004. Representative examples are depicted in Fig. 13. Common reaction pathways for these complexes include reaction with nucleophiles to form vinylmetal species (**638**), reaction with alcohols (or amines) to form Fischer carbene complexes (**639**) or water to form metal acyls (**637**), and deprotonation at the β-position to form alkynylmetal complexes (**636**). Other common synthetic routes to metal vinylidenes include addition of electrophiles to metal acetylide complexes (e.g. the reverse of the reaction synthesizing **636**), and treatment of acylmetal complexes with dehydrating agents (i.e. the reverse of the reaction synthesizing **637**).

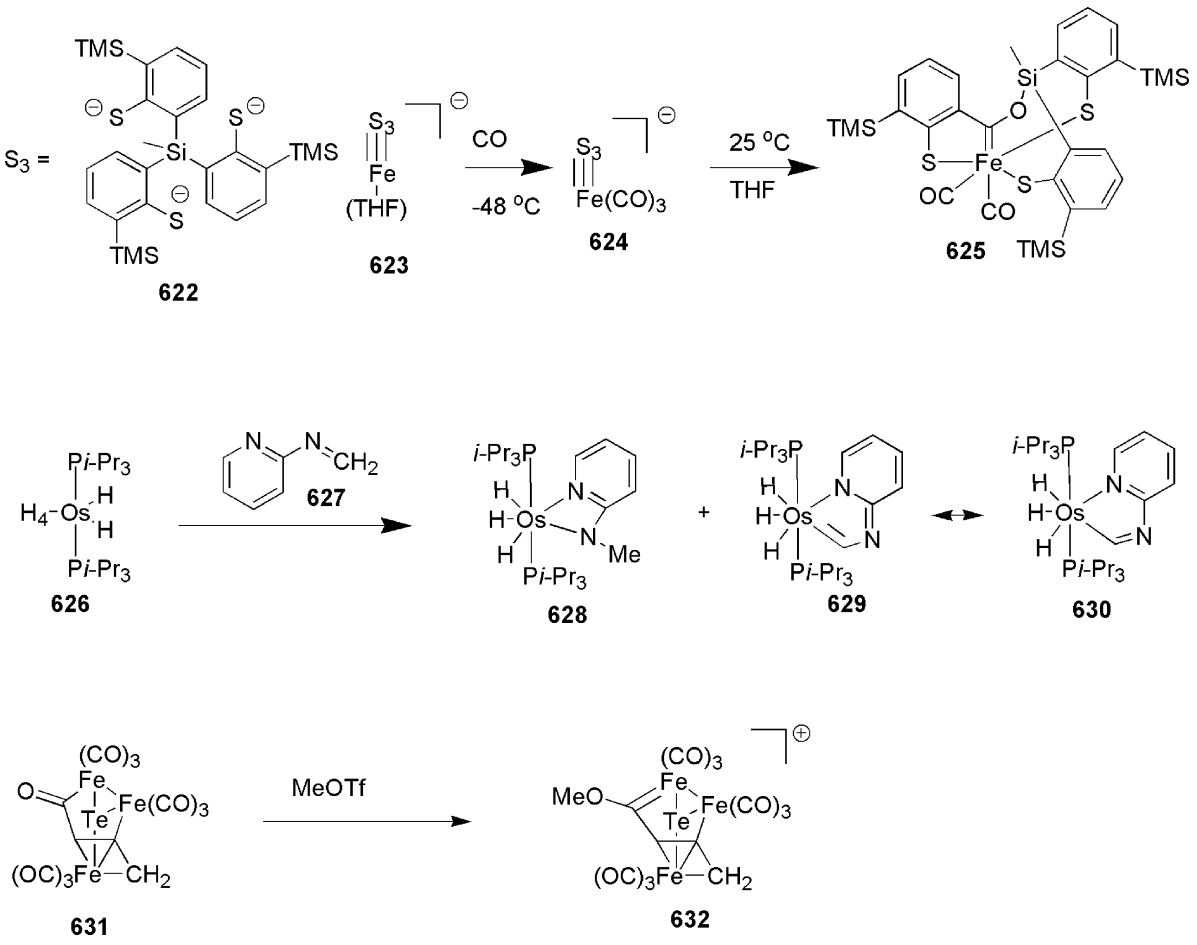


Scheme 61.



Scheme 62.

Specific reports which highlight the reaction pathways of Scheme 64 are depicted in Fig. 13 and include: (1) formation of cationic ruthenium vinylidene complexes (e.g. **640**) substituted by a pyrimidine ring and subsequent conversion to Fischer carbene complexes (e.g. **641**) [689]; (2) formation of cationic ruthenium vinylidenes and allenylidenes featuring a tetradentate cyclam ligand and subsequent electrochemical studies [690]; (3) conversion of alkynylruthenium complexes to the corresponding methoxycarbene complexes and photochemical and electrochemical studies [691]; (4) formation of mononuclear vinylidene complexes (e.g. **642**) from a chloride-bridged dimeric ruthenium complex and *t*-butylacetylene followed by treatment with titanium phenoxide derivatives to replace chloride ligands and thus break the dimers [692]; (5) formation of ruthenium–vinylidene complexes (e.g. **643**) and conversion to the alkynylruthenium complex or dicarbonyl complex (e.g. **645**) by treatment with water, presumably via the acylruthenium complex (e.g. **644**) [693]; (6) formation of bis(ruthenium–vinylidene) complex (**646**) from reaction of an alkyne (*o*-*N*,*N*-dimethylaminophenylacetylene) with ruthenium(III) acetylacetonate in the presence of zinc [694]; (7) formation of ruthenium–vinylidene complexes from an alkynylphenylalanine derivative [695]; (8) synthesis and electrochemical studies of cationic ruthenium vinylidene complexes that contain bipyridyl ligands (e.g. **647**) [696]; (9) formation of ruthenium vinylidene complexes (e.g. **648**) followed by reaction with oxygen to the afford the corresponding carbonyl compounds [697]; (10) formation of a cationic ruthenium vinylidene complex (e.g. **649**) from an alkyne-carbohydrate derivative followed addition reactions of water and ammonia [698]. Use of a ruthenium catalyst (**650**) for the conversion of 4-alkynols to six-membered ring cyclic enol ethers was also reported [699]. This



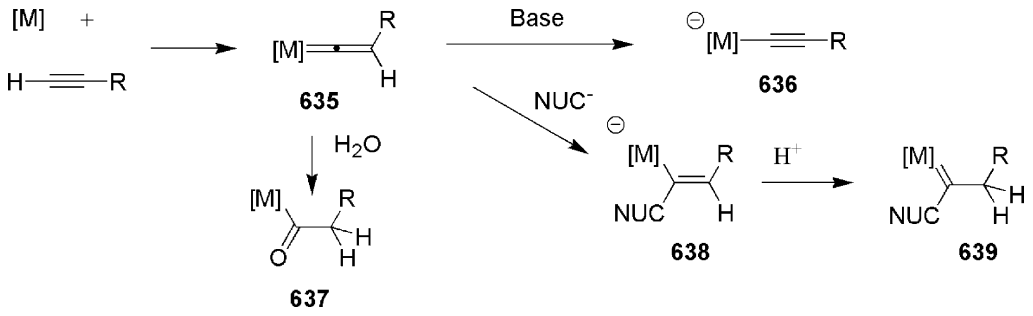
Scheme 63.

process likely involves the sequence of vinylidene formation, followed by conversion to a cyclic Fischer carbene complex, followed by conversion of the carbene complex to the corresponding alkene. Ruthenium vinylidene complexes have been observed in a novel [4 + 2]-cycloaddition reaction of ynoate esters and arylalkynes, however the proposed mechanism for the cycloaddition process involves the π-alkyne complex and not the vinylidene complex [700].

The formation of chelated enamine complex **654** (Scheme 65) from ruthenium halide **651** and phenylacetylene was reported [701]. An observable π-acetylene complex (**652**) was formed initially, which converts to **654**. This process presumably involves the formation of a vinylidene (**653**) followed by intramolecular nucleophilic attack by the nitrogen at the carbene carbon. DFT studies were employed to evaluate the vinylidene–π-alkyne complex equilibria.

The formation of cyanomethylruthenium–vinylidenes (e.g. **656**, Scheme 66) and their subsequent conversion to cyclopropenylruthenium carbene complexes (e.g. **657**) by deprotonation followed by cyclization was reported [702]. Treatment of vinylidene complex **656** with iodine led to the iodomethyl vinylidene complex **658**.

The reaction of cationic terminal vinylidene ruthenium complexes (e.g. **659**, **662**, Scheme 67) with phosphines was reported [703]. The reaction of vinylidene complex **659** with triphenylphosphine led to internally coordinated vinylphosphonium



Scheme 64.

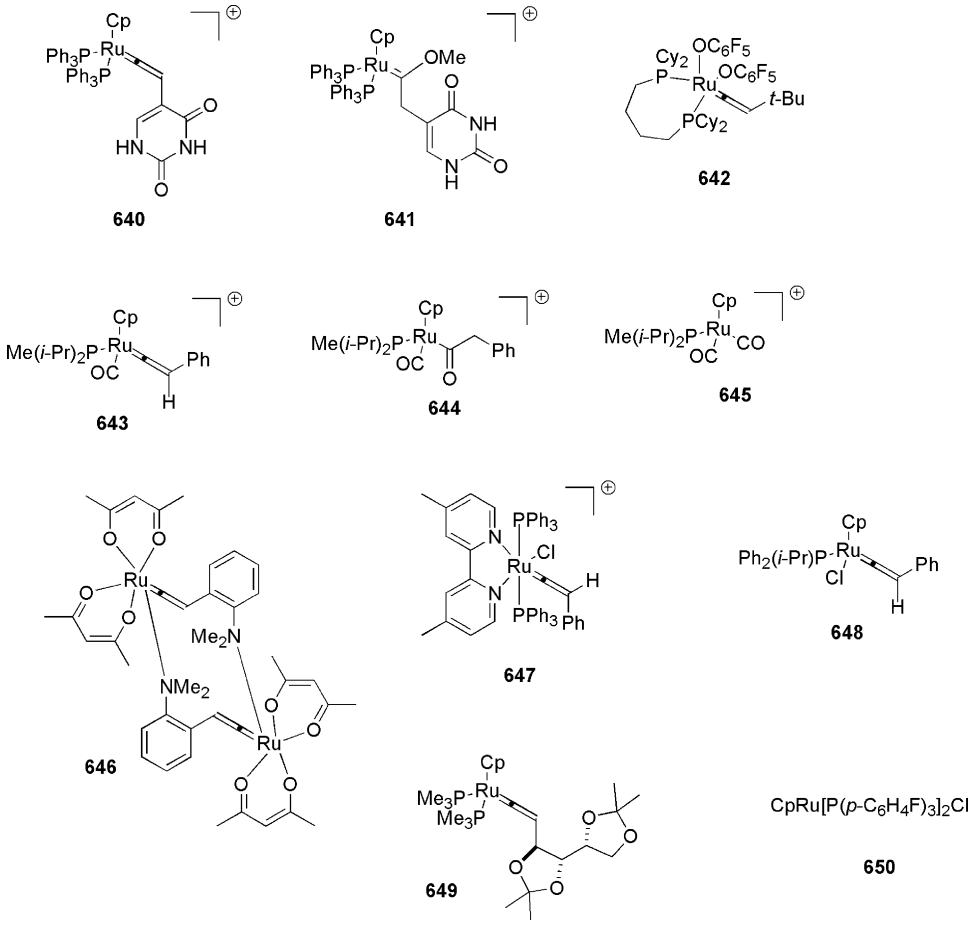
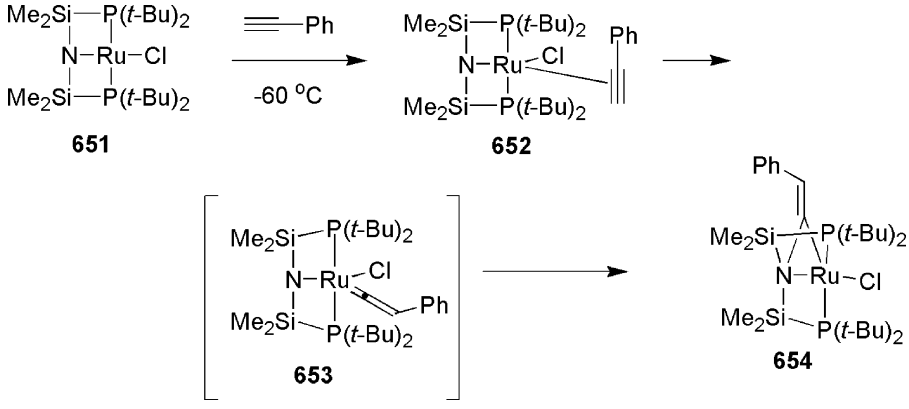


Fig. 13. Representative Group VIII metal–vinylidene complexes, precusors, and reaction products reported in 2004.

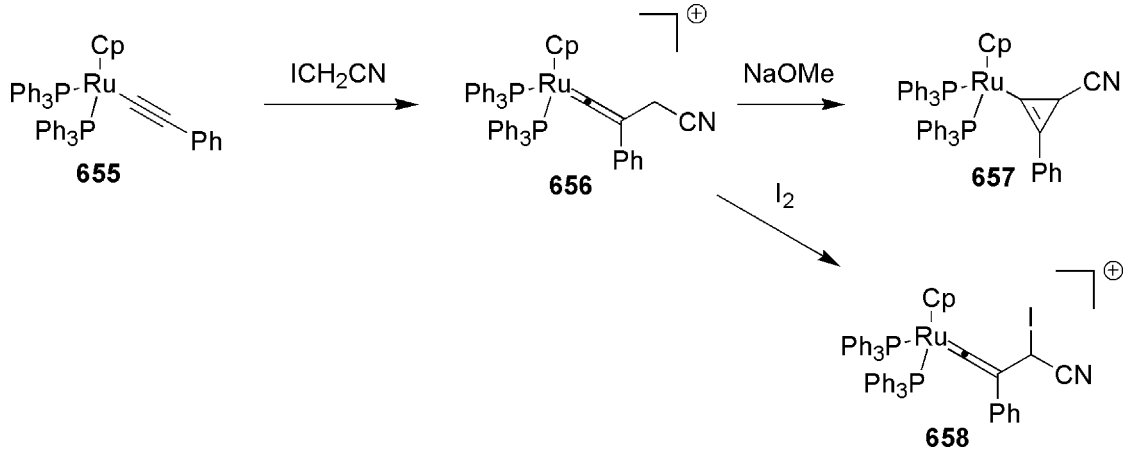
salts (e.g. **661**). A mechanism involving nucleophilic addition of the phosphine to the carbene carbon followed by intramolecular C–H activation was proposed. This mechanism was supported through deuterium labeling studies. The analogous reaction with phenyldimethylphosphine led to the simple nucleophilic addition product **663**.

Several reaction processes were reported for ruthenium vinylidene hydrides (e.g. **665**, Scheme 68) [704]. Several ligand exchange reactions were reported for these complexes. Protonation of these complexes led to the cationic carbyne complexes (e.g. **666**). Reaction noncoordinating counterions in acetonitrile led to the cationic alkenylmetal complexes (e.g. **667**), which could be protonated to afford the dicationic carbene complexes (e.g. **668**). Reaction of the vinylidene hydride complexes with CO led to the neutral alkenylmetal complexes.

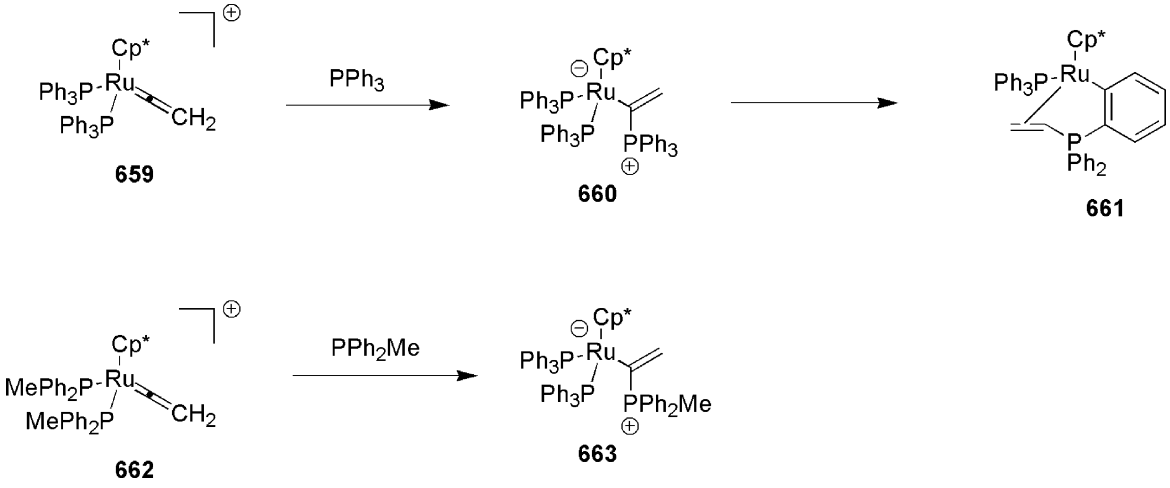
Alkenylindenes (e.g. **672**, Scheme 69) were prepared by treatment of alkynylstyrene derivatives (e.g. **670**) with cationic ruthenium complex **671** [705]. The proposed mechanism involves formation of the cationic vinylidene complex (**673**) followed by conversion to the alkylidenecyclopropane derivative **675**,



Scheme 65.

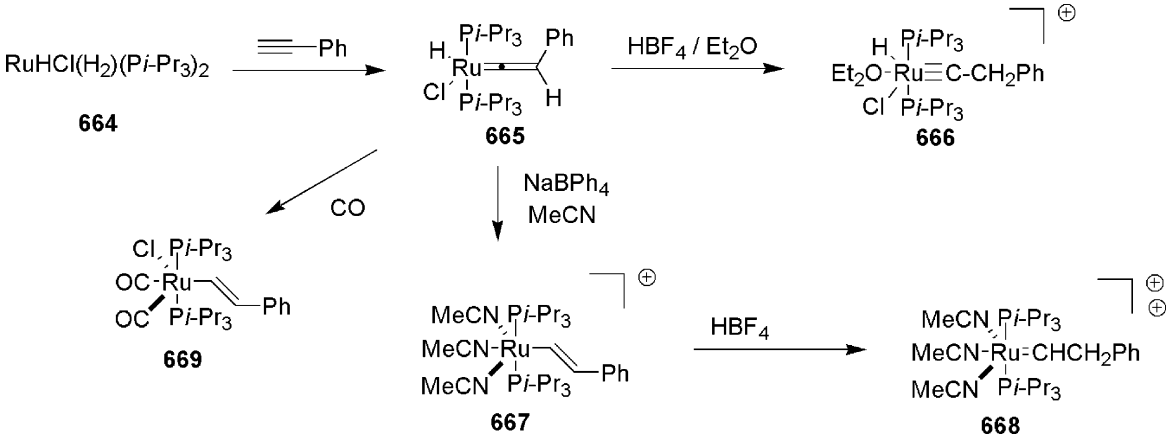


Scheme 66.

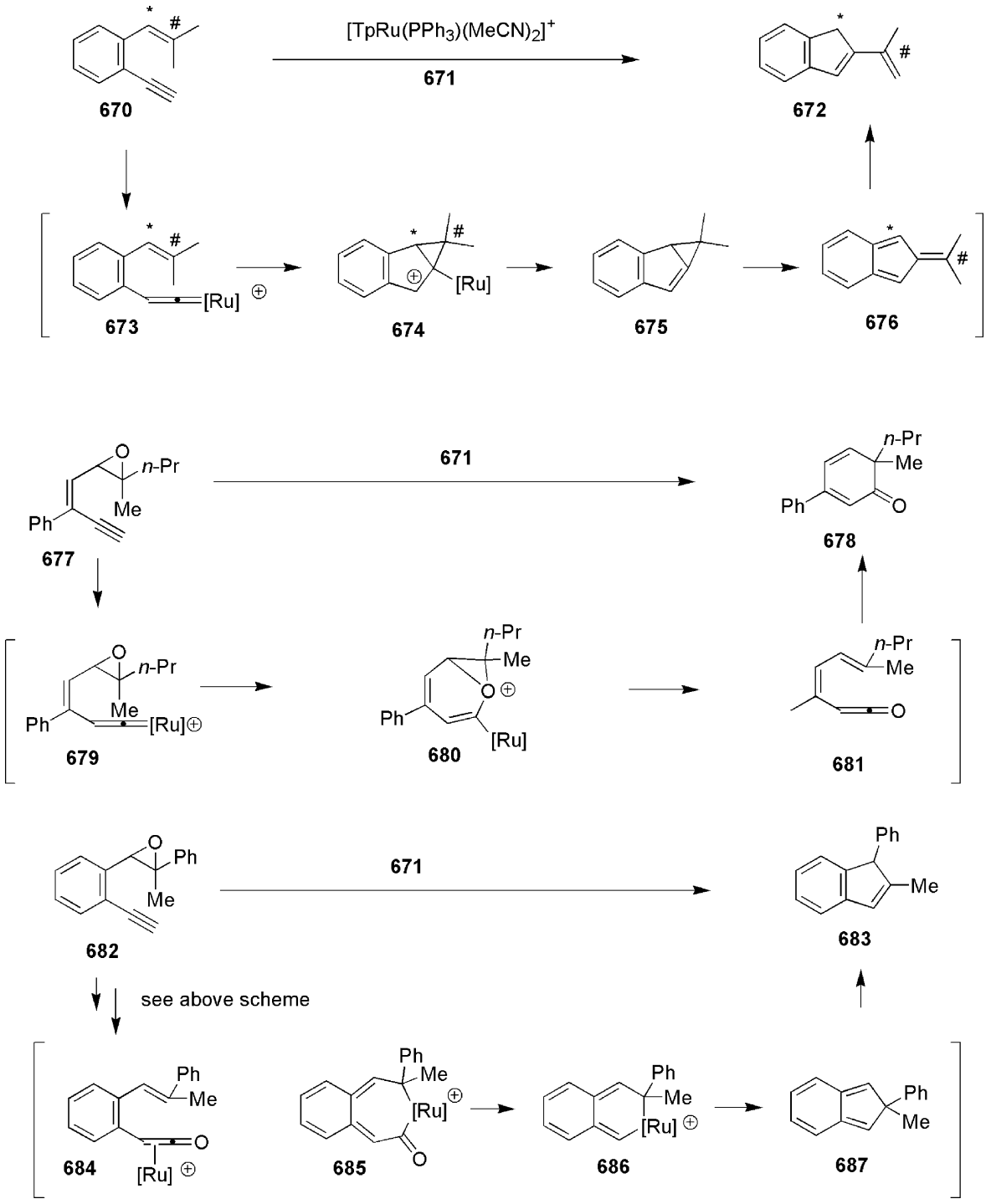


Scheme 67.

which opens to the *o*-quinonemethide **676** followed by a ruthenium assisted hydride shift to afford the observed product. This mechanism was supported through C-13 labeling studies. Ruthenium–vinylidenes have also been proposed as intermediates in the conversion of enyne-epoxides (e.g. **677**) to phenols or cyclohexadienones (e.g. **678**) and *o*-alkynylstyrene oxides (e.g. **682**) to rearranged indenes (e.g. **683**) [706]. For the formation of phenols/cyclohexadienones, a mechanism involving nucleophilic attack of the epoxide oxygen on the carbene carbon of the vinylidene, followed by net transfer of the oxygen to form the



Scheme 68.

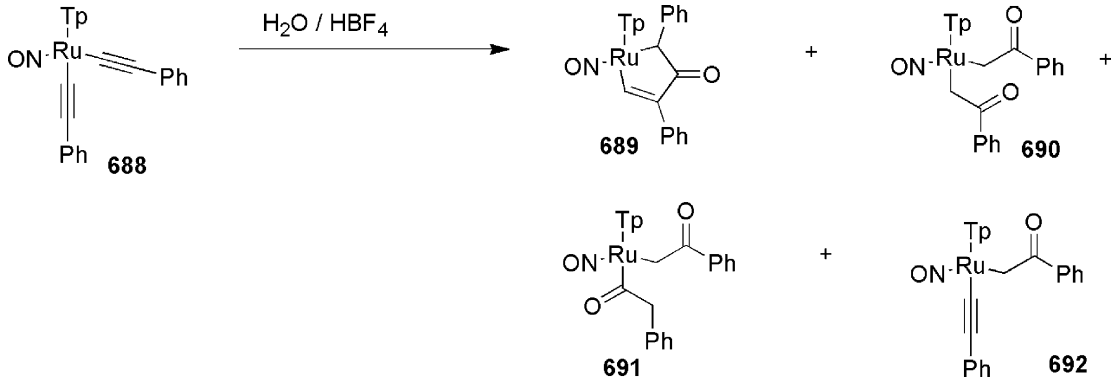


Scheme 69.

dienylketene (**681**) followed by electrocyclization was proposed. A more complex process was proposed for indene formation. Additional examples of the reaction of styrene oxides and complex **671** lead to naphthols or alkylideneindanones [707].

Additional reaction processes that involve metal vinylidenes are depicted in Scheme 70. Metal vinylidene complexes are possibly involved in the hydrative coupling of the alkynyl ligands in bis(alkynyl)complex **688** resulting in ruthenacyclopentenone complex **689** and bis(acetophenonyl) complex **691** [708]. A theoretical study of barriers to rotation of osmium vinylidene complexes was reported [709].

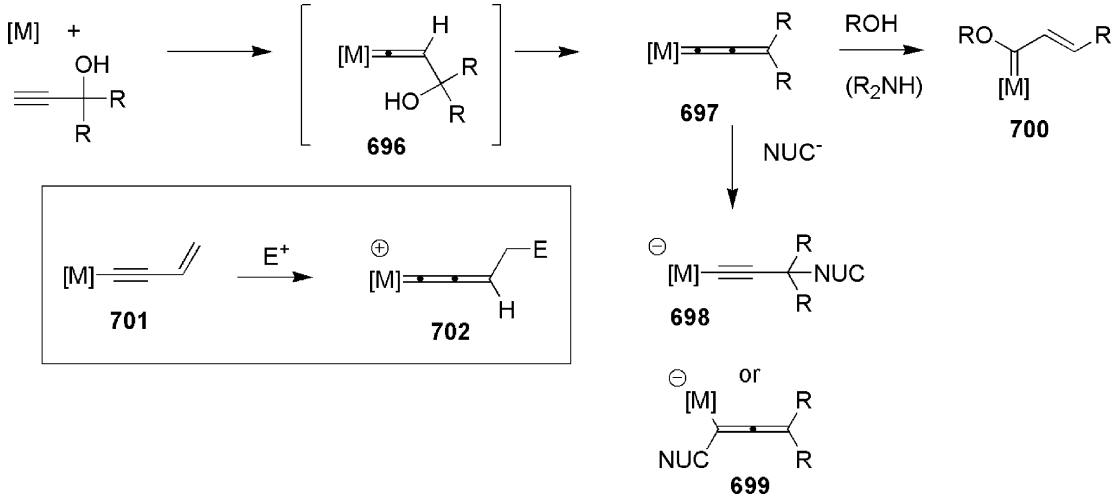
1.1.3.5.6. Group VIII metal complexes of higher cumulenes. Metal-higher cumulene complexes (**697**, **702**, Scheme 71) were produced from the coupling of coordinatively unsaturated Group VIII metal complexes with propargyl alcohols (usually those that contain no hydrogens β- to the OH group), or by addition of electrophiles to the δ-carbon of alkenylethynyl–metal complexes (**701**). A variety of reaction processes of Group VIII



Scheme 70.

metal–cumulene complexes were reported in 2004. Common reaction pathways for these complexes include reaction with nucleophiles at the γ-position, resulting in alkynylmetal complexes (**698**), or attack at the γ-position, resulting in allenylmetal complexes (**699**). Reaction with alcohols or amines can lead to α,β-unsaturated Fischer carbene complexes (**700**). Representative examples of this class of compounds are depicted in Fig. 14.

Specific reports which highlight the reaction pathways depicted in Scheme 71 are depicted in Fig. 14, and include: (1) the addition of a variety of nucleophiles to cationic ruthenium allenylidene complex **704** [710]; (2) formation of a ruthenium allenylidene complex (**705**) and its use as a cycloisomerization catalyst [711]; (3) formation of a dicationic ruthenium allenylidene complex from a cationic ruthenium chloride complex and 1,1-diphenyl-2-propyn-1-ol [712]; (4) formation of a ruthe-



Scheme 71.

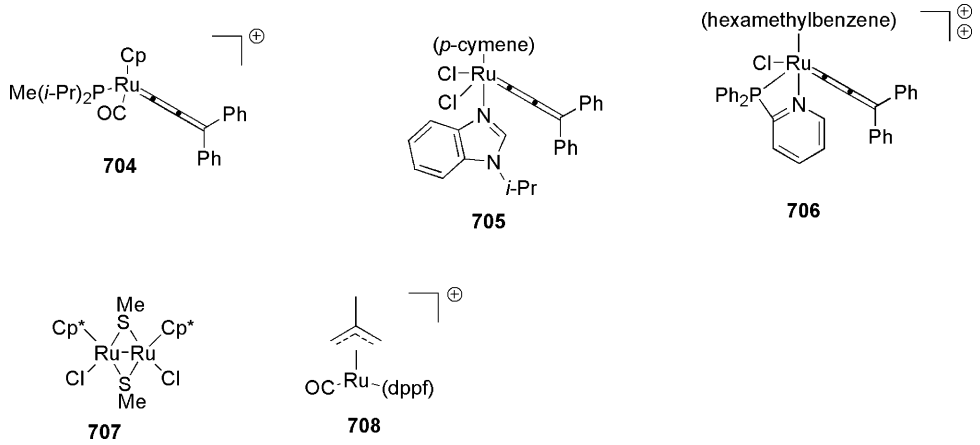
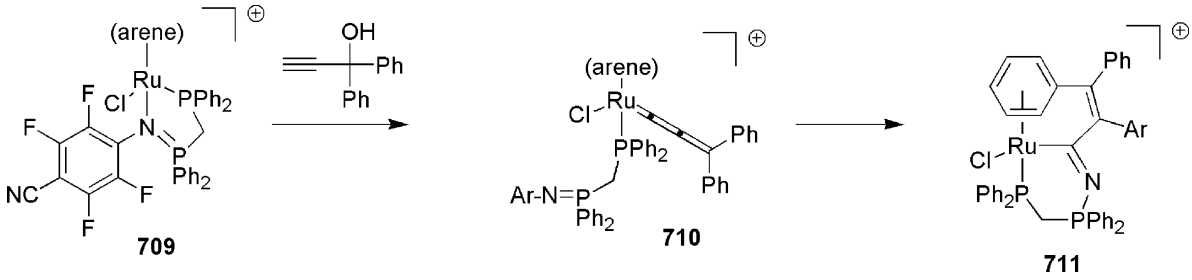


Fig. 14. Representative Group VII metal–higher cumulene complexes, products, and precursor complexes reported in 2004.



Scheme 72.

nium allenylidene complex featuring chiral and enantiomerically pure phosphine ligands [713]. Several processes reported in 2004 invoke metal–higher cumulene complexes as intermediates, including: (1) a novel cycloaddition reaction between 1,3-diketones and propargyl alcohols leading to six-membered ring oxygen heterocycles catalyzed by bis(ruthenium) complex **707** [714]; (2) isomerization of propargyl alcohols to α,β-unsaturated aldehydes using ruthenium complex **708** [715].

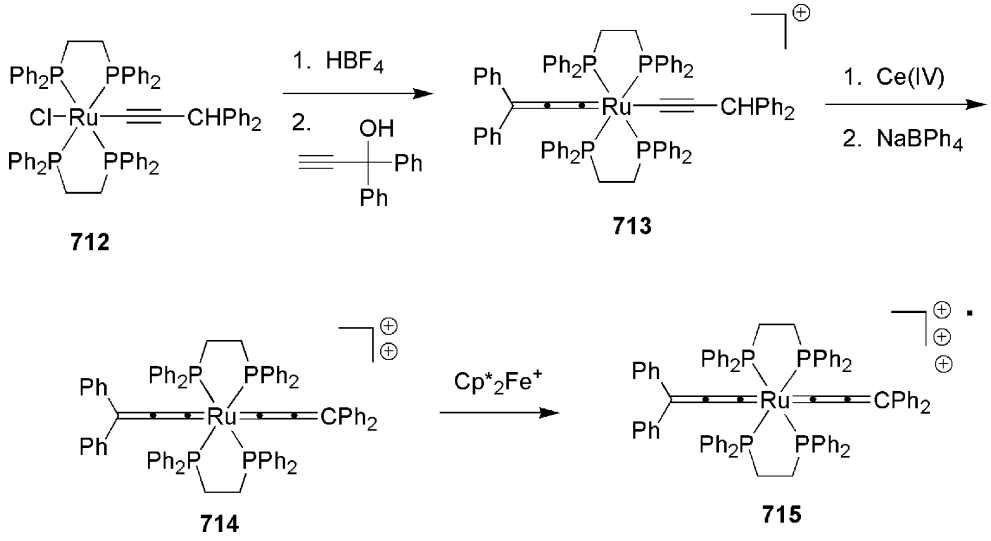
The coupling of cationic arene ruthenium complexes (e.g. **709**, Scheme 72) with propargyl alcohol derivatives was reported [716]. Coupling of the *p*-cymene (arene = *p*-cymene) complex diphenylpropargyl alcohol led directly to the bridged arene complex **711**. Reaction with the mesitylene analog of complex **709** afforded an intermediate allenylidene complex **710**, which converted to **711** after 10 days at room temperature.

Alkynyl allenylidene ruthenium complexes (e.g. **713**, Scheme 73) were prepared through coupling of alkynylruthenium chloride complex **712** with diphenylpropargyl alcohol [717]. This complex could be converted to dicationic bis(allenylidene) complex **714**. This complex could be further oxidized using the permethylferrocenyl cation.

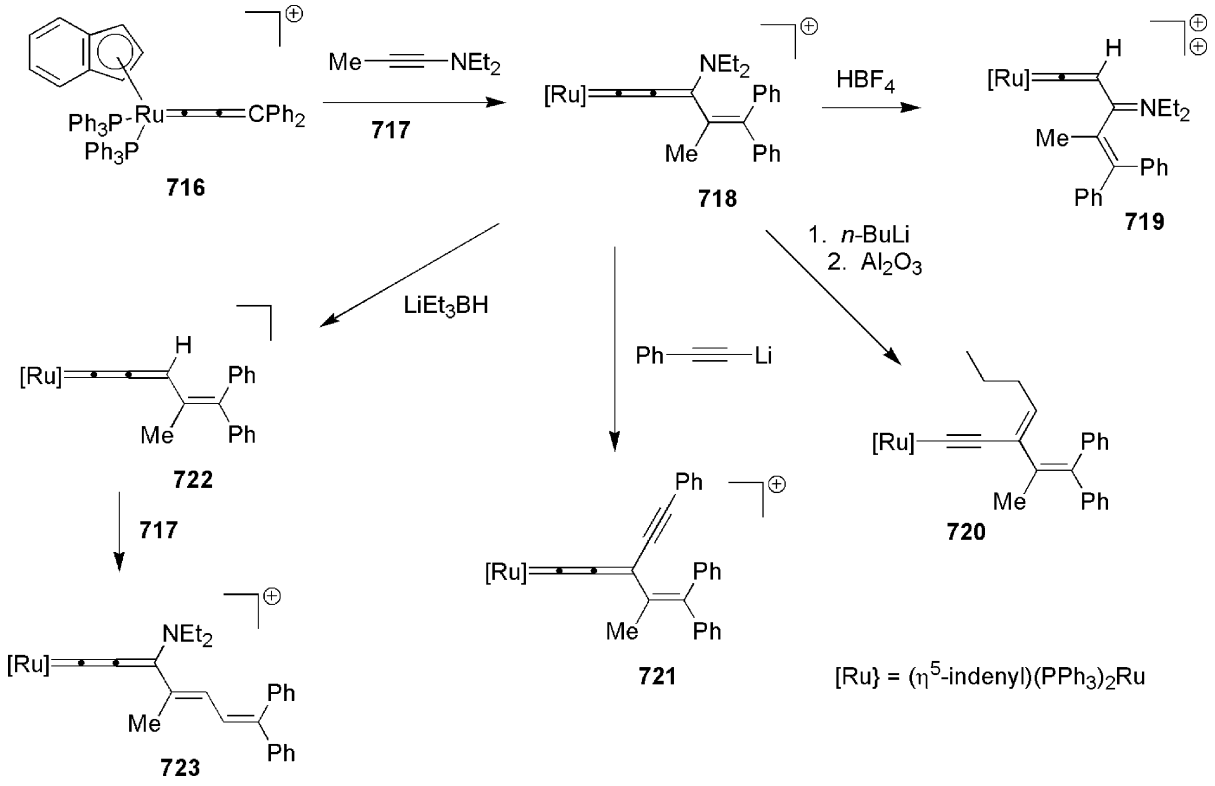
Reaction of ruthenium allenylidene complexes (e.g. **716**, Scheme 74) with ynamines was reported [718]. The elongated allenylidene complexes (e.g. **718**) were produced. A dicationic vinylidene complex (**719**) was formed upon protonation of alkenylallenylidene complex **718**. Treatment of complex **718** with nucleophiles led to the γ-substitution products (e.g. **720–722**). A second insertion of the ynamine affords the dienylallenylidene complex **723**.

Stepwise formation of allenylidene–osmium complex **727** (Scheme 75) from propargyl alcohol complex **724** was reported [719]. Treatment with CO led initially to the CO(alkyne) complex **725** which proceeded to the allenylidene complex **727** at room temperature through observable intermediates. Protonation initially afforded dicationic carbyne complex **728**, which transformed to the indenylidene complex **729**. A similar set of transformations could be induced by diphenylphosphine. Allenylidene complex **727** could be transformed to the Fischer carbene complexes by treatment with alcohols or amines, or the acyl complex by treatment with water. Reaction of allenylidene complex **727** with carbodiimides led to products derived from [2 + 2]-cycloaddition with the β,γ-double bond. Formation of osmium-allenylidene and vinylidene complexes containing Cp-bridged phosphine ligands was also reported [720].

Formation of allenylidene–osmium complexes (e.g. **731**, Scheme 76) from diphenylpropargyl alcohol and osmium bromide **730** was reported [721]. An unusual cycloaddition reaction resulting in bis(osmium) complex **734** was observed using dimethylpropargyl alcohol. The key steps involve nucleophilic attack of the alkene group of the intermediate alkenylvinylidene complex **733** at the α-carbon of allenylidene complex **732**, followed by subsequent ring closure.



Scheme 73.

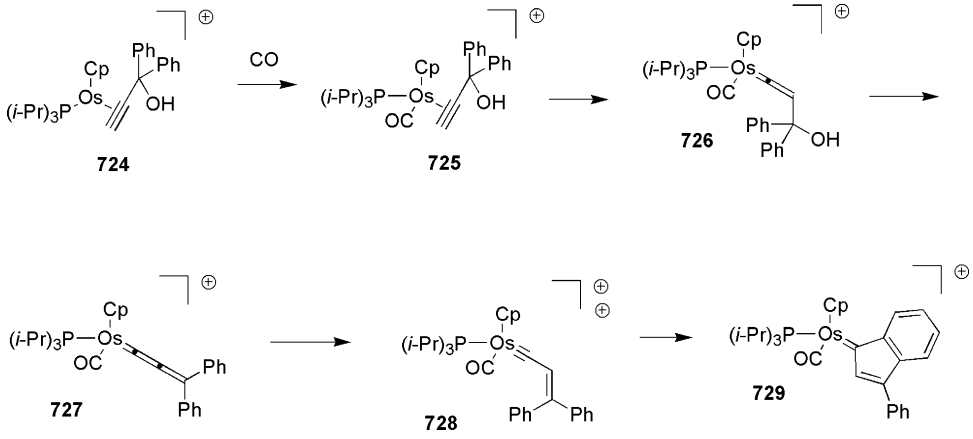


Scheme 74.

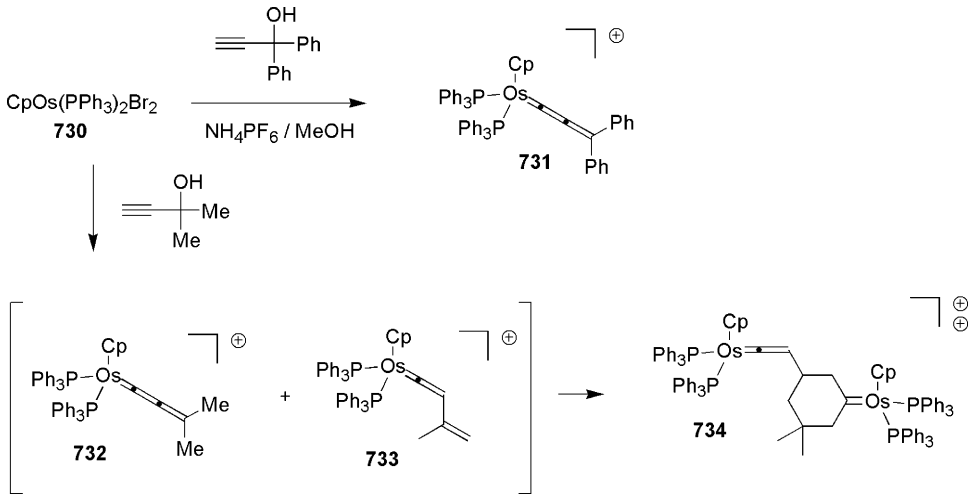
Ruthenium allenylidene complexes (e.g. **736**, Scheme 77) were proposed as intermediates in the formation of enynes (e.g. **737**) from propargyl alcohol **735** [722]. These products were further subjected to platinum catalyzed cycloisomerization, also proceeding through a carbene complex (**738**), to afford fused cyclopropanes (**739**). A one-pot reaction was also demonstrated. A related process involving the coupling of propargyl alcohols and ketones to form γ,δ-alkyne-ketones was also reported [723]. Nucleophilic addition of the acetone enolate to the γ-carbon of the allenylidene was proposed.

Cationic ruthenium allenylidene complexes (e.g. **743**, Scheme 78) were proposed as intermediates in the conversion of propargyl ethers (e.g. **740**) into alkynyl ketones (e.g. **746**) catalyzed by ruthenium complex **671** [724]. The proposed mechanism involves splitting the starting compound into propargyl alcohol **742** and allenylidene complex **743**, followed by formation of propargyloxy Fischer carbene complex **744**, followed by transfer of hydrogen to ruthenium, followed by hydrolysis to afford the alkynone. Similar processes were proposed for the ruthenium-catalyzed reductive conversion of benzyl propargyl ethers to 1,3-dienes and benzaldehyde [725].

The coupling of in situ-generated butatrienylidene complex **747** (Scheme 79) with heteroarylamines (e.g. pyrroles) was reported [726]. The reaction occurs between the 2-position of the pyrrole and the γ-carbon of the cumulene ligand to afford the intermediate enynyl complex (**748**), which undergoes proton transfer to afford the substituted allenylidene complex (e.g. **749**). Reaction occurs at the 3-position of the heteroaro-



Scheme 75.



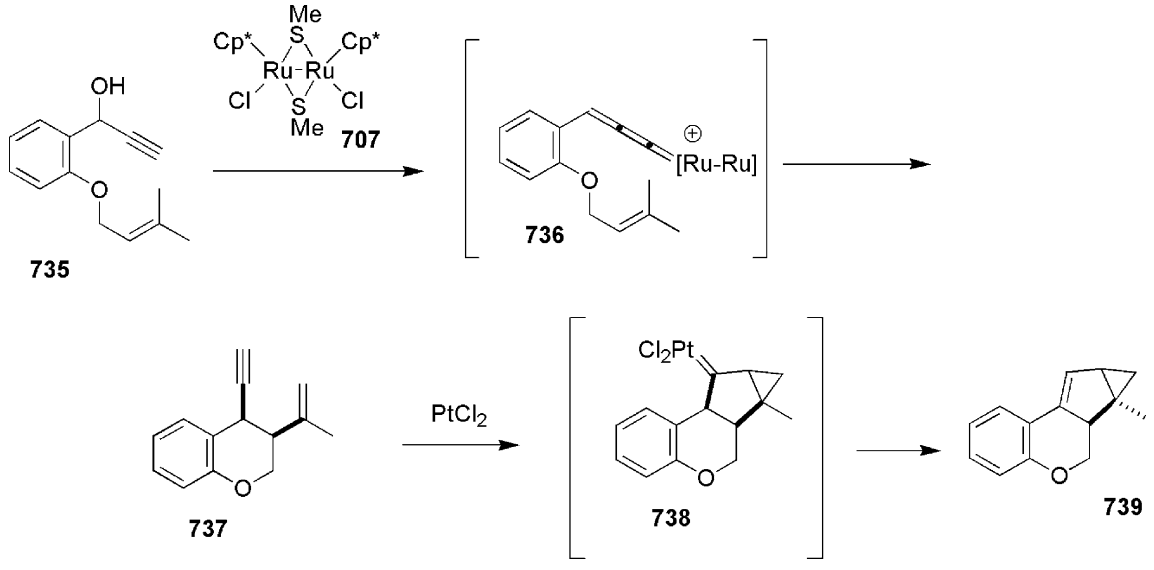
Scheme 76.

matic ring if indoles or 2,5-disubstituted pyrroles were used. Spectroelectrochemical studies were also reported for these complexes. Butatrienylidene complexes (e.g. **752**) were also suggested as intermediates in the conversion of ferrocenylbutadiyne (**751**) to alkynylruthenium complex **753** [727]. Nucleophilic addition of triethylamine to the γ-position of intermediate butatrienylidene–ruthenium complex **752** was proposed.

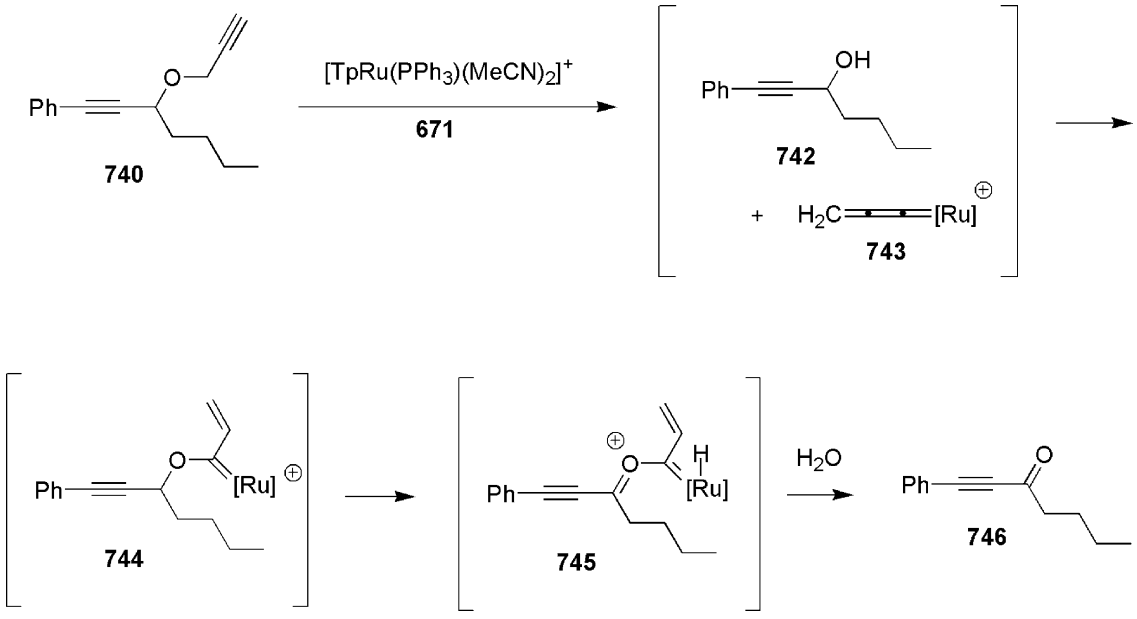
Electrochemical oxidation products from Ar-C≡C-Fe(dppe)(Cp^*) complexes feature substantial contribution from an allenylidene complex resonance form [728].

1.1.3.6. Group IX metal–carbene complexes.

1.1.3.6.1. Simple carbene complexes. The reaction of rhodium halides (e.g. **760**, Scheme 80) with diazo compounds was reported [729]. Reaction of the complex where L = PPh_3 led to a mixture of the carbene complex **761** and the bis(imine) derivative **762**. This process was more efficient if induced by a laser at 514 nm than if induced by photolysis using a mercury lamp. Several reaction processes were reported for these carbene complexes. Reaction with ethylene afforded ethylene–rhodium complex **764**. Reaction with triethylsilane led to the oxidative addition product **763**. Reaction with hydrogen (L = P*i*-Pr_3) led to the bridged structure **765**. The reaction of chelated rhodium chlorophenol complexes (e.g. **766**) and diazo compounds was reported [730]. Reaction of complex **766** with diphenyldiazomethane and ethylene led to the alkene **767**. Isomeric alkene **772** was produced from the coupling of structurally similar rhodium–ethylene complex **768** with diphenyldiazomethane. A mechanism involving formation of the carbene complex, followed by oxidative addition into the C–H bond of ethylene, followed by hydrogen migration to afford the vinyl(diphenylmethyl)rhodium complex **771**, followed by reductive elimination was proposed to explain the formation of alkene **772**. Rhodium carbene complex **775** was prepared through the coupling of rhodium complex **773** with chloroform and an amine [731]. Reaction of complex **773** with chloroform



Scheme 77.



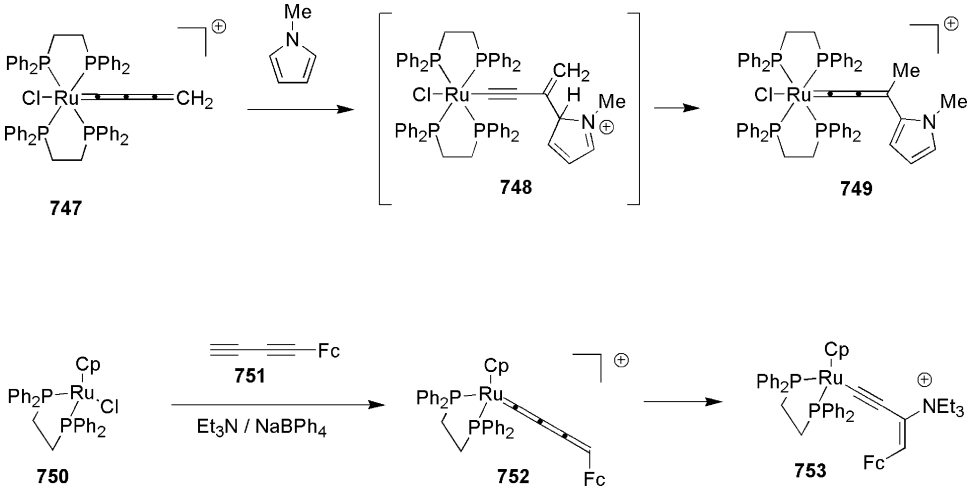
Scheme 78.

initially affords dichloromethyl complex **774**, which affords the aminocarbene complex upon treatment with an amine.

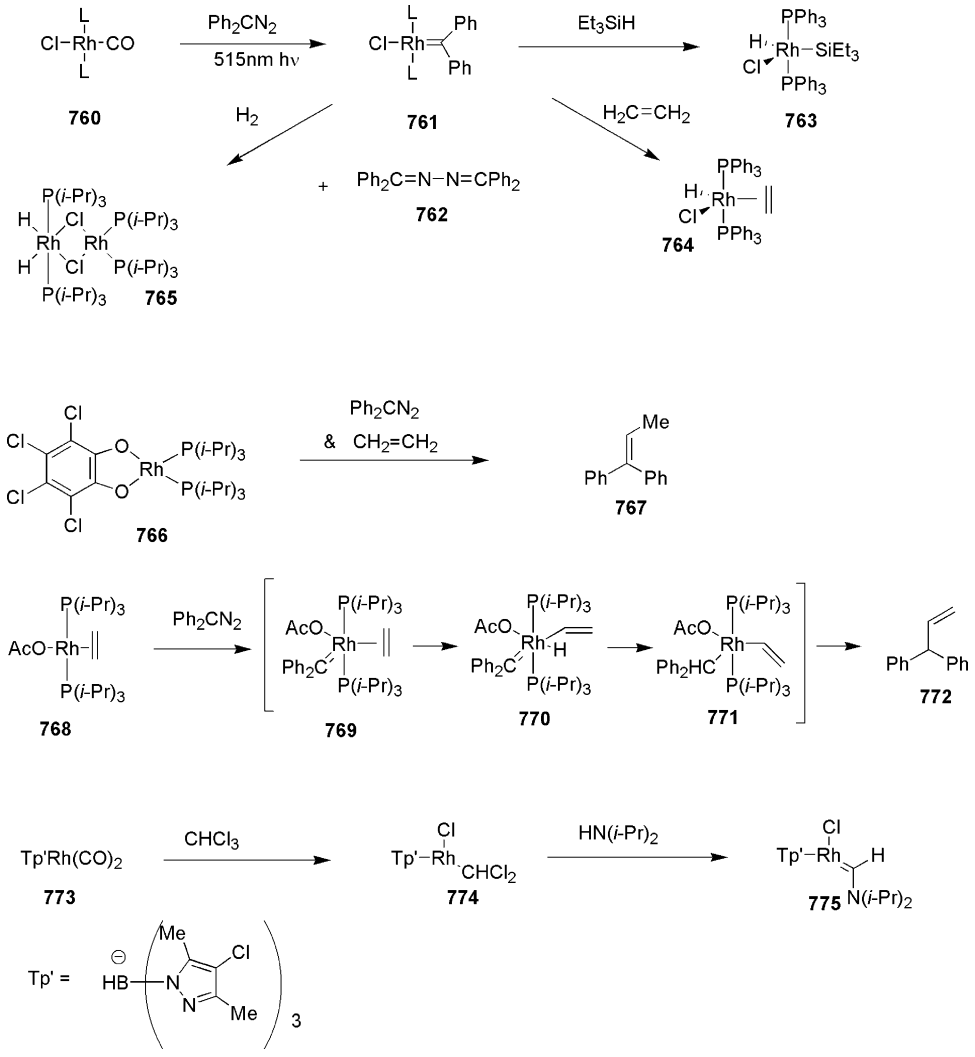
Chelated iridium carbene complex hydrides (e.g. **778**, Scheme 81) were prepared by the direct reaction of complex **776** with ethylphenol derivatives [732]. Carbene complex **778** is in equilibrium with the alkene complex **779**; equilibrium favors the carbene complex. Reaction with acetonitrile at 60 °C establishes an equilibrium with chelated alkyl complex **780**. Related compounds were produced in the reaction of iridium complex **776** with 1,2-dimethoxyethane [733]. Reaction at 60 °C leads to dihydrido carbene complex **781**, which converts to a mixture of complex **782** and *o*-substituted complex **783** upon heating to 80 °C in acetonitrile. A mechanism involving a benzyne–rhodium complex intermediate was proposed for the conversion of **782**–**783**. Compounds **784** and **785** were produced if the initial carbene-forming reaction was conducted at 80 °C in benzene.

Iridium carbene complexes (e.g. **789**, Scheme 81) were generated at equilibrium by the reaction of iridium complex **786** with *N*,*N*-dimethyl-2-aminopyridine [734]. The mechanism involves formation of an NMR-observable agostic complex **787**, followed by C–H oxidative addition and α-hydride elimination. Treatment of this complex with hydrogen regenerates complex **786**. These reaction processes were also evaluated computationally. Reaction of the **788**/**789** system with a monosubstituted alkene led to the elongated carbene complex **792** [735]. A mechanism involving alkene insertion into the Ir–H bond, followed by reductive elimination followed by an intermolecular C–H activation was proposed. Reaction of complex **788** with methyl vinyl ketone led to the β-metalloenone complex **793**, which has the carbene complex **794** (a metallafuran) as a contributing resonance form (Scheme 82).

Protonation of cationic iridium complexes (e.g. **795**, Scheme 83) led to dicationic iridabenzene complex (e.g. **796**)



Scheme 79.



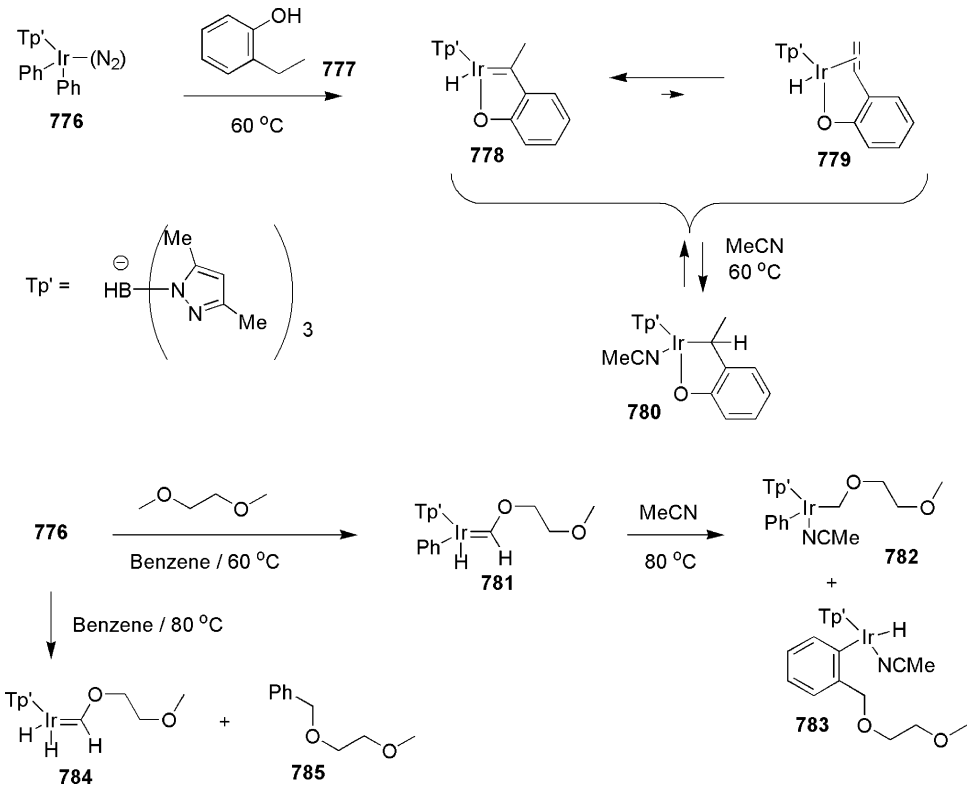
Scheme 80.

[736]. Protonation of the ethynyl(hydrido)iridium analogs (e.g. **797**) led to the methyl(CO)iridium complexes (e.g. **800**). Formation of a vinylidene, followed by addition of water and deinsertion of CO was proposed. The reactivity of iridathiabenzene complexes (e.g. **801**) was reported [737]. Ligand exchange occurred upon treatment with *t*-butyl thiolate to provide an equilibrium mixture of stereoisomeric complexes **802** and **803**. Further ligation with acetonitrile and trimethylphosphine was also reported. A dimeric complex (**806**) was formed upon treatment of complex **802/803** with triflic acid and acetonitrile. The aromatic ring was also successfully complexed to a $RuCp^+$ (η^5-ligation to all of the atoms of the aromatic ring except Ir).

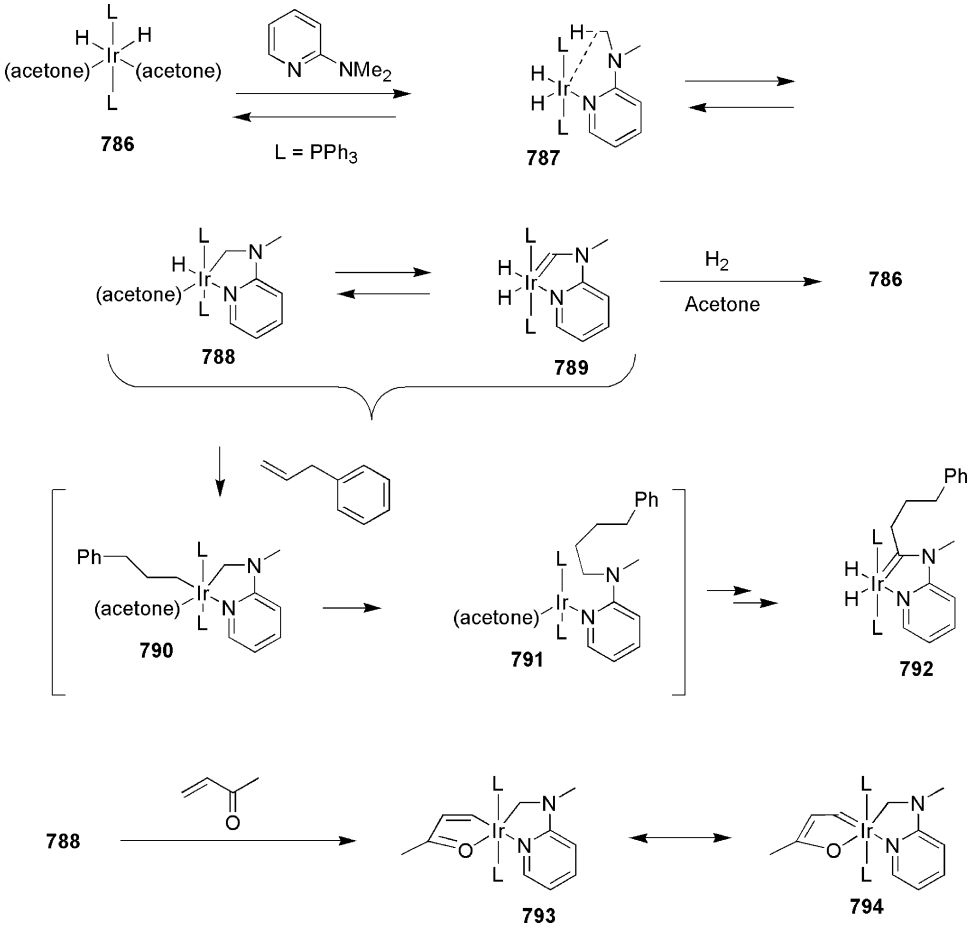
Rhodium carbene complexes (e.g. **808**, Scheme 84) were proposed as intermediates in a novel synthesis of furan derivatives from enyne-ketone derivatives and $Rh_2(OAc)_4$ [738]. Reaction in the presence of benzaldehyde and triphenylphosphine led to vinylfuran derivatives. A mechanism involving formation of the π-alkyne complex followed by intramolecular nucleophilic addition of the carbonyl oxygen to the alkyne complex to afford the furylcarbene intermediate was proposed (see Scheme 37 for a similar process induced by chromium). Carbonyl olefination products (e.g. **809**) were observed if an aldehyde and triphenylphosphine were present in the reaction. A mechanism involving conversion of the carbene complex to a phosphorane, followed by Wittig reaction was proposed. A polymeric material (e.g. **812**) was formed when the enyne-ketone contains remote alkene functionality and the aldehyde/triphenylphosphine additives were omitted. In this case the carbene complex intermediate (**811**) undergoes intermolecular cyclopropanation. Polymeric materials could also be produced if the enyne-ketone contains remote aldehyde functionality and triphenylphosphine was present.

The preparation of rhodium–Bertrand carbene complexes from the free carbenes was reported [739–741]. The bonding in these complexes was predominantly of a σ-donor nature. The π-acceptor ability of these complexes was rather weak.

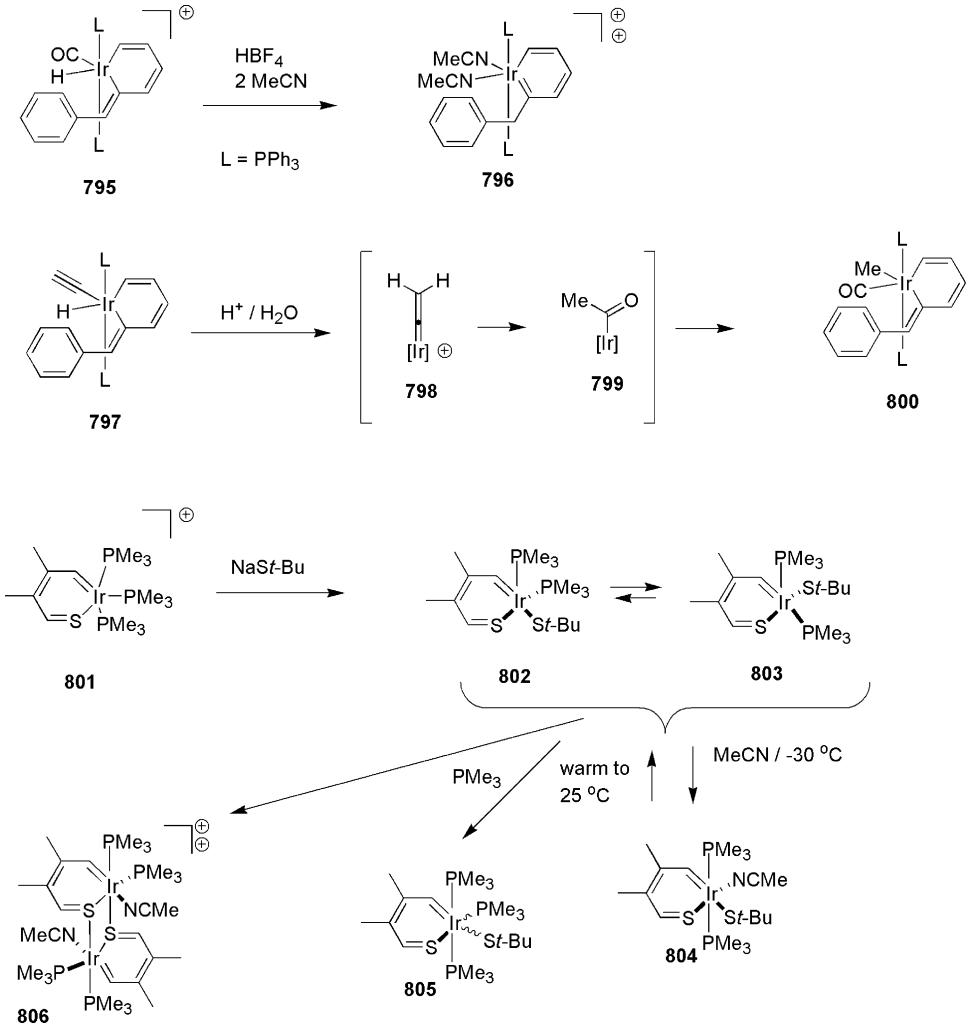
Other studies of Group IX metal–carbene complexes (excluding cumulenes) include: (1) possible involvement of iridium carbene complexes in the conversion of iridacyclopentenes to iridacycloheptarienes [742]; (2) asymmetric cyclopropenation reactions using diazo compounds, rhodium(II) acetate, and alkynes, including a detailed discussion of carbene intermediates



Scheme 81.



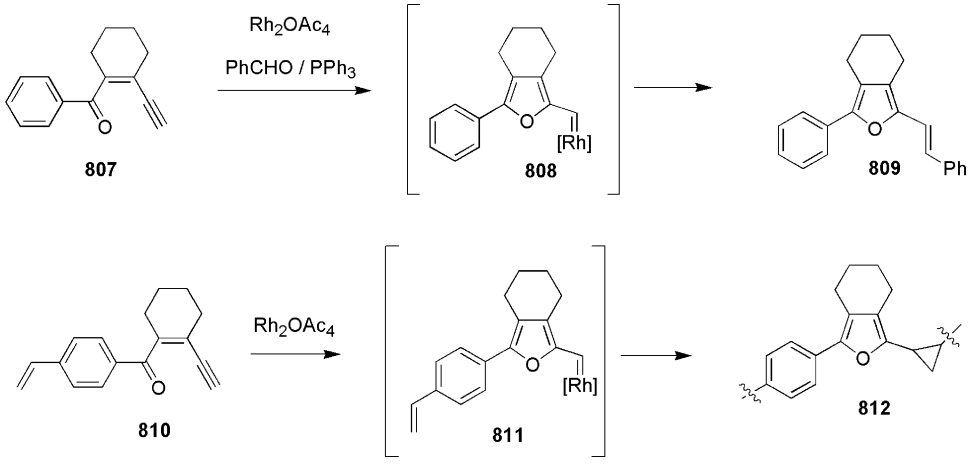
Scheme 82.



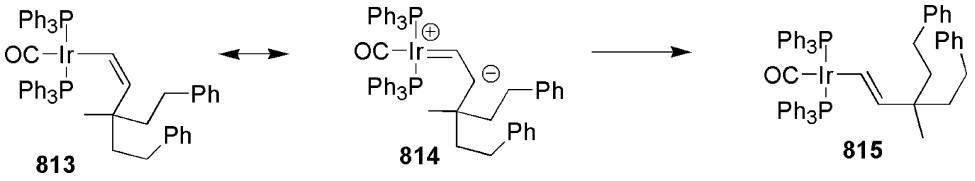
Scheme 83.

in the reaction [743]; (3) implication of an iridium carbene complex resonance form (**814**, Scheme 85) to explain unusually low barriers to rotation for alkenylruthenium complexes [744].

1.1.3.6.2. Cumulene complexes. Similar synthetic procedures and reactivity patterns were generally observed for Group IX and Group VIII metal–cumulene complexes (Schemes 64 and 71). Several rhodium–cumulene(alkynyl) complexes (e.g. **821**–**822**, Scheme 86) were prepared through coupling of two equivalents of a terminal alkyne with a rhodium–allyl complex (e.g. **820**) [745]. Chiral rhodium vinylidene complexes (e.g. **825**) were prepared from rhodium complexes featuring chiral ligands (**824**) and terminal alkynes



Scheme 84.



Scheme 85.

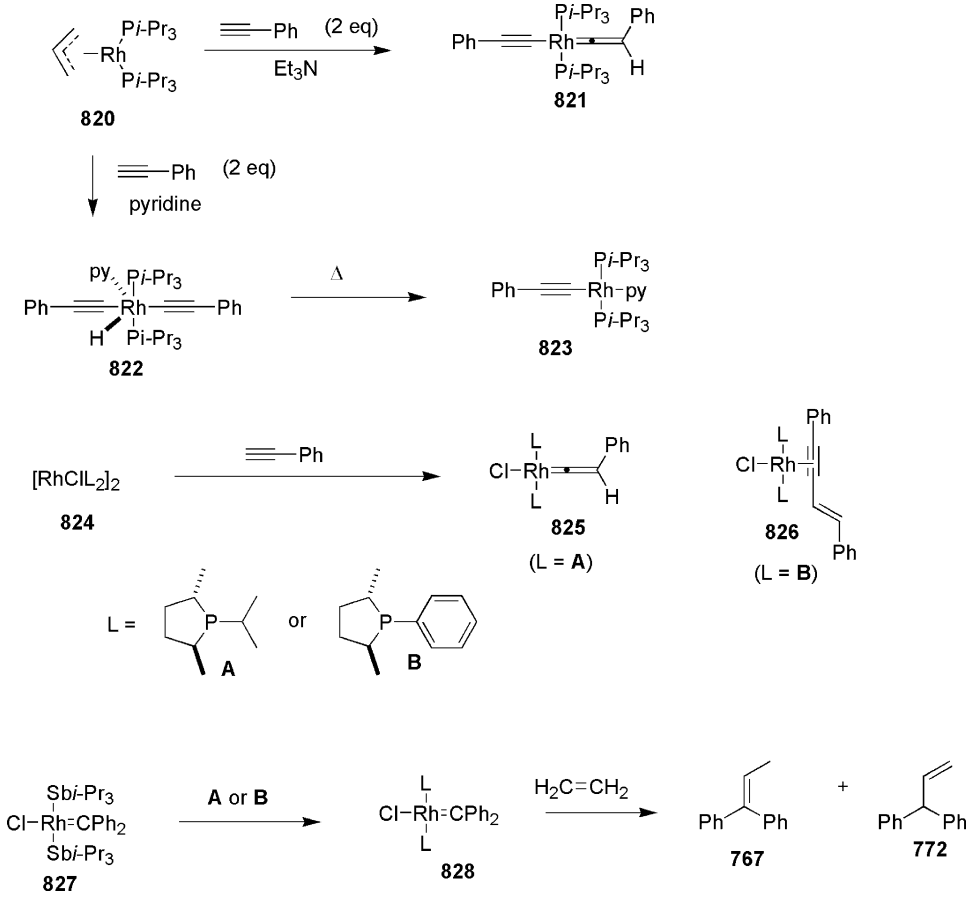
[746]. In the formation of **825**, both the π-alkyne and alkynyl(hydrido)ruthenium complex intermediates were observable by NMR. An alkyne-coupled product (**826**) was obtained when the P-phenyl ligand (**B**) was employed. Simple rhodium carbene complexes featuring these ligands were also prepared. Reaction of these complexes with ethylene led to alkene derivatives **767** and **772**.

Hydrative alkyne dimerization (conversion of **829** to **830** or **831**, Scheme 87) using Wilkinson's catalyst and 2-amino-3-picoline was reported [747]. A mechanism involving conversion of the alkyne to the vinylidene (**832**) followed by conversion to the iminoacyl complex (**834**), followed by alkyne insertion was proposed. Reaction using with the *N*-methyl analog of the amine led to the enamine.

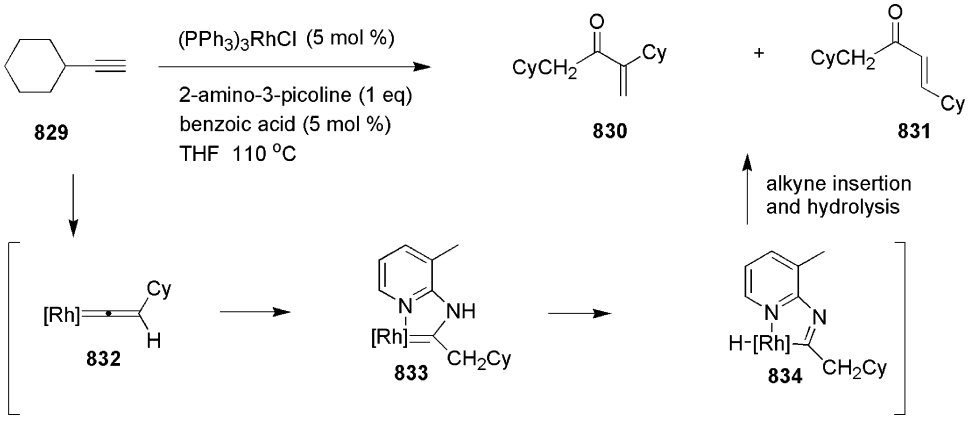
1.1.3.7. Group X metal–carbene complexes. Palladium– and platinum–carbene complexes (e.g. **838**, Scheme 88) were prepared from the coupling of chloro-substituted iminium salt **836** with $Pd(PPh_3)_4$ or the platinum analog [748]. The same complexes could be prepared through reaction of the neutral β-chloro-α,β-unsaturated amide **835** with the palladium or platinum(0) species followed by a methylation reaction. Manganese carbene complex **839** was also produced from these same organic starting materials.

The preparation of palladium carbene complexes featuring pincer ligands (e.g. **842**, Scheme 89) was reported [749]. The carbene–palladium bond was longer than typical palladium carbene complexes and thus is more consistent with a single bond than a double bond. DFT calculations revealed that there is significant anionic character at the carbene carbon. Reaction with iodomethane led to the cationic methylated complex **843**.

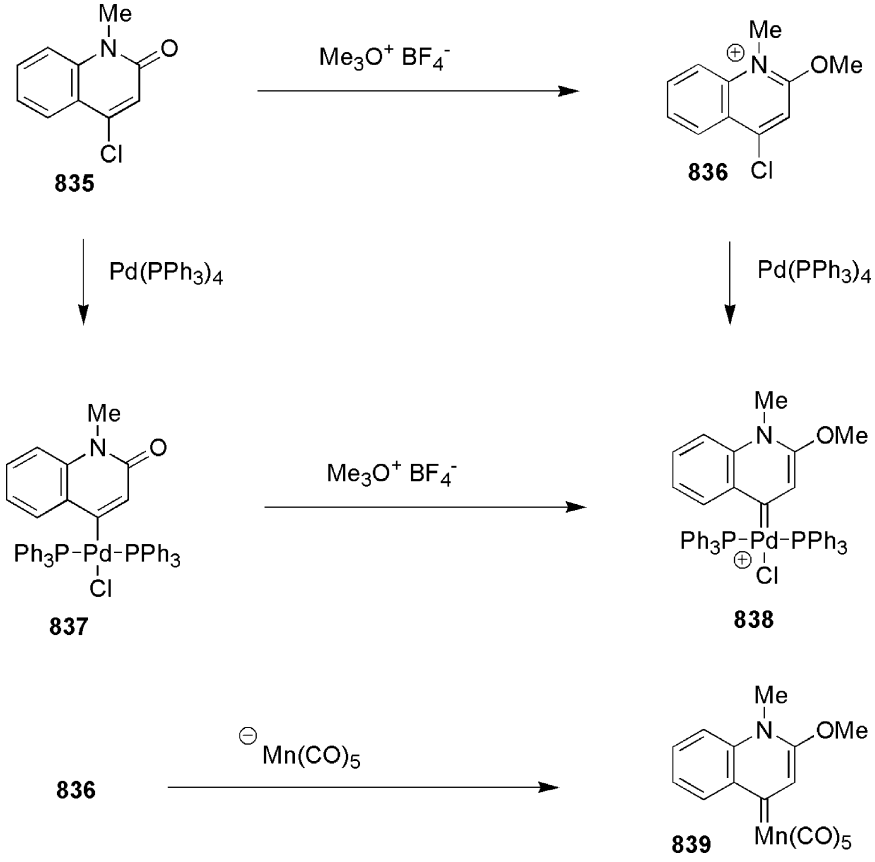
The preparation of platinabenzenes derivatives (e.g. **847**, Scheme 90) was reported [750]. Treatment of the organolithium reagent derived from iodide **844** with iodoplatinum complex **845** afforded a mixture of the transmetallation product **846** and the



Scheme 86.



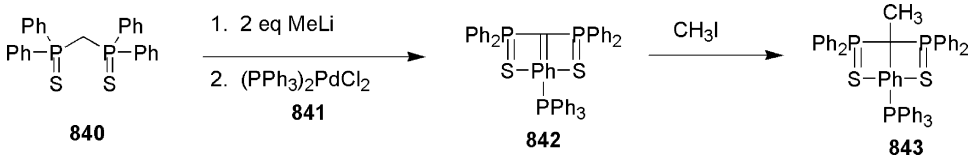
Scheme 87.



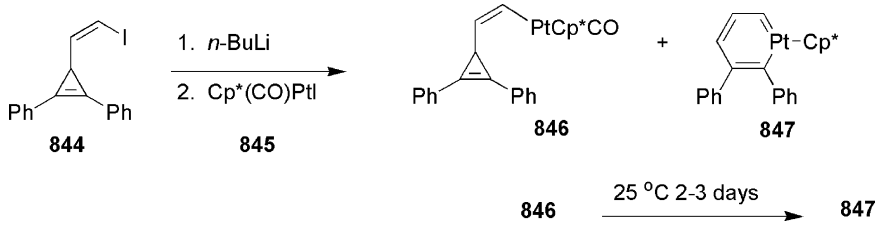
Scheme 88.

platinabenzene **847**, which was air stable. Mild thermolysis of **846** led to the platinabenzene **847**.

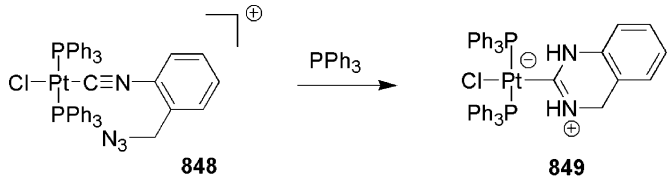
Several examples of the preparation of *N*-heterocyclic carbene complexes from isocyanide–Group X metal complexes were reported in 2004; examples are depicted in Scheme 91. Intramolecular addition of azide-derived phosphimines [751] and arsonium ylides [752] was reported. Preparation of palladium– (e.g. **851**) [753] and nickel–carbene complexes [754]

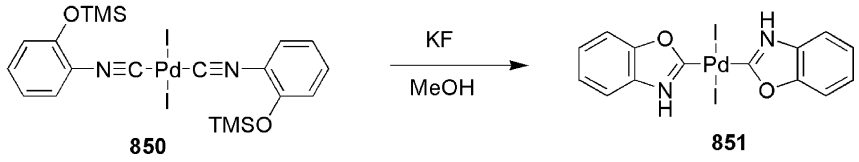


Scheme 89.



Scheme 90.





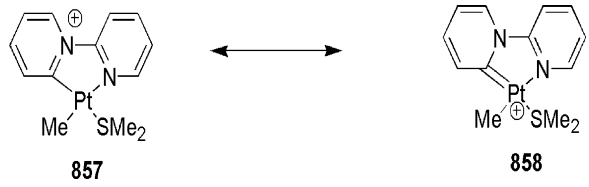
Scheme 91.

by reaction of 2-trimethylsilyloxyphenyl isocyanide complexes (e.g. **850**) with fluoride sources was reported.

Formation of the hydroazulene ring system (e.g. **853**, Scheme 92) through the nickel-catalyzed coupling of dieneynes (e.g. **852**) with trimethylsilyldiazomethane was reported [755]. A mechanism involving carbene complex formation, followed by alkyne insertion and intramolecular cyclopropanation was proposed. Cope rearrangement of the resulting divinylcyclopropane (**856**) affords the observed product (**857**).

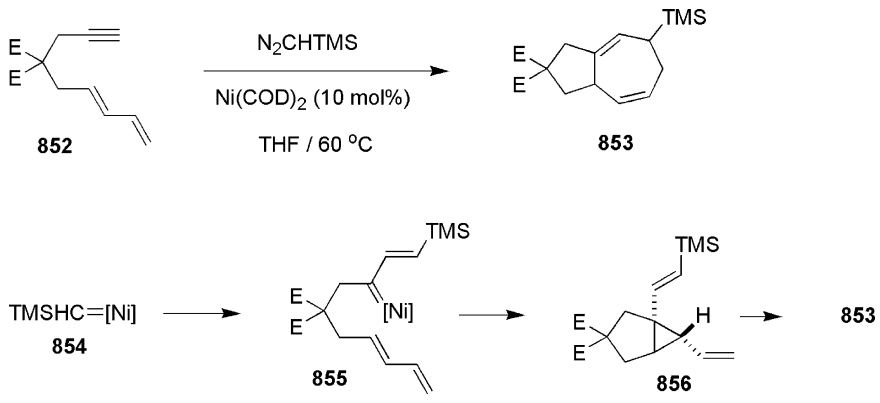
A carbene complex (**858**, Scheme 93) is a major contributing resonance form to cationic pyridylpyridinium complex **857** based on NMR and X-ray data [756].

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 94. Platinum carbene

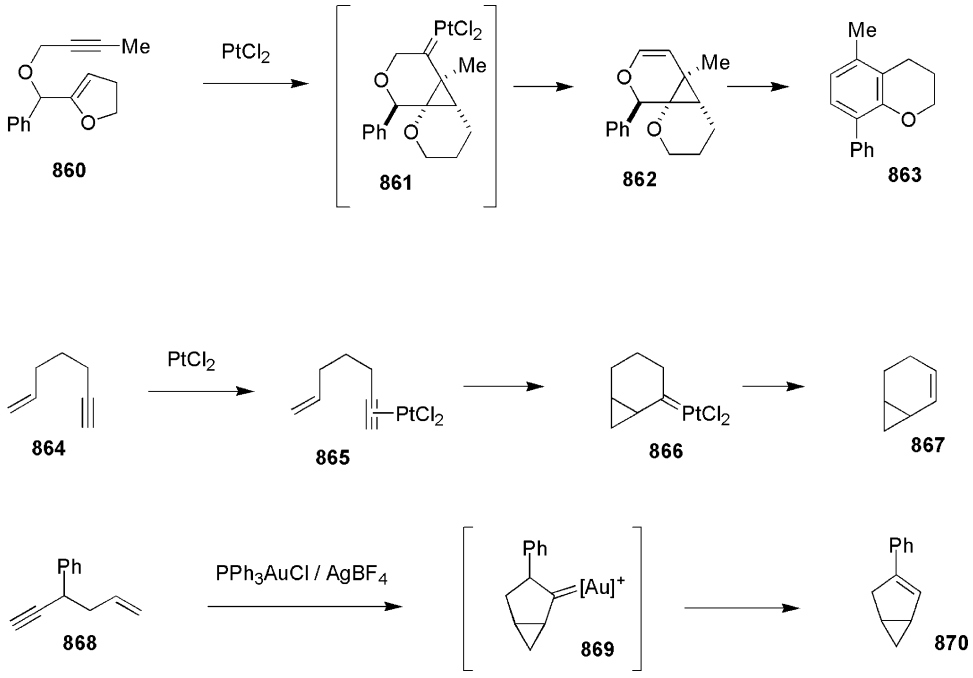


Scheme 93.

complexes (e.g. **861**) were proposed as intermediates in the isomerization of propargyl ethers (e.g. **860**) to benzene rings fused to oxygen heterocycles (e.g. **863**) [757]. A mechanism involving formation of cyclopropylcarbene–platinum complex **861**, followed by conversion to alkene-cyclopropane **862**, followed by an acid-catalyzed net dehydration was proposed. The platinum-catalyzed cycloisomerization of enynes (conversion of **864**–**867**) was studied computationally [758]. Formation of the π-alkyne



Scheme 92.



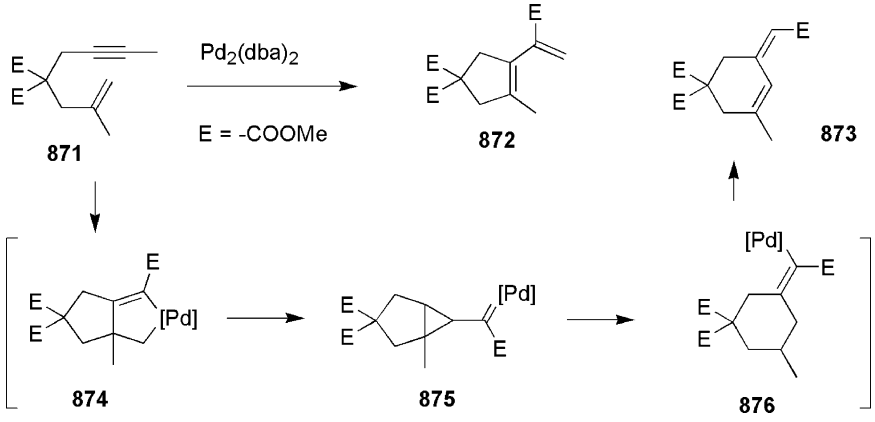
Scheme 94.

complex, followed by endo cyclization to the cyclopropylcarbene complex followed by decomposition to the alkene was the preferred mechanistic pathway. An additional example of this chemistry is depicted in Scheme 77. A similar reaction process (conversion of **868**–**870**) was catalyzed by gold salts [759]. A mechanism involving the cyclopropylcarbene–gold complex (**869**) was proposed.

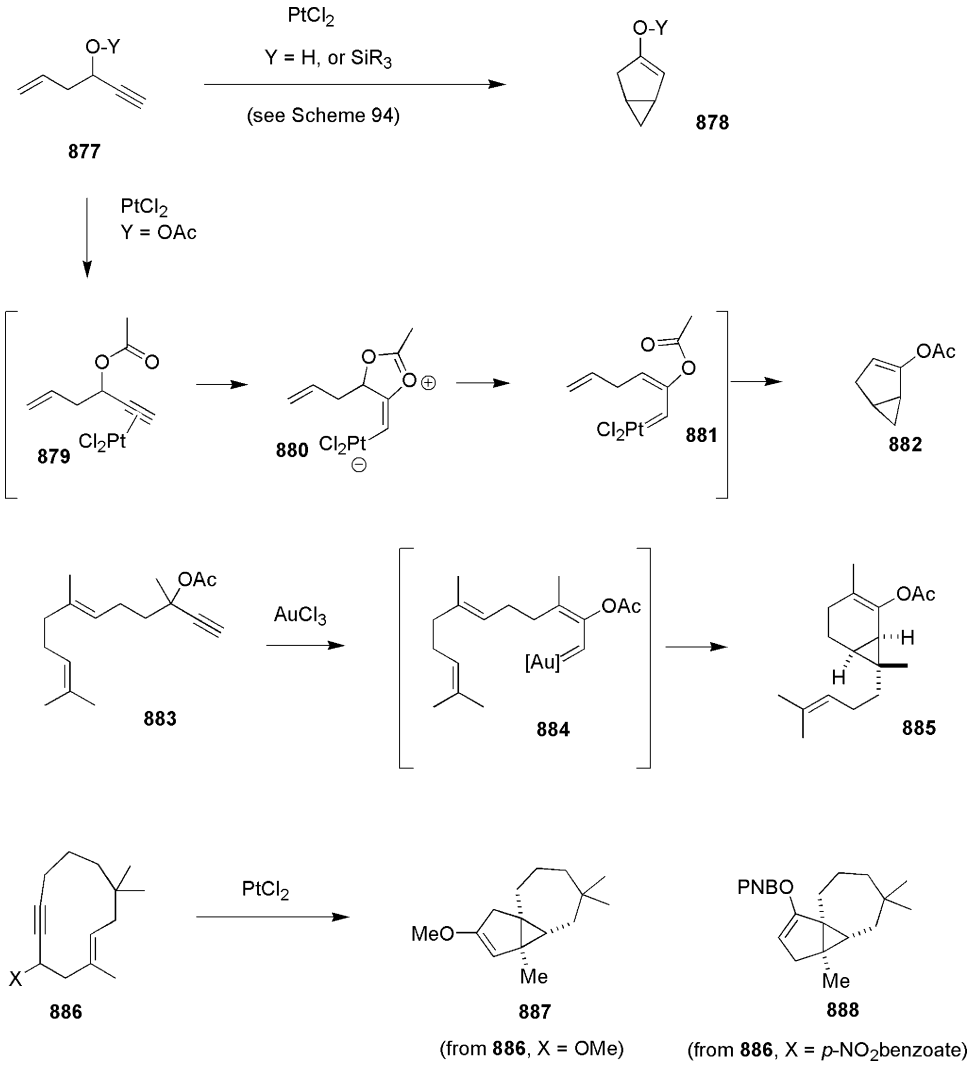
Palladium carbene complexes (e.g. **875**, Scheme 95) were proposed as intermediates in the conversion of enynes (e.g. **871**) to the cyclic compounds (e.g. **873**) accompanied by enyne metathesis products (e.g. **872**) [760]. A mechanism involving rearrangement of metallacyclopentene **874** to the cyclopropylcarbene complex **875**, followed by cationic cyclopropane ring opening was proposed to account for the formation of six-membered ring derivative **873**.

Carbene complexes were also generated from 1,2-shift of propargyl ester derivatives in the presence of platinum and gold complexes (see Scheme 96). Coupling of propargyl functionalized compound **877** with platinum chloride led to bicyclo[3.1.0]hexene derivatives (e.g. **878** and **882**) [761]. The course of the reaction was determined by identity of the Y group in **877**. Propargyl alcohols and ethers led to **878**; this reaction is analogous to that in Scheme 94. Propargyl esters led to **882** through a process involving a net 1,2-shift of the ester group and simultaneous formation of a platinum carbene complex (**881**) followed by intramolecular cyclopropanation. Similar results were obtained for internal alkynes [762]. This reaction was used as the key step in the synthesis of carene terpenoids (e.g. conversion of **883**–**885**) [763]. Reaction of cyclic enynes of general structure **886** with platinum(II) chloride led to tricyclic ketones **887** or **888** [764]. The reaction course depends upon whether X is an ether or an ester group.

A mechanistically related reaction process involving alkoxyacetylene analogs (e.g. **889**, Scheme 97) was reported [765]. The reaction affords cyclohexadiene intermediates (e.g. **891**). The proposed mechanism involves formation of a



Scheme 95.

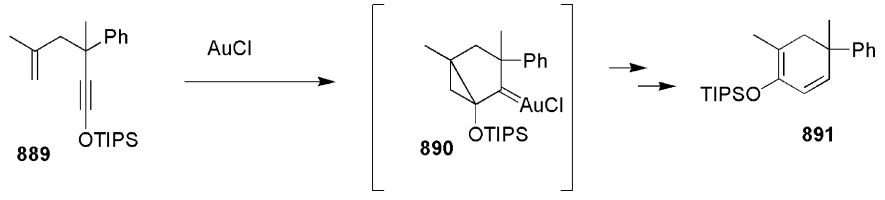


Scheme 96.

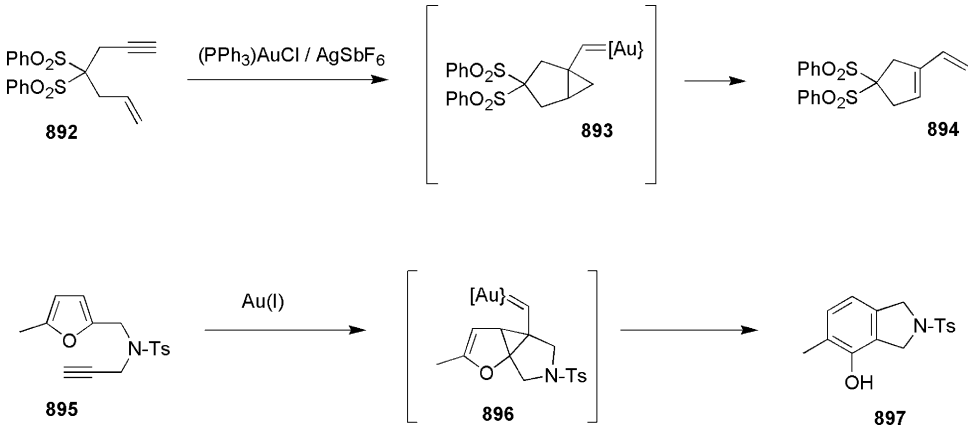
cyclopropylcarbene–gold complex **890**. This carbene complex cannot directly afford an alkene due to the lack of α-hydrogens. A series of cyclopropylcarbinyl-type rearrangements leads to the eventual product.

Several other reaction processes were reported from the reaction of alkynes and platinum or gold complexes that might involve carbene complex intermediates (see Scheme 98). Several papers reported on platinum-catalyzed enyne metathesis in 2004, which may involve metal carbene complex intermediates [766]. Apparent enyne metathesis was observed upon treatment of enyne **892** with gold(I) complexes [767]. DFT calculations showed that the most reasonable intermediates are cyclopropylcarbene–gold complexes. Cyclopropylcarbene complexes were also proposed as intermediates in the conversion of furanyldienes (e.g. **895**) to phenols (e.g. **897**) [768]. Platinum carbene complexes were mentioned as likely intermediates in the platinum-catalyzed conversion of 2-alkynylbiphenyl derivatives to phenanthrenes [769].

1.1.3.8. Group XI carbene complexes. A copper–carbene complex (**901**, Scheme 99) was generated by mild thermolysis of bridging carbene complex **900** and could be observed spectroscopically [770]. A stable copper carbene complex (**904**) could be generated by treatment of **903** with a diazo compound, and an X-ray structure was obtained for the complex. Treatment of the carbene complex with styrene at room temperature led to



Scheme 97.



Scheme 98.

the cyclopropanation product. The copper–carbon bond length in **904** is 1.834 Å, which is consistent with significant double bond character. One paper in 2004 suggested that there is a small degree of backbonding in Group XI *N*-heterocyclic carbene complexes [771]. The paper suggested that there is a similar degree of backbonding in these complexes and in dialkoxy Fischer carbene complexes.

A major discussion of metal carbene complexes in the copper-catalyzed cyclopropanation of 2,5-dimethyl-2,4-hexadiene was reported [772]. The effect of halide on copper catalyzed enantioselective cyclopropanation was studied by DFT calculations [773].

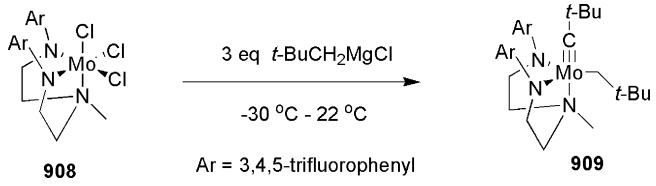
1.2. Metal–carbyne or metal–alkylidyne complexes

1.2.1. Review articles

A review of transition metal silyl complexes includes a significant number of carbyne complexes in addition to carbene complexes [774]. Some reviews of alkene metathesis feature alkyne metathesis segments [27,28].

1.2.2. Synthesis and/or generation

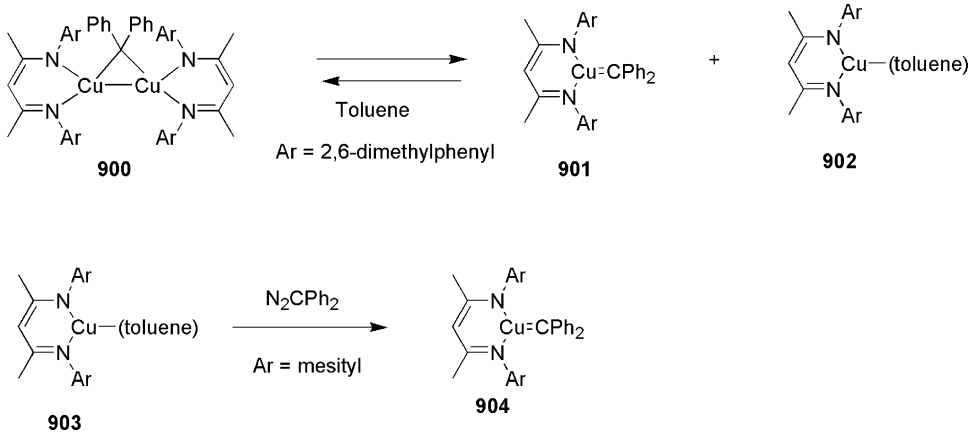
Several examples of the preparation of bis(amido)amine molybdenum–carbyne complexes (e.g. **909**, Scheme 100) from molybdenum halide complex **908** were reported [775]. Reaction



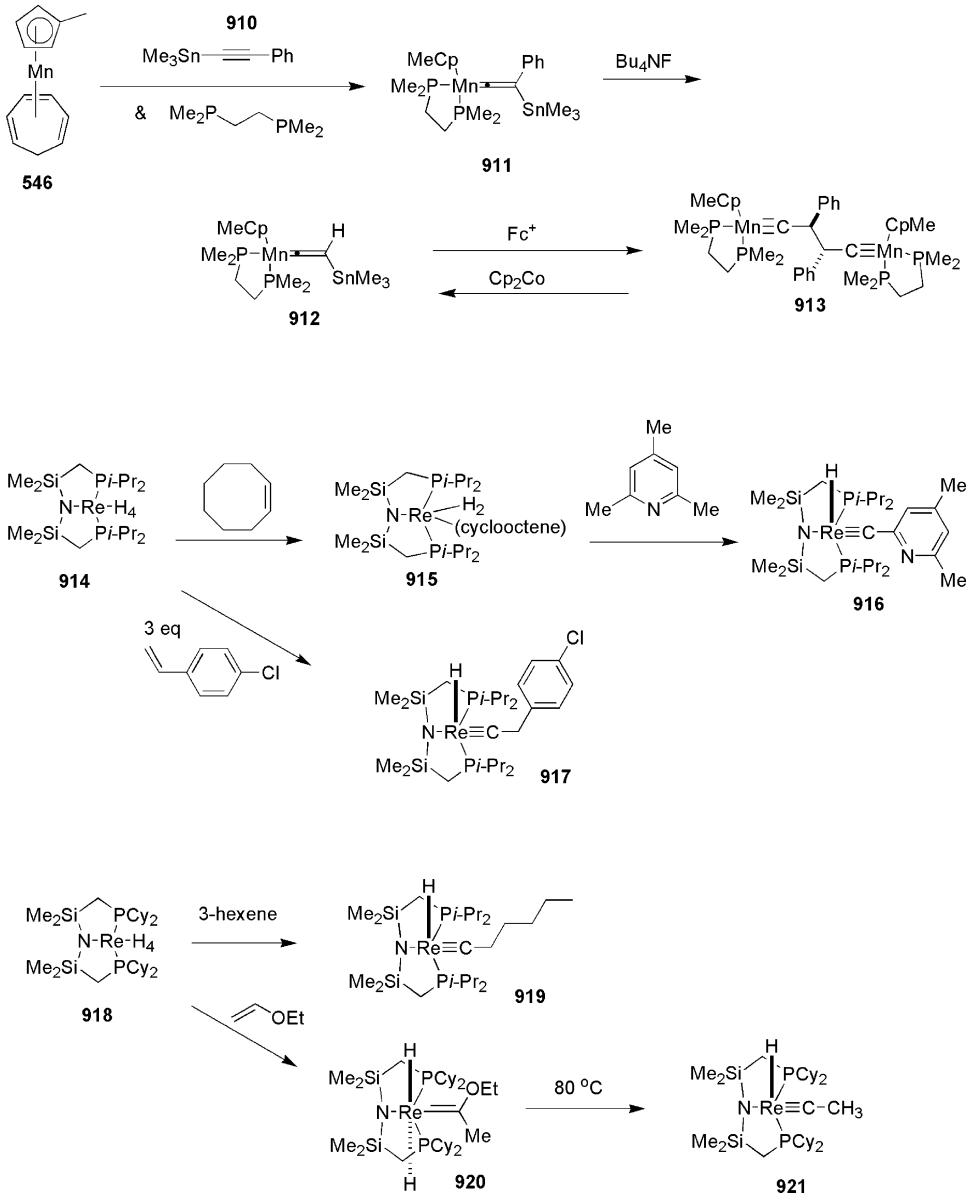
Scheme 100.

of this complex with neopentyllithium results in direct formation of the carbyne complex. The carbyne-forming reaction did not occur if Ar = C_6H_5 or when trimethylsilylmethyllithium was used in place of neopentyllithium. Numerous tungsten carbyne complexes were prepared through ligand substitution reactions of R–C≡W(CO)$_4$OTf derivatives [776]

Formation of bis(carbyne) complexes (e.g. **913**, Scheme 101) through oxidative dimerization manganese vinylidene complexes (e.g. **912**) was reported [777]. The dimerization process was stereoselective. Treatment of the bis(carbyne) complex with a reducing agent (cobaltacene) induced fragmentation back to the vinylidene complex. The coupling of rhenium tetrahydride complex **914** with cyclooctene followed by collidine resulted in the carbyne complex **916** [778]. A carbyne complex (**917**) was also formed by reaction of complex **914** with *p*-chlorostyrene. The structure of the complexes was studied by DFT calculations. Even 3-hexene afforded a carbyne complex (**919**) upon



Scheme 99.



Scheme 101.

treatment with complex **918**, presumably through isomerization to 1-hexene [779]. A carbene dihydride (**920**) was obtained from the analogous reaction with ethyl vinyl ether. This complex could be converted to the carbyne complex **921** by thermolysis. Carbyne complexes did not form from the coupling of the diphenylphosphino analogs of ruthenium tetrahydride complexes **914/918** and alkynes, despite the fact that this reaction is incredibly exothermic according to DFT calculations [780].

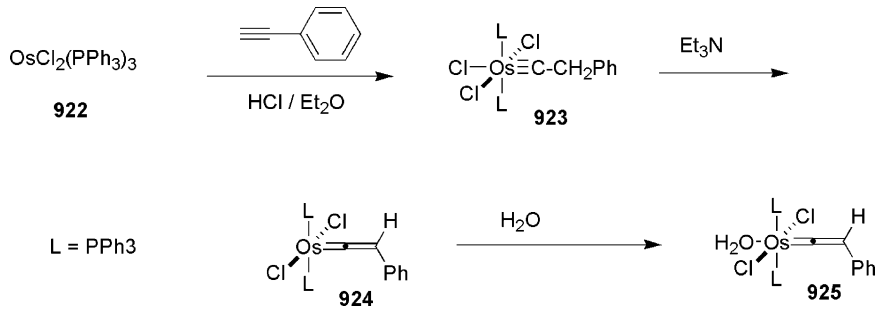
Synthesis of carbyne complexes from $OsCl_2(PPh_3)_3$ (**922**, Scheme 102) and terminal alkynes was reported [781]. Coupling of these partners in the presence of HCl leads to the carbyne complexes (e.g. **923**). An elimination leading to the vinylidene complex (**924**) was observed upon treatment with triethylamine.

Additional carbyne complexes prepared in 2004 include the generation of carbyne complexes at a platinum surface from 1,1,1-trichloroethane [782]. Some papers in the metathesis and carbene sections feature segments on carbyne chemistry. These studies include references [159,568,676,704].

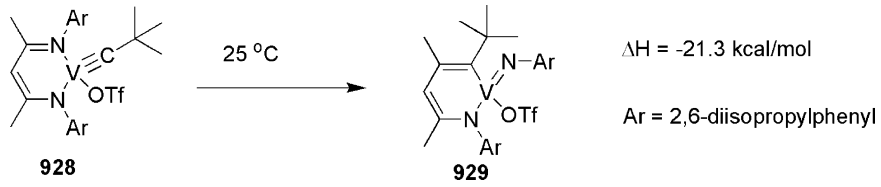
1.2.3. Reactivity

1.2.3.1. Addition reactions of metal–carbyne complexes. Vanadium carbyne complex **928** (Scheme 103) was generated and found to undergo an intramolecular metathesis reaction at room temperature, resulting in vinylvanadium complex **929** [783]. The reaction followed first order kinetics and was energetically favorable by 21.3 kcal/mol.

Complexation of the carbon–tungsten triple bond with other metals was reported [784]. Reaction of complex **930** (Scheme 104) with $Fe_2(CO)_9$ led to bimetallic complex **931**. The reaction employing the phenyl analog of **930** proceeded in much lower yield. Reaction with tellurium afforded to trimetallic alkynyltungsten complex **932**. Addition of $SOCl_2$ to the tungsten



Scheme 102.

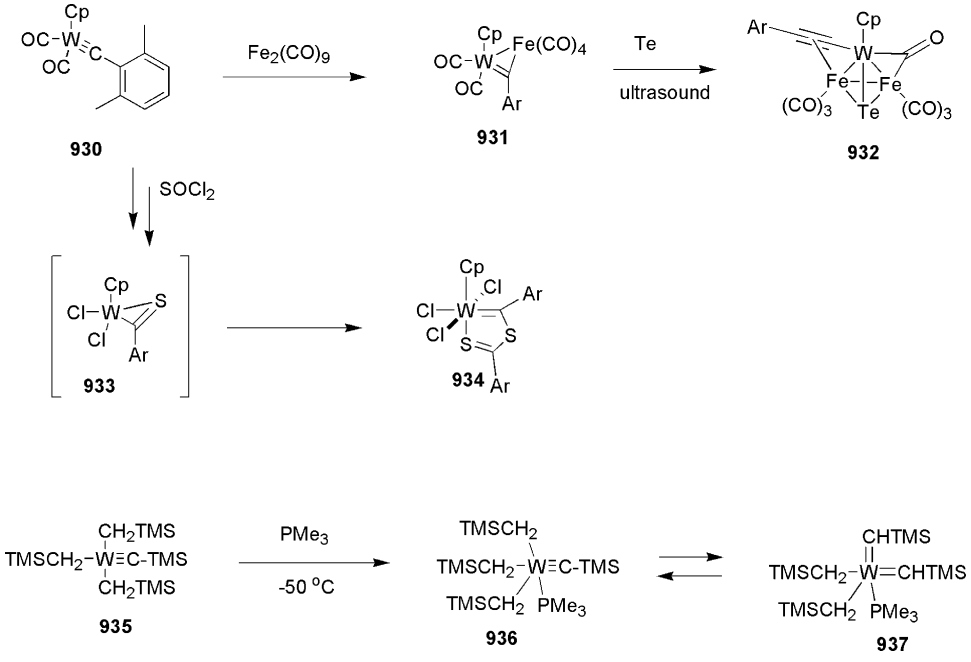


Scheme 103.

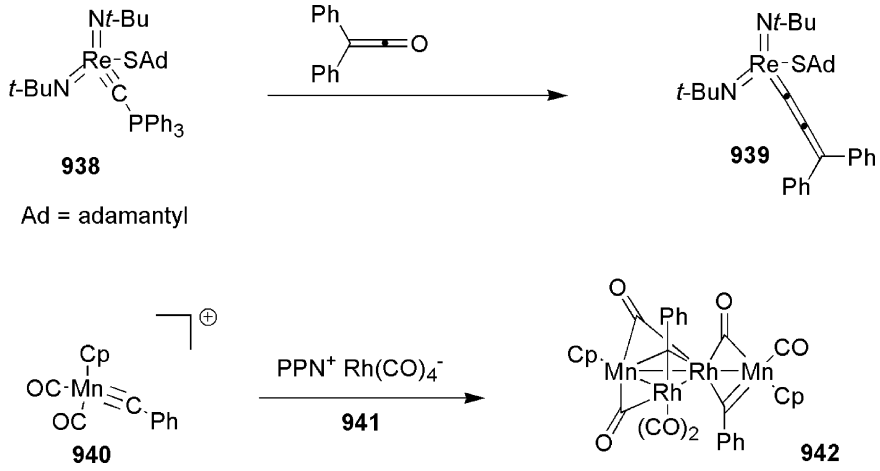
carbon triple bond of complex **930** was also reported, resulting in complex **934** [785]. The formation of complex **934** was proposed to occur via a thioacyl complex intermediate. Addition of HCl to triphenyl Group XIV metal-substituted carbyne complexes [Ph_3E–C≡W(O-*t*-Bu)$_3$] was also reported [786]. The reaction afforded the carbene complex [Ph_3E–CH=WCl_2(O-*t*-Bu)$_c$] and *t*-butyl alcohol. Generation of tris(trimethylsilylmethyl)tungsten carbyne complex **935** followed by addition of trimethylphosphine at −50 °C led to carbyne complex **936** [787]. Upon warming, an equilibration between the bis(carbene) complex **937** and carbyne complex **936** was observed. Theoretical calculation revealed that the bis(carbene) complex is more stable by 2.1 kcal/mol.

The coupling of rhenium carbyne complexes (e.g. **938**, Scheme 105) with ketenes was reported [788]. The reaction leads to the allenylidene complex **939**. Addition of the nucleophilic carbyne carbon to the ketene group followed by elimination of triphenylphosphine oxide was proposed. The coupling cationic manganese carbyne complex **940** with rhodium carbonyl anions was reported [789]. The coupling resulted in the polynuclear manganese carbene complex **942**, which functioned as a hydroformylation catalyst. The electrochemistry of this complex was also reported.

Reaction of chelating *o*-acetophenone osmium complex **943** (Scheme 106) with HBF_4 in the presence of phenylacetylene led to carbyne–osmium complex **944** [790]. Reaction of the



Scheme 104.



Scheme 105.

carbyne complex with CO led to osmium complex **945** and 1,4-diphenylbutadiene (**946**). Reaction with sodium chloride led to cyclic vinylidene complex **948**. A mechanism involving 1,2-migration of the styryl group followed by a cyclization reaction involving the resulting alkynylcarbene ligand and the alkynyl ligand in intermediate complex **947** was proposed.

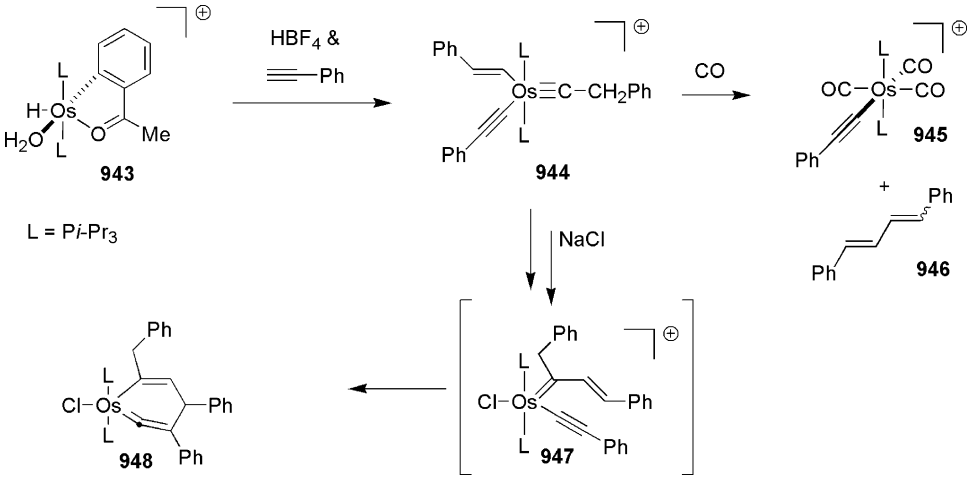
1.2.3.2. Alkyne metathesis. Alkyne metathesis, which involves metal carbyne complexes as intermediates, has been covered comprehensively regardless of whether the initiator is a carbyne complex. General equations describing the mechanism and precedented modes are presented in Scheme 107. Several reports using alkyne metathesis for natural product synthesis and for polymer synthesis appeared in 2004; representative substrates and products are depicted in Fig. 15.

Several examples of alkyne metathesis were reported in 2004. Representative examples are depicted in Fig. 15 Examples include: (1) alkyne cross-metathesis of **950** and bis(trimethylsilyl)acetylene using catalyst **952** and dichloromethane [791]; (2) use of RCAM (see Scheme 107) for the preparation of cyclic enynes (e.g. **953**) employing carbyne complex **955** [792]; (3) use of threefold RCAM in the coordination sphere of a metal for the preparation of interligand-bridged transition metal phosphine complexes (e.g. **956**) using catalyst **955** [793]; (4) preparation of macrocyclic bis(lactones) using molybdenum hexacarbonyl and fluorinated phenol derivatives [794]; (5) ADMET-type polymerization of bis(alkyne) derivatives (e.g. **958**) using carbyne complex **960** [795,796].

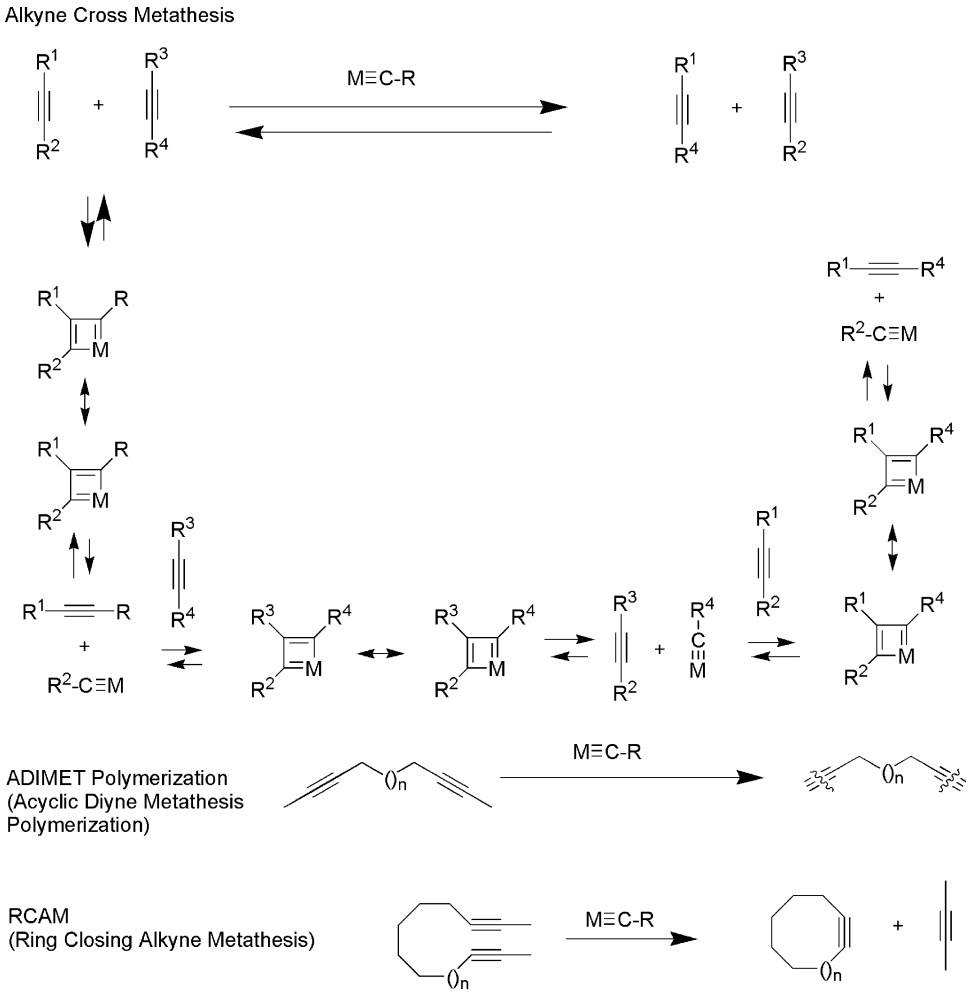
Molybdenum carbyne complex **962** (Scheme 108) was generated from the reaction of tris(amido)molybdenum complex **952** and 1,1-dihaloalkanes[797]. The yield of the carbyne complex could be improved by a reductive recycle approach. Phenoxy derivatives (e.g. **960**) could be prepared by reaction of the carbene complexes with phenols. The tris(*p*-nitrophenoxy) complex **960** was an effective alkyne metathesis catalyst. Various metathesis dimerization reactions (e.g. conversion of **963–964**) were reported for this complex.

Patents were awarded for new alkyne metathesis catalysts [798] and for the synthesis of enediynes using alkyne metathesis [799].

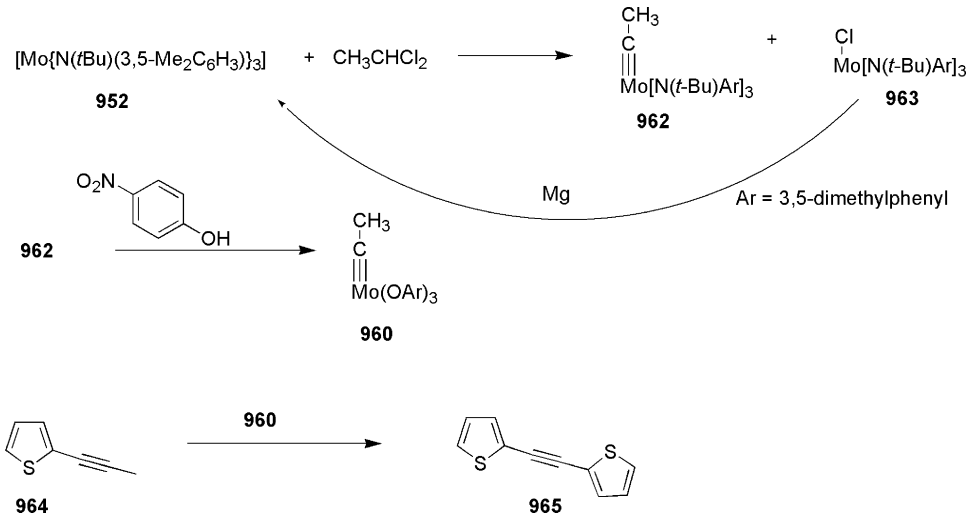
1.2.3.3. Other processes involving metal–carbyne complexes. Several examples of bimetallic compounds bridged through an ethynylcarbyne linker were reported in 2004; repre-



Scheme 106.



Scheme 107.



Scheme 108.

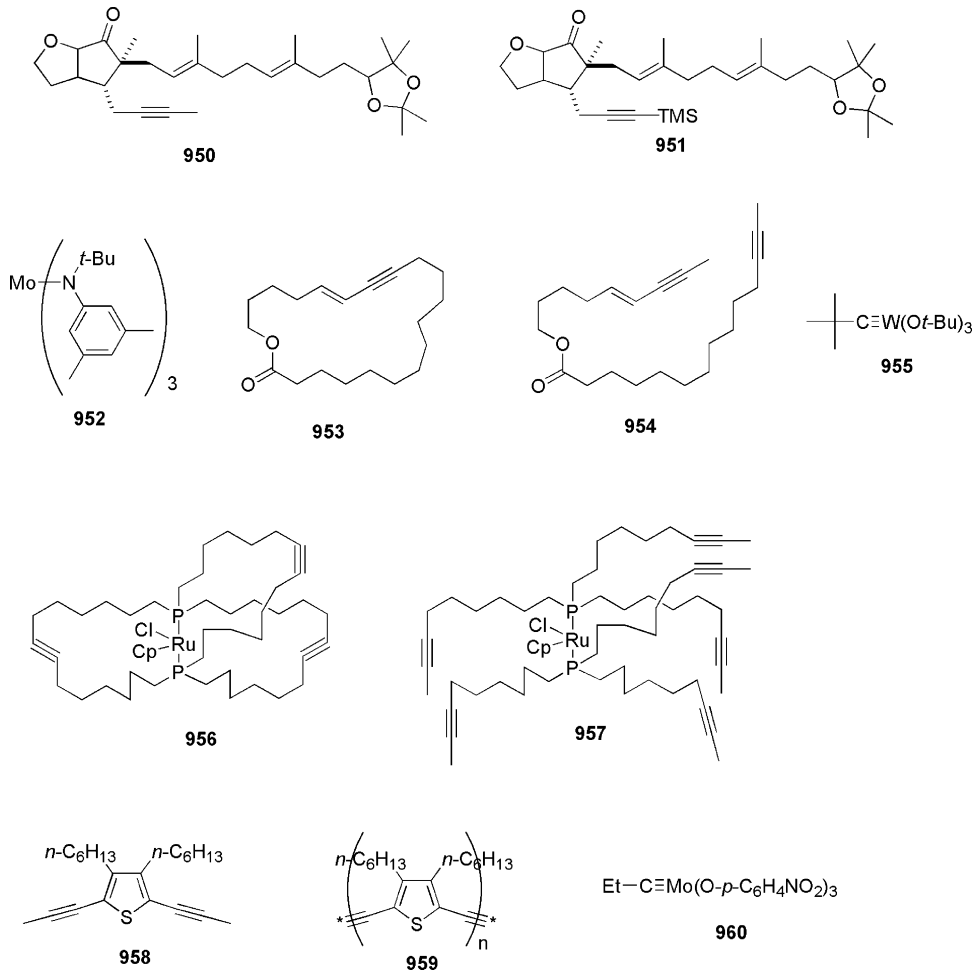
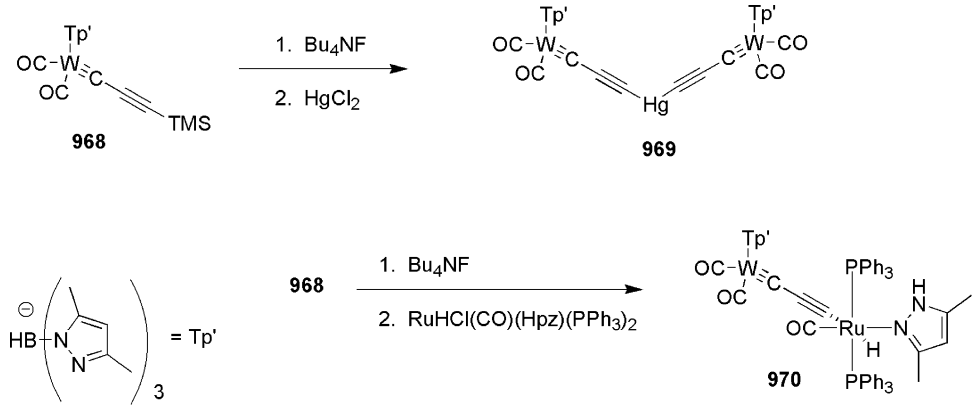


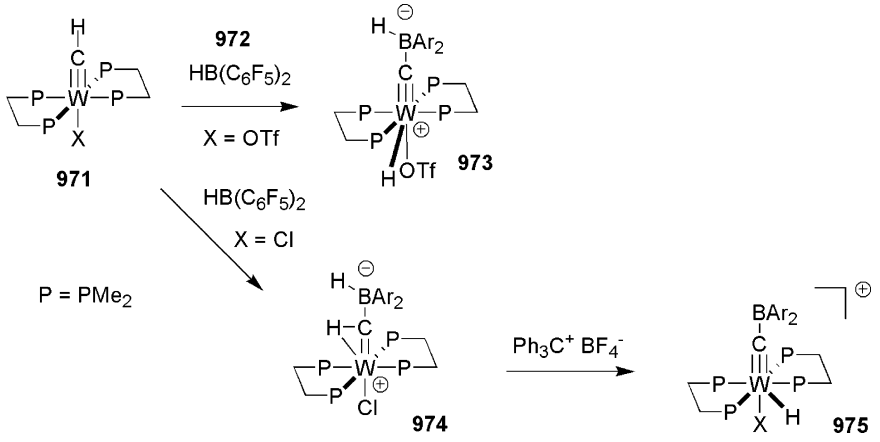
Fig. 15. Alkyne metathesis substrates, products, and catalysts.

sentative examples are depicted in Scheme 109. Examples include: (1) the formation of bis(metal carbene-alkynyl)mercury compounds (e.g. **969**) [800]; (2) formation of a bis(alkynylcarbyne)–iridium complex [801]; (3) formation of tungsten carbyne–alkynylruthenium complexes (e.g. **970**) [802]; (4) formation of tungsten carbyne–alkynylrhodium complexes [803].

The synthesis and reactivity of terminal carbyne–tungsten complex **971** (Scheme 110) was reported [804]. Reaction of the triflate complex with diarylborane derivative **972** led to the borylcarbyne–tungsten complex **973**. Reaction with the chlorotungsten carbyne complex led to the agnostic complex **974**. Hydride abstraction afforded the borylcarbyne complex **975**.



Scheme 109.



Scheme 110.

Compounds featuring molybdenum–lead triple bonds were reported [805]. Computationally based comparisons of these complexes with analogous metal–carbyne complexes were studied.

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