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Review

The chemistry of the carbon–transition metal double and triple bond: annual survey covering the year 2002☆

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Abstract

This is a review of papers published in the year 2002 that focus on the synthesis, reactivity, or properties of compounds containing a carbon–transition metal double or triple bond.

Keywords: Carbon; Transition; Survey

1. Introduction

This survey is intended to be a comprehensive summary of articles that report on the synthesis, reactivity, or properties of compounds featuring a multiple bond between carbon and a transition metal. Reactions that employ metal carbene complexes as transient intermediates generated through well-established routes are not covered, unless there is some effort to characterize the carbene complex intermediate. This area was reviewed in 2002 [1,2]. Although a determined effort has been made to include patents, in general only patents that are listed in or at the end of the Organometallics section of *Chemical Abstracts* (Section 29) are included; patents that appeared in Chemical Abstracts in the year 2002, have been included. Only compounds which feature a multiple bond between one carbon atom and one transition metal are discussed in this survey, thus bridging carbene and carbyne complexes are not covered unless there is a multiple bond to at least one transition metal. The complexes of stable carbenes with transition metals have not been included; since the π-donation component of these complexes is minimal, there is no formal carbon–metal multiple bond [3,4]. This area was reviewed several times in 2002 [5–9]. 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 [10] 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* [11]).

DFT	density functional theory
Grubbs catalyst I	structure **1** (Fig. 1),
Grubbs catalyst II	structure **2** (Fig. 1),
Nolan catalyst	structure **3** (Fig. 1),
Schrock catalyst	structure **4** (Fig. 1).

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

2. Metal–carbene or metal–alkylidene complexes

2.1. Review articles

Several reviews covering aspects of metal–carbene complex chemistry appeared in 2002. Many reviews focusing on some aspect of carbene complex-initiated olefin metathesis were published, including the following specific subjects: (1) an overview of modern alkene metathesis [12]; (2) metathesis polymerization [13–15]; (3) ROMP using ruthenium catalysts [16,17]; (4) the mechanism of alkene metathesis [18]; (5) use of ruthenium–carbene complexes in both alkene metathesis and radical reactions [19]; (6) alkene metathesis for C–C multiple bond formation [20]; (7) industrial applications of alkene metathesis [21]; (8) applications of alkene metathesis in green chemistry [22]; (9) the early history of alkene metathesis [23]; (10) tandem ROMP-hydrogenation reactions [24]; (11) stereoselectivity in ROMP reactions [25]; (12) alkene and alkyne polymerization using seven-coordinated tungsten and molybdenum compounds [26]; (13) titanium-based alkene metathesis [27]; (14) metathesis using catalysts generated in situ from $[RuCl_2$ (*p*-cymene)$]_2$ [28]; (15) catalyst and synthesis issues in ADMET polymerization [29]; (16) formation of metathesis-based polymers for separation applications [30]; (17) preparation of C–C coupling and polymerization catalysts through ROMP [31]; (18) synthesis of cyclic polymers [32]; (19) ADMET polymerization of divinylbenzene [33]; (20) metathesis-like processes using alkenylsilicon compounds [34]; (21) use of ROMP for preparation of separation

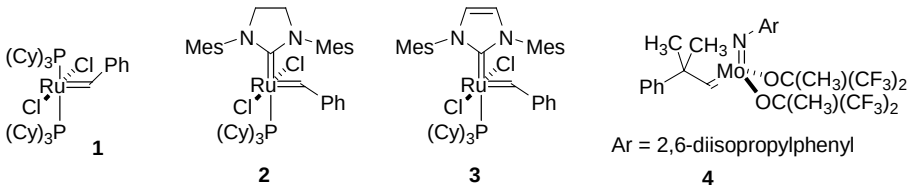
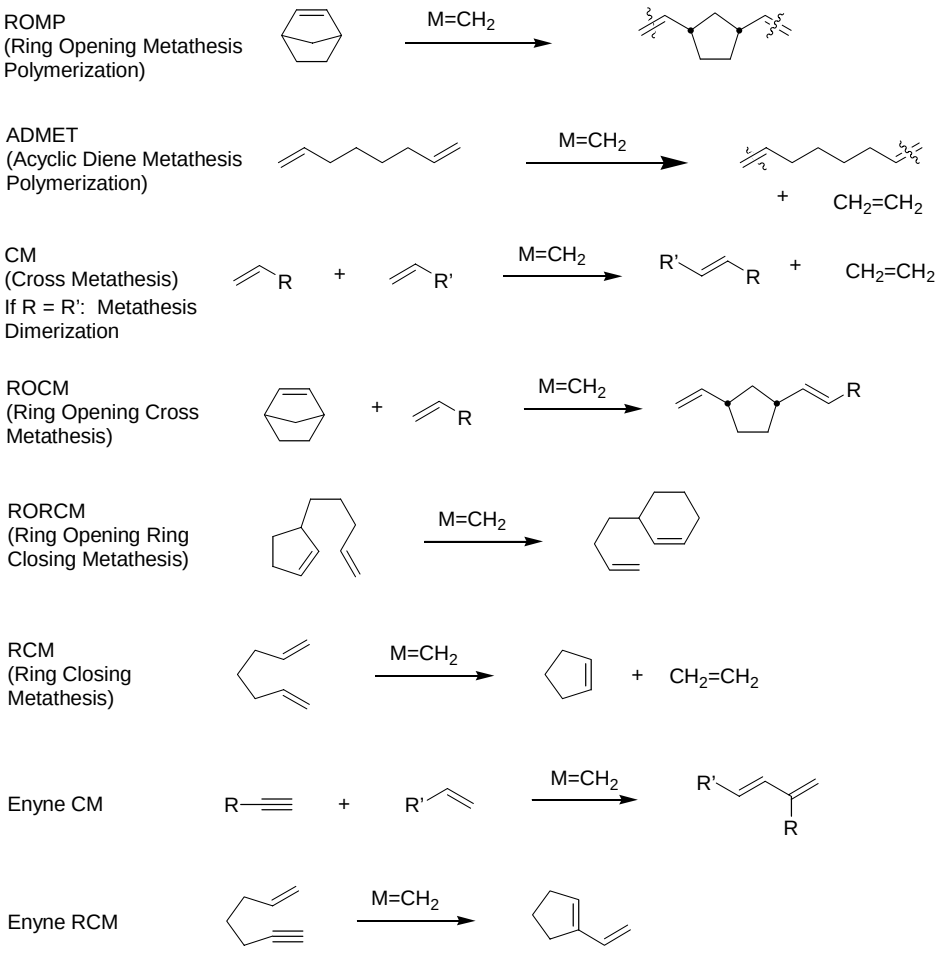


Fig. 1. Structures of alkene metathesis catalysts **1**–**4**.

media [35]; (22) applications of metathesis in oleochemistry [36]; (23) preparation of new materials through ROMP [37]; (24) synthesis of new materials based on ROMP and radical-based processes [38]; (25) dπ–pπ interactions in transition metal polymerization catalysts [39]; and (26) theoretical studies of molybdenum-based alkene metathesis catalysts [40]. Several comments about the current state of the art in alkene metathesis initiated by well-defined catalysts appeared in 2002 [41–43]. Several review articles report on organic synthesis of various compound classes, often through olefin metathesis. Specific compound classes represented include: (1) cyclic amino acids [44], (2) saturated oxygen heterocycles [45], (3) marine toxins [46], (4) sucrose derivatives [47], (5) homoallylamines [48], (6) catenanes [49], and (7) benzannulated heterocycles [50]. A review of polymerization catalysts features a section on metathesis [51]. Additional aspects of carbene complex chemistry have been reviewed in 2002, including: (1) high oxidation state multiple carbon–metal bonds [52]; (2) titanium alkylidenation reagents [53]; (3) use of Fischer carbene complexes for heterocycle synthesis [54]; (4) reaction of phosphaalkenes toward carbene complexes [55]; (5) the physical organic chemistry of Fischer carbene complexes [56]; (6) tungsten–pentacarbonyl-catalyzed construction of carbocyclic frameworks [57]; (7) metal–calixarene carbene complexes [58]; (8) ruthenium and osmium porphyrin carbene complexes [59]; (9) half sandwich group VIII metal carbene complexes [60]; (10) iridium-containing cumulenes



Scheme 1.

[61]; and (11) reactions of palladium–carbene and carbyne complexes [62]. Although not specifically focusing on metal–carbene complexes, some review articles place a heavy emphasis on this subject. Subjects reviewed in this category include: (1) stoichiometric use of transition metal complexes in organic synthesis [63]; (2) the chemistry of λ3-2*H*-azaphosphirene metal complexes [64]; (3) metal–ligand multiple bond chemistry [65]; (4) catalytic cyclopropanation [66]; (5) polymer-supported ligands and metal complexes useful for catalysis [67,68]; (6) biological applications of organometallics, which includes some discussion on carbene complexes [69]; (7) carbon–metal σ-bonded species for the groups titanium and manganese [70]; and (8) carbon–metal σ-bonded species for the groups iron, cobalt, and nickel [71].

2.2. Alkene metathesis

Alkene metathesis was the most common reaction process reported for metal–carbene complexes in 2002, and this special section is devoted to papers that focus on this process. Many examples of both polymerization [mostly ring opening metathesis polymerization (ROMP)] reactions and small-molecule syntheses appeared. Only metathesis reactions initiated by a discreet transition metal–carbene complex or metathesis reactions that discuss the carbene complex intermediates of this reaction have been included here. Distinct modes of alkene metathesis are depicted in Scheme 1.

2.2.1. General studies of alkene metathesis catalysts

Numerous attempts to develop new catalysts for alkene metathesis were reported in 2002; some representative examples are depicted in Fig. 2. Several derivatives of the Grubbs and Schrock catalysts were synthesized and tested in their ability to undergo either ROMP or RCM processes, including: (1) analogs of the Grubbs and Nolan catalysts that feature internal coordination to an ester carbonyl group (e.g. **5**) [72]; (2) new chiral analogs of the Schrock catalyst that feature partially hydrogenated binaphthyl ligands (e.g. **6**) [73]; (3) various tungsten- and molybdenum analogs of the Schrock catalyst [74]; (4) a chelating ruthenium–dicarbene complex (e.g. **7**) that provides cyclic polymers in ROMP of cyclooctene [75]; (5) heteroatom-substituted analogs of the Grubbs catalyst [76]; (6) a ruthenium-based asymmetric olefin metathesis catalyst (**8**) [77]; (7) a ruthenium-hydride vinylidene complex and the isomeric ruthenium ethylidene complex [78]; (**8**) a phosphine-free ruthenium–carbene complex featuring a chelating salicylimide ligand (**9**) [79–81]; (9) ruthenium–carbene complexes that feature a chelating 2-hydroxymethylenepyridine ligand [82]; (10) simple ruthenium complexes that contain an *N*-heterocyclic carbene ligand as the only carbene ligand [83]; (11) chelating *o*-isopropoxyarylcarbene–ruthenium complexes (e.g. **10**) [84–87]; (12) cationic ruthenium allenylidene complexes [88]; (13) a highly active ruthenium–carbene complex (**11**) containing 3-bromopyridine ligands [89]; (14) bimetallic titanocene-containing cationic ruthenium allenylidene

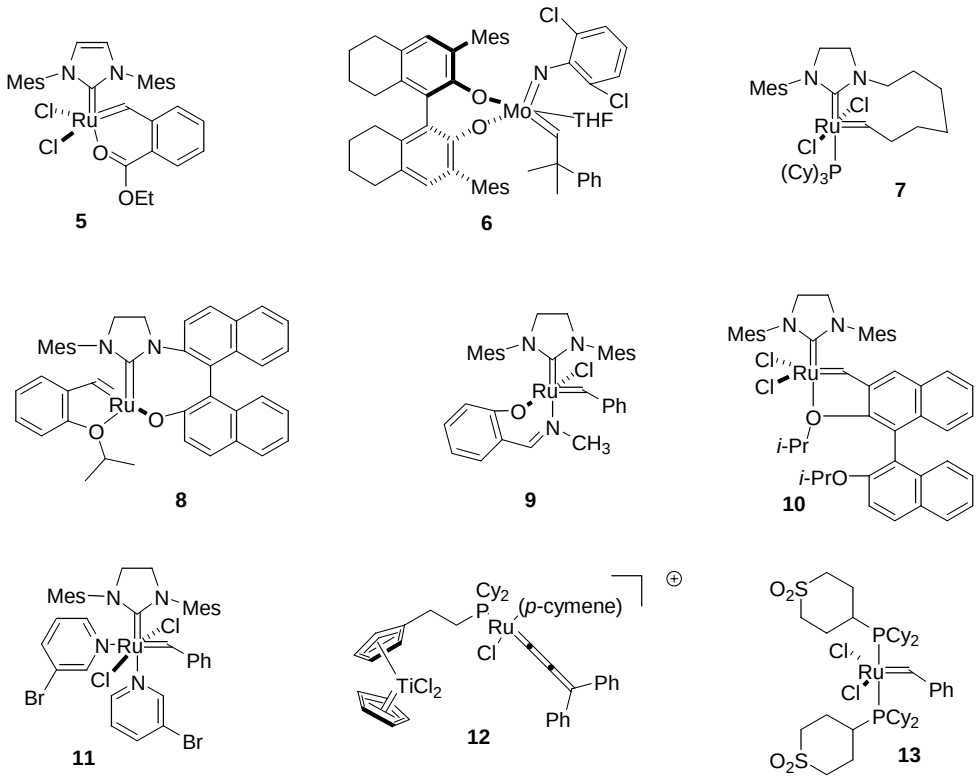


Fig. 2. Representative examples of new catalysts for alkene metathesis.

complexes (e.g. **12**) [90,91]; (15) a more polar analog of Grubbs catalyst I featuring sulfone-containing phosphine ligands (**13**) [92]; (16) a recyclable polymer-bound phosphine-free ruthenium–carbene complex [93]; (17) metathesis catalysts that have been microencapsulated in polystyrene [94]; (18) silica-bound analogs of Grubbs catalyst II [95]; (16) a polymer-bound chiral molybdenum carbene catalyst [96]; (19) a polymer-supported ruthenium vinylidene complex [97]; (20) polymer-bound recoverable and recyclable ruthenium catalysts [98,99]; (21) a dendritic polycarbene–ruthenium complex [100]; (22) rhenium–organogermanium systems [101]; (23) ruthenium(III) chloride–alkyne systems [102]; (24) in situ-generated tungsten–carbene complexes [103,104]; (25) a noncarbene-containing indenylruthenium complex [105]; (26) a trimethylsilylmethyl molybdenum halide complex [106]; (27) a ferrocenylcarbene analog of Grubbs catalyst I [107]; and (28) ruthenium–carbenes bound to cadmium selenide nanoparticles [108]. Several patents were issued for the synthesis and development of metal–carbene containing olefin metathesis catalysts [109–122]. An improved synthetic route to the Nolan olefin metathesis catalyst was reported [123]. A patent was issued for an alternative synthesis of Grubbs catalyst I and numerous other carbene complexes [124].

Other general studies of alkene metathesis where carbene complexes were discussed include: (1) comparison of turnover numbers for various ruthenium–carbene complex alkene metathesis catalysts [125]; (2) comparison of the rate and efficiency of alkene metathesis using Grubbs catalyst I versus tungsten halide/tetraalkyltin based catalysts [126]; (3) RCM in aqueous solvent [127]; (4) deactivation of metathesis catalysts through formation of chloro-bridged dimmers [128]; and (5) an attempt to rationalized previously-documented effects from RCM in supercritical CO_2 by studying the inter- versus intramolecular interactions in similar alkene substrates that contain fluorophore substituents [129].

Several theoretical studies of alkene metathesis appeared in 2002. A theoretical study of alkene metathesis by ruthenium–carbene complexes was reported [130]. The high rotational barrier for bis(phosphine) complexes was suggested as an important factor in the superior reactivity of Grubbs catalyst II versus Grubbs catalyst I. Another study of alkene metathesis using ruthenium–carbene complexes was reported using DFT [131]. These calculations suggest that the dissociative mechanism is favored over the associative mechanism for the reaction of ethylene with various complexes of general structure $LL'Cl_2Ru{=}CH_2$ [L and L′ are PH_3, PR_3, or :C(NHCH=CHNH)]. The relative energies of the reactive intermediates are affected by the electron-donating ability of phosphine ligands, for example in $(PMe_3)_2Cl_2Ru{=}CH_2$, where phosphine dissociation is suppressed and alkene insertion is facilitated relative to the analogous PH_3 complex. An additional study of the mechanism of alkene metathesis was reported using DFT [132]. Catalysts featuring either two phosphine ligands, one phosphine and one heterocyclic carbene ligand, or cis chelating phosphines were examined. The phosphine is more strongly bound in the *N*-heterocyclic carbene-ligated species. Ethylene coordination and insertion for the coordinatively unsaturated intermediates was also examined. In this process, metallacyclic structures represent energy minima along this segment of the reaction coordinate and are higher in energy than the corresponding carbene–alkene complexes. The major role played by the bulky mesityl substituents is to exert steric pressure on the alkylidene group. The heterocyclic carbene ligands promote alkene coordination, lower the metathesis reaction barrier, and stabilize metallacyclic intermediates, which accounts for the overall increase in activity of these catalysts. One study emphasizing metathesis at molybdenum centers using DFT was reported, with emphasis on the molybdacyclobutane intermediate [133].

2.2.2. *Polymerization reactions*

Initiation of the ring opening metathesis polymerization (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 2002 (Fig. 3). Numerous cycloalkenes have been subjected to ROMP using metal carbene complexes, including: (1) biphenyl-substituted norbornenes (e.g. **14**) [134]; (2) phosphine-substituted norbornenes [135]; (3) carbazole-substituted norbornenes (e.g. **15**) [136]; (4) norbornenedicarboxylate esters attached to enantiomerically-pure proline derivatives [137]; (5) norbornene derivatives featuring an additional alkene or chlorosilane groups [138]; (6) tetracyclic analogs of norbornene (e.g. **16**) [139]; (7) norbornenes connected to pincer-ligated phenylpalladium(II) derivatives (e.g. **17**) [140,141]; (8) norbornenes fused to the *N*-hydroxysuccinimide ring system [142]; (9) norbornenes and oxanorbornenes of general structure **18** [143]; (10) norbornenecarboxylate esters of complex fluorinated benzyl alcohol derivatives [144]; (11) polyethylene glycol-bound norbornenes [145]; (12) adenine-containing norbornene derivatives [146]; (13) norbornene derivatives featuring a thymidine ring associated with a 1,6-diamidopyridine derivative (**19**) [147]; (14) bicyclo[3.2.0]hept-6-ene [148]; (15) norbornene-fused succinimides [149]; (16) norbornenes attached to oligothiophene units (e.g. **20**) [150]; (17) 3,5-siloxane-bridged cyclopentenes (e.g. **21**) [151]; and (18) ROMP of eight-membered ring cyclic lactams (e.g. **22**) [152]. Numerous papers reported on the preparation of various copolymers and end-capped polymers through ROMP of cycloalkene derivatives, including: (1) co-ROMP of oxanorbornene-fused succinimides (e.g. **23**) with cyclooctene [153]; (2) co-ROMP of norbornene and norbornenedicarboxylate silyl esters [154]; (3) ROMP of various norbornene ester derivatives and polymer modification

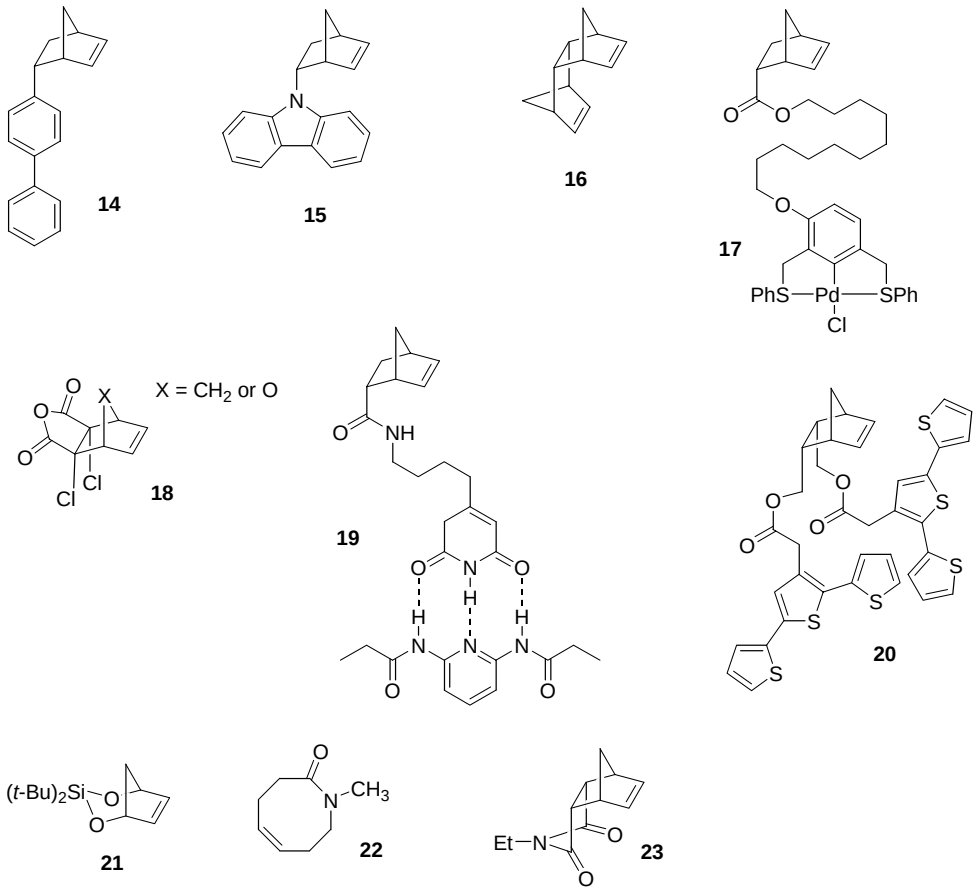


Fig. 3. Representative substrates for the ROMP reaction.

through retro-ADMET reactions of alkene-containing polymers [155]; (4) synthesis of block copolymers consisting of units prepared through ROMP of norbornene and anionic polymerization of styrene derivatives [156]; (5) ROMP of norbornenecarboxamides followed by end capping of the living polymers with enol ether quenchers [157]; (6) ROMP of norbornene using the Schrock catalyst followed by addition of 4-pyridinecarboxaldehyde to the living polymer [158]; (7) ROMP of norbornene followed by end-capping using enol ethers that contain α-haloester groups for eventual free radical polymerization [159]; (8) co-ROMP of cyclooctene with polyethylene glycol-bound cyclooctene derivatives [160]; and (9) ROMP of cyclooctene followed by end-capping of the living polymer with ethyl vinyl ether [161]. Other studies related to carbene complex-induced ROMP include: (1) ROMP of norbornenedicarboxylate esters in polar solvents [162]; (2) ROMP of norbornene in an ionic liquid [163]; (3) ROMP of carbamate and ester-substituted norbornenes as part of a method to remove excess acylating agents from organic reactions [164]; (4) ROMP of norbornene using molybdenum and tungsten catalysts [165]; (5) comparison of ROMP for endo and exo dicyclopentadiene and partially saturated analogs [166]; and (6) ROMP initiation with a vanadium catalyst [167].

Several examples using carbene complexes to initiate acyclic diene metathesis (ADMET, see Scheme 1) polymerization reactions were reported in 2002. Substrates subjected to ADMET are depicted in Fig. 4, and include: (1) phosphazine-containing dienes (e.g. **24**) [168]; (2) silicon-containing dienes (e.g. **25**) [169]; (3) co-ADMET polymerization of 1,9-decadiene and (divinyl)(tetraethoxy)disiloxane [CH_2=CHSi(OEt)$_2$OSi(OEt)$_2$CH=CH_2] [170]; and (4) co-ADMET polymerization of 1,9-decadiene and epoxy-containing monoolefins [171]. A combination ROMP-ADMET polymer was prepared by exposure of strained alkenes and bis(α,β-unsaturated carbonyl) compounds (e.g. **26**) to Grubbs catalyst I [172]. A study comparing the effectiveness of various metal alkylidenes as ADMET initiators was also reported [173].

2.2.3. Nonpolymer-forming ring opening metathesis reactions

Several examples of the tandem RORCM (see Scheme 1) reaction were reported in 2002. Representative reaction equations are presented in Scheme 2. Norbornene **28** was transformed to bicyclic compound **29** by treatment with Grubbs catalyst I [174]. A similar transformation was reported for other norbornene derivatives [175], various oxanorbornenes and oxabicyclo[3.2.1]octane derivatives

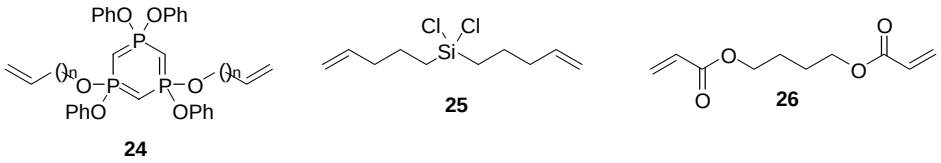
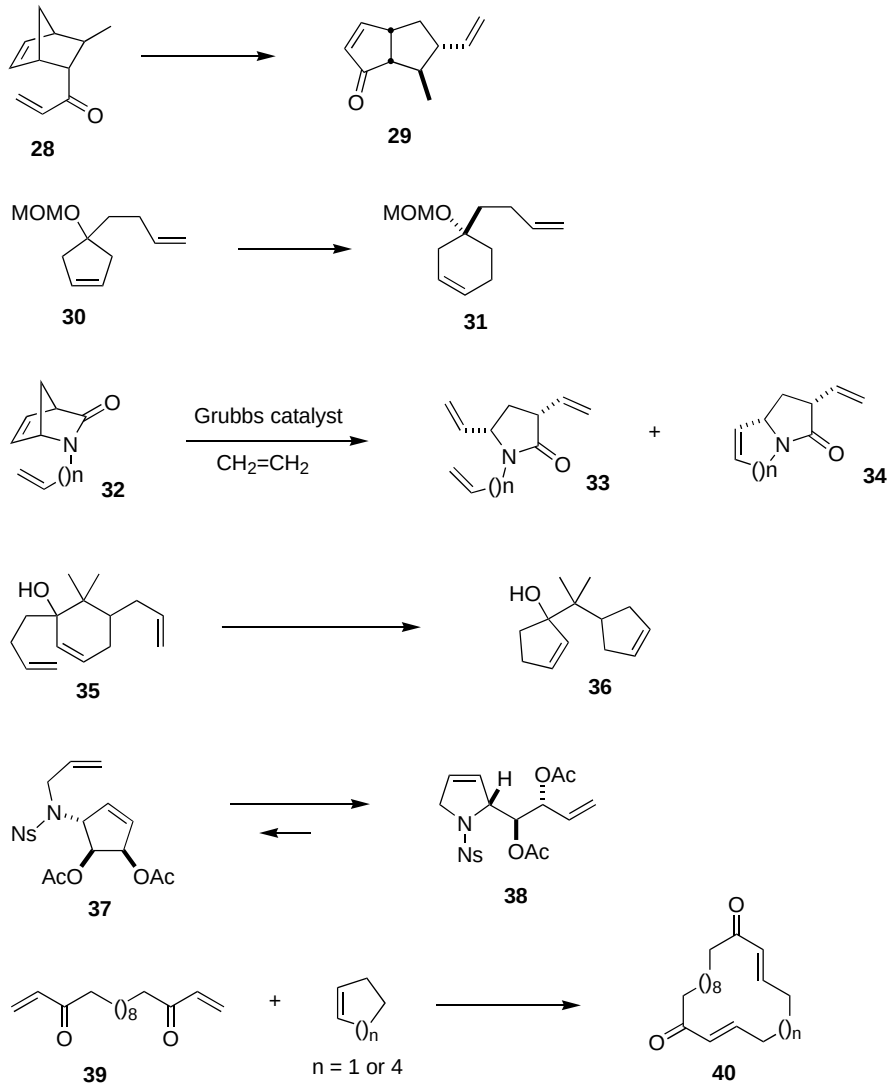


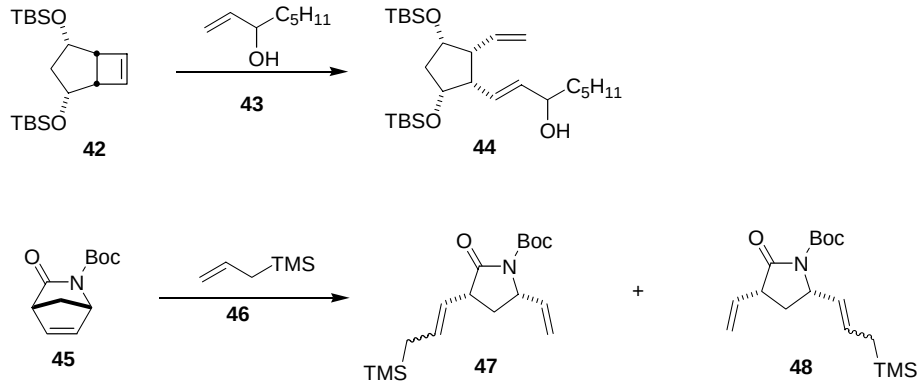
Fig. 4. Representative substrates for ADMET polymerization.

[176], and a bicyclo[2.2.2]octene derivative [177]. An asymmetric RORCM of various achiral ethers (e.g. **30**) was effected using a chiral molybdenum carbene complex catalyst [178]. RORCM was used as the key step in a total synthesis of the alkaloid swainsonine [179]. RORCM in competition with RO-CM was reported for the treatment of **32** with ruthenium–carbene complex catalysts and ethylene [180]. A double RORCM was demonstrated for cyclohexane derivative **35** [181]. An analogous process was reported for an *N*-allylcycoheptenylamine derivative [182]. A double RORCM was used as the key step in a total synthesis of the alkaloid dihydrocuscohydrine [183]. Compounds **37** and **38** were equilibrated through a RORCM using Grubbs catalyst I [184]. Intermolecular RORCM was observed in the coupling of bis(enones) (e.g. **39**) or bis(enoates) with cyclic alkenes [185]. Related products from coupling more than one cycloalkene unit were also obtained. RORCM in competition with ROMP was observed in the cometathesis of vinylsilanes and cyclooctene [186]. RO-CM was also reported for these systems.

Several examples of RO-CM (see Scheme 1) were reported in 2002. A stereodivergent synthesis of all 15-F_2 isoprostanes was developed utilizing bicyclo[3.2.0]heptane ring systems (e.g. **42**, Scheme 3) as the key step [187].



Scheme 2.



Scheme 3.

Moderately regioselective RO-CM was observed in the metathesis of alkene **45** and allyltrimethylsilane [188]. The major product was regioisomer **47**. The regioselectivity was determined after hydrogenation of the initially-obtained alkenes. Other examples of RO-CM include: (1) coupling of diazanorbornene derivatives with styrene derivatives [189]; (2) coupling of norbornene esters with allyltrimethylsilane [190]; (3) coupling of various five- and eight-membered ring cycloalkenes with α,β-unsaturated esters [191]; and (4) coupling of cyclobutene derivatives with monosubstituted alkenes [192]. A theoretical study of RO-CM of 1,5-cyclooctadiene and ethylene was reported [193].

2.2.4. Cross metathesis and metathesis-dimerization reactions

Many examples of the cross metathesis reaction (see Scheme 1) of various dissimilar alkenes (usually monosubstituted) were reported in 2002. Representative examples are depicted in Fig. 5. Specific pairs of compounds subjected to cross metathesis include: (1) alkene **49** and crotonaldehyde (**50**) for total synthesis of callipeltoside A [194]; (2) vinyl siloxanes and allylic ethers [195,196]; (3) simple alkenes (e.g. **51**) and γ,δ-unsaturated Fischer carbene complexes (e.g. **52**) [197]; (4) *O*-allyl glycosides (e.g. **53**) and vinylglycine derivatives (e.g. **54**) [198]; (5) *O*-allylic glycosides and simple monosubstituted alkenes [199]; (6) allylsilanes and enoates (followed by hydrogenation in the same pot) [200]; (7) allylsilanes and α,β-unsaturated carbonyl compounds [201]; (8) styrene and various monosubstituted alkenes [202]; (9) vinylferrocene (**55**) and styrene derivatives [203]; (10) alkylboranes (e.g. **57**) and 1,4-diacetoxy-2-butene (**58**) [204]; (11) simple alkenes and either vinylboranes or methacrolein [205]; (12) vinylboronates (e.g. **59**) and monosubstituted alkenes featuring a high degree of oxygenation (e.g. **60**) [206]; (13) chiral allylboronates and simple alkenes [207]; (14) dissimilar vinyl epoxide derivatives [208]; (15) vinyl epoxides and alkenylsilanes [209]; (16) resin-bound alkenes and *N*-hydroxysuccinnimide esters of 4-pentenoic acid [210]; (17) C-allyl glycosides and either allyl chloride [211] or alkene-containing amino acids [212]; (18) vinylcyclopentane derivative **61** with alkene-ester **62** for total synthesis of brefeldin A [213]; (19) the propargylic/allylic alcohol falcarindiol (**63**) with ethylene [214]; (20) vinylpyrrolidine derivatives and vinyl acetate esters [215]; (21) dissimilar 1,2-dialkyl-substituted alkenes for insect pheromone synthesis [216]; (22) monosubstituted alkenes and 2-methyl-2-butene in concentrated solutions of 2-methyl-2-butene [217,218]; (23) allylic phosphonate esters and simple alkenes [219]; (24) alkene-containing phosphonate esters and alkenes attached to a solid support [220]; (25) methyl vinyl ketone and alkenes containing distant leaving groups [221]; and (26) the allyl-containing immunosuppressant FK-506 and monosubstituted alkenes [222]. A comparison of the Schrock catalyst and Grubbs catalyst I in cross metathesis of vinyl aromatics with monosubstituted alkenes was also reported [223,224].

Several examples of dimerization via metathesis (see Scheme 1) were reported in 2002. Compounds subjected to metathesis dimerization are depicted in Fig. 6, and include: (1) indolocarbazole derivatives (e.g. **64**) [225]; (2) allylic ether derivatives (e.g. **65**) [226], including carbohydrates [227]; (3) *O*-allylcarbohydrate derivatives (e.g. **66**) and formation of macrocycle-bridged carbohydrates through RCM [228]; (4) gold nanoclusters [229]; and (5) polymer-supported 10-undecenoic acid derivatives [230].

2.2.5. Ring closing metathesis

The ring-closing metathesis reaction (RCM) (see Scheme 1) has emerged as a very pimportant method for organic synthesis. Many examples forming diverse ring sizes have been reported in 2002, including macrocycles and medium-size rings, as well as the traditional five- and six-membered ring-forming reactions. Reactions have been classified according to the type of ring system formed as a result of RCM.

The RCM reaction has been employed for the synthesis of a variety of carbocyclic ring systems (Fig. 7), the indicated bond was formed via the RCM reaction). Examples include: (1) synthesis of cyclopentene derivatives [231–237]; (2) formation of indenol derivatives (e.g. **68**) [238]; (3) simultaneous allylic isomerization and

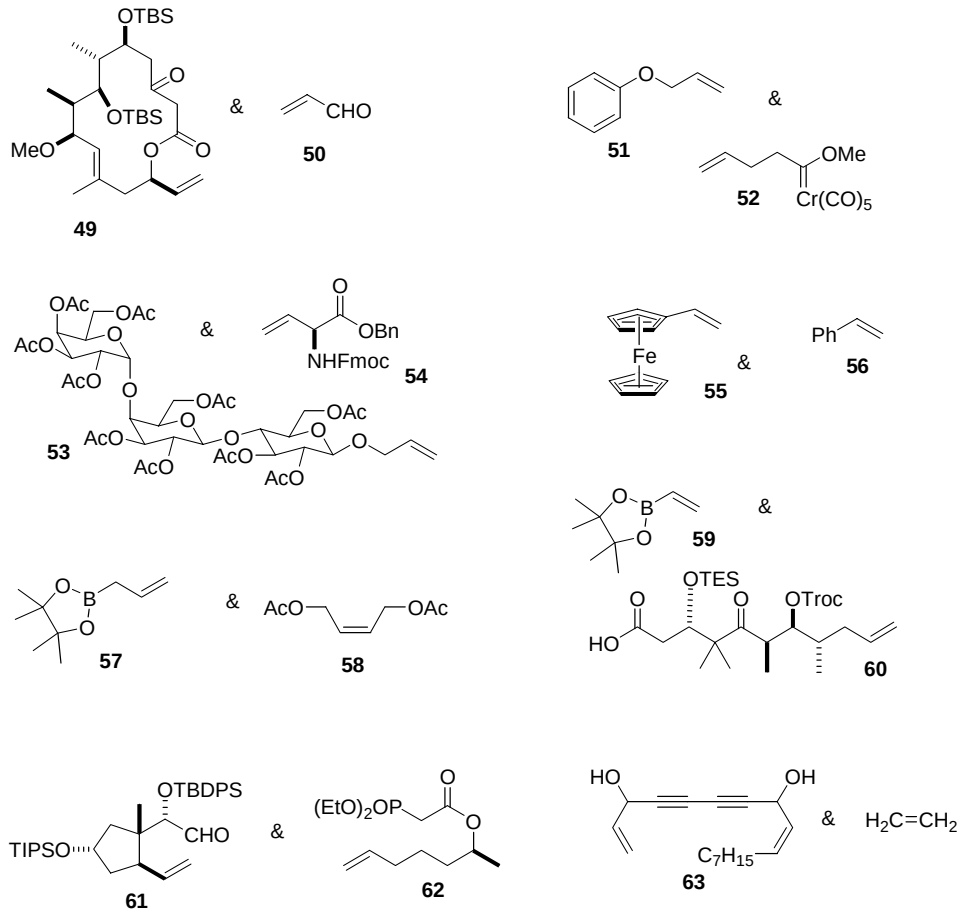


Fig. 5. Represent pairs of alkenes subjected to cross metathesis.

RCM using a mixed palladium–ruthenium system [239]; (4) use of five-membered ring forming RCM to release alkene-containing compounds from resins [240]; (5) synthesis of highly-oxygenated cyclopentene derivatives (e.g. **69**) [241,242]; (6) synthesis of aminocyclopentenes for aminoprostaglandin synthesis [243]; (7) moderately diastereoselective formation of cyclohexene derivatives from precursors featuring diastereotopic vinyl groups [244]; (5) evaluation of electronic and steric effects in the formation of cyclohexenes by RCM from precursors featuring a functionalized conjugated diene group [245]; (6) formation of six-membered rings fused to γ-butyrolactones (e.g. **70**) [246]; (7) formation of a six-membered ring carbocycle fused to a polycyclic ring system (e.g. **71**) [247,248]; (8) formation of six-membered ring allylic alcohol derivatives [249]; (9) formation of cycloalkenes spiro-fused to the pyrazine ring system [250,251]; (10) formation of six-membered ring enol ethers (e.g. **72**) [252]; (11) formation of highly oxygenated six-membered rings [253]; (12) formation of cyclic β-amino acid derivatives (e.g. **73**) [254]; (13) formation of both a cyclohexene ring (e.g. **74**) and a dihydropyran ring by RCM in the total synthesis of ricciocarpin A and B [255]; (14) formation of six-membered rings fused to norbornane at the 1- and 7-positions (e.g. **75**) [256]; (15) formation of six-membered rings fused to the indole ring system [257]; (16) formation of cycloheptene

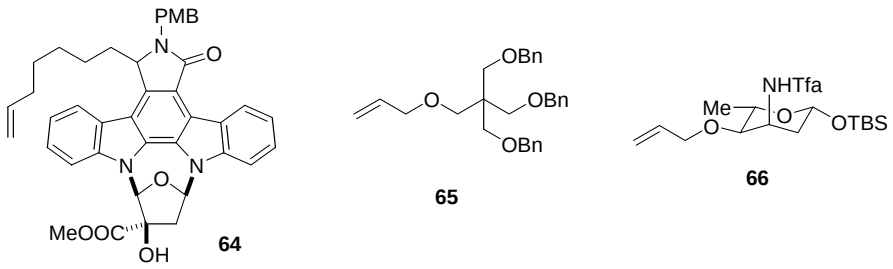


Fig. 6. Representative alkenes subjected to metathesis dimerization.

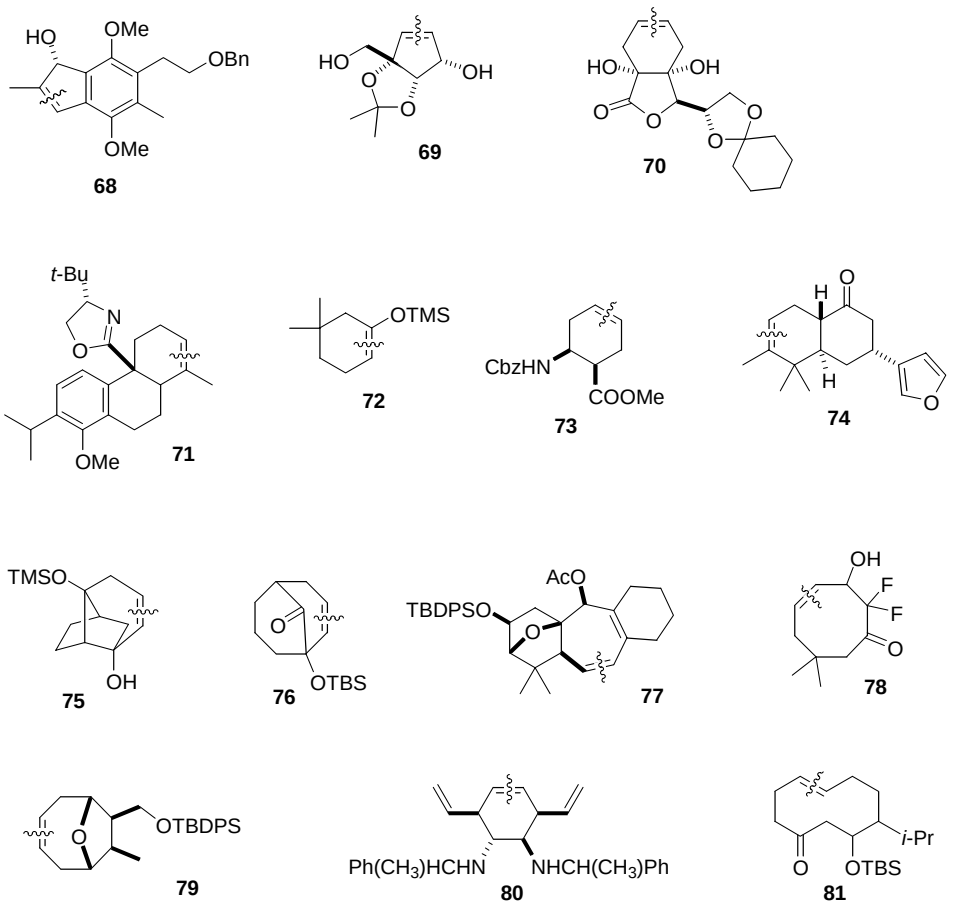


Fig. 7. Representative carbocycles produced through an RCM reaction (bond constructed through RCM indicated).

derivatives fused to other ring systems [258–260]; (17) formation of six- to seven-membered ring systems present in bicyclo[*x*.*y*.1]alkane ring systems (e.g. **76**) [261]; (18) formation of a six-membered ring for total synthesis of dysinosin A [262]; (19) synthesis of cycloheptene derivatives for liverwort diterpene syntheses [263]; (20) formation of ring-fused cycloheptenes (e.g. **77**) for synthesis of solanoecleptin A analogs [264]; (21) formation of cycloheptene derivatives for africanol total synthesis [265]; (22) formation of fluorinated cyclooctenone derivatives (e.g. **78**) [266]; (23) formation of eight-membered rings fused to other ring systems [267,268]; (24) synthesis of an oxygen-bridged eight-membered ring (**79**) for mycoepoxydiene total synthesis [269]; (25) formation of various spiro-fused bicyclic ring systems [270]; (26) diastereoselective formation of 3,6-divinylcyclohexenes (e.g. **80**) from optically pure tetravinyl diamine derivatives [271]; and (27) formation of 10-membered ring carbocycles (e.g. **81**) [272].

Numerous examples of the formation of nitrogen heterocycles using the RCM reaction (Fig. 8) were reported in 2002, including: (1) formation of five-membered ring enamines (e.g. **83**) [273]; (2) formation of indoles from a tandem alkene isomerization-RCM sequence [274]; (3) formation of dihydropyrroles in an ionic liquid [275]; (4) formation of dihydropyrroles (e.g. **84**) for synthesis of dihydroxyproline [276] and swainsonine [277]; (5) formation of cyclic amino acids [278]; (6) formation of six-membered ring cyclic lactams (e.g. **85**) for total synthesis of lentiginosine [279]; (7) formation of tetrahydropyridine derivatives [280,281]; (8) asymmetric formation of tetrahydropyridine derivatives [282]; (9) formation of tetrahydropyridine derivatives for total synthesis of aspidosperma alkaloids [283]; (10) formation of 9-azabicyclo[3.3.1]nonane derivatives (e.g. **86**) for total synthesis of adaline [284]; (11) formation of methylenedihydropyridines (e.g. **88**) via RCM of a conjugated diene with a remote alkene [285]; (12) formation of bicyclic δ-lactams (e.g. **89**) in competition with formation of *N*-cyclopentenyl-γ-lactams (e.g. **90**) in RCM of acyclic amide-tetraene derivatives [286]; (13) formation of bicyclo[*x*.3.1]-amine derivatives [287]; (14) formation of nitrogen heterocycles fused to benzoxazepine rings (e.g. **91**) [288]; (15) formation of α,β-unsaturated δ-lactams [289]; (16) formation of dihydropiperidine rings spiro fused to a cyclohexene ring (e.g. **92**) from an acyclic tetraene starting material [290]; (17) formation of nitrogen and oxygen heterocycles by RCM of divinyl-containing *O*,*N*- and *O*,*O*-ketal derivatives [291]; (18) formation of competitive ring sizes in the RCM-based synthesis of diheterocyclic (N and O)

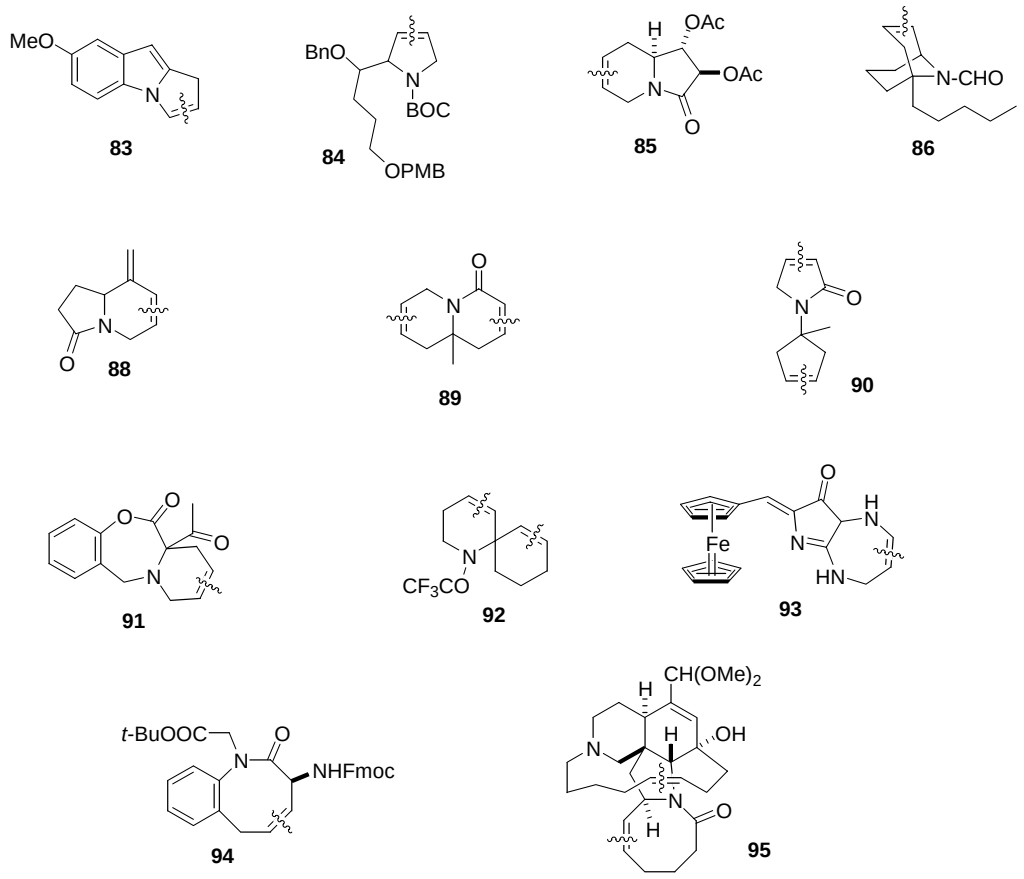


Fig. 8. Representative *N*-heterocycles produced through an RCM reaction (bond constructed through RCM indicated).

compounds fused to a benzene ring using triene derivatives [292]; (19) formation of various cyclic amines including a total synthesis of coniine [293]; (20) formation of a seven-membered ring for tuberstemonine total synthesis [294]; (21) formation of diazepines attached to a ferrocene unit (e.g. **93**) [295]; (22) formation of eight-membered ring lactam derivatives (e.g. **94**) [296]; (23) formation of nine-membered rings fused to the indole ring system [297]; (24) formation of an eight-membered ring cyclic lactam and a macrocyclic amine in separate reactions (see **95**) for the total synthesis of manzamine A [298]; (25) formation eight-membered ring diamine derivatives [299]; and (26) formation of medium-ring cyclic amino acid derivatives [300].

Many examples of oxygen heterocycle synthesis using the RCM reaction were reported in 2002 (Fig. 9), including: (1) synthesis of five-membered ring oxygen heterocycles (e.g. **97**) for nucleoside synthesis [301]; (2) synthesis of 2,5-dihydrofurans [302]; (3) synthesis of an α,β-unsaturated five-membered ring lactone for acaterin total synthesis [303]; (4) synthesis of six-membered ring oxygen heterocycles [304]; (5) synthesis of six-membered ring oxygen heterocycles (e.g. **98**) for total synthesis of cascospongiolide B [305]; (6) synthesis of six-membered ring oxygen heterocycles (e.g. **99**) for laulimalide total synthesis [306–310]; (7) formation of six-membered ring oxacycles fused to a ribonucleoside ring (e.g. **100**) [311]; (8) formation of six-membered ring lactones for fostriecin total synthesis [312,313]; (9) diastereoselective formation of bicyclic six-membered ring containing oxygen heterocycles (e.g. **101**) [314,315]; (10) formation of six-membered ring α,β-unsaturated lactones [316–320]; (11) formation of six-membered ring α,β-unsaturated lactones for total synthesis of methynolide [321], goniodiol (see **102**) [322], and osmundalatone [323]; (12) formation of β,γ-unsaturated six-membered ring lactones [324]; (13) formation of six-membered ring cyclic ethers for total synthesis of ambruticin [325]; (14) tandem alkene-isomerization and RCM to form various cyclic enol ethers (e.g. **103**) from the corresponding acyclic allylic ethers (e.g. **104**) using Grubbs catalyst II pretreated with hydrogen [326]; (15) asymmetric formation of oxygen heterocycles using a chiral molybdenum carbene complex catalyst [327]; (16) formation of six- to nine-membered ring oxygen heterocycles for total synthesis of ciguatoxin and related compounds (e.g. **105**, **106**) [328–338]; (17) synthesis of various α,β-unsaturated oxacyclic ketone derivatives [339]; (18) synthesis of various oxacycles fused to aromatic rings (e.g. **107**) [340–344]; (19) synthesis of eight-membered ring cyclic lactones (e.g. **108**) [345]; (20) competitive formation of carbocycles and oxacycles in the double RCM of various dioxygen-containing

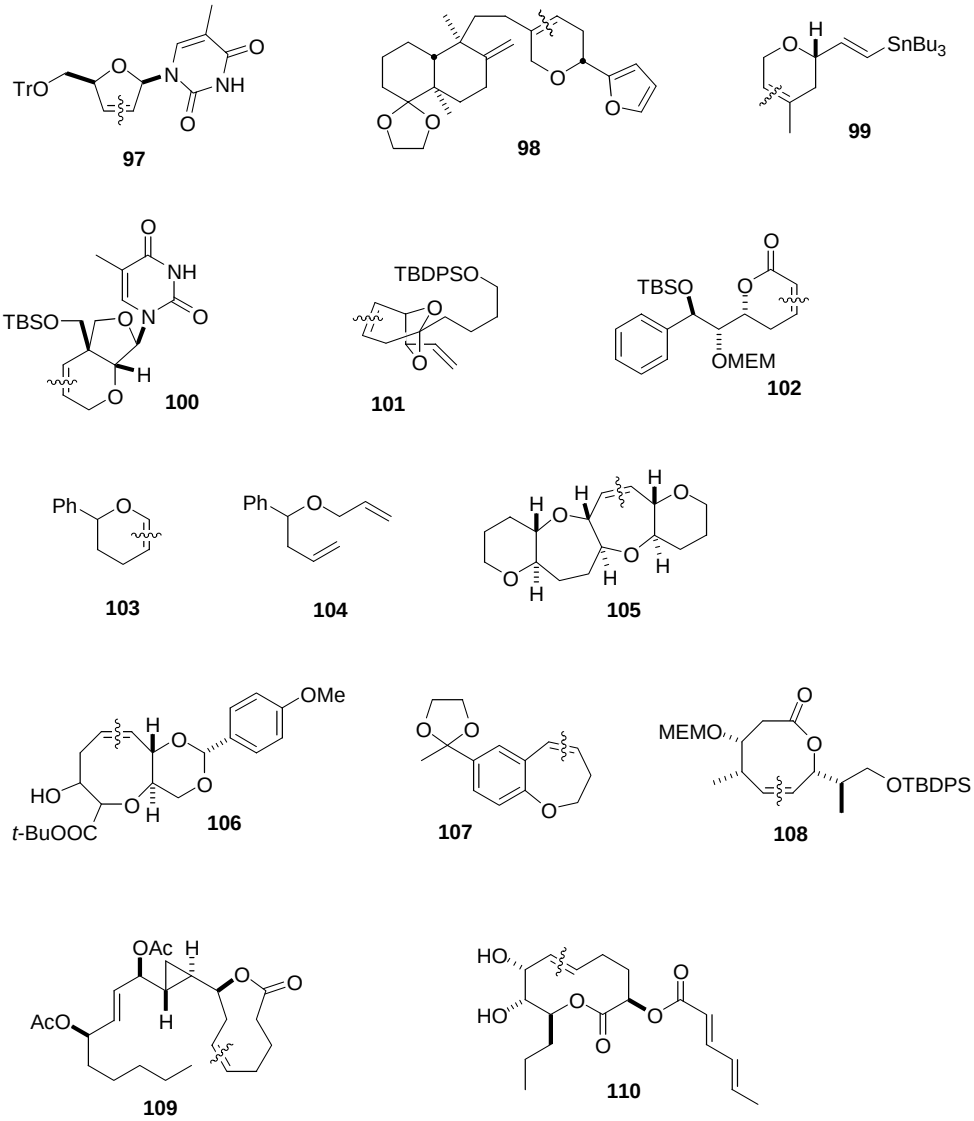


Fig. 9. Representative oxygen-heterocycles produced through an RCM reaction (bond constructed through RCM indicated).

tetraenes [346]; (21) synthesis of a nine-membered ring lactone (e.g. **109**) for halicholactone total synthesis [347]; (22) synthesis of a 10-membered ring lactone for total synthesis of ascidiatrienolide A [348]; (23) synthesis of a 10-membered ring lactone (e.g. **110**) for pinoldoxin total synthesis [349]; and (24) synthesis of 10-membered ring lactones for total synthesis or herbarumin and pioldoxin, and control of alkene geometry through choice of metathesis catalyst [350];

Other heterocyclic compounds were also constructed via the RCM reaction (Fig. 10). Examples include: (1) synthesis of metallacyclic sterically-shielded dirhenium complexes through alkene metathesis of polyalkyne-bridged complex (e.g. **112**) [351]; (2) formation of bridging zirconacene derivatives (e.g. **113**) through RCM of 5-hexenylzirconacenes [352]; (3) synthesis of bridged ferrocenes; this reaction proceeds with a high degree of kinetic resolution [353]; (4) synthesis of an encased all-carbon ligand through RCM of an octatetrayne-bridged platinum complex featuring 7-octen-1-ylphosphine ligands [354]; (5) synthesis of cyclic siloxanes through RCM of vinyl siloxanes [355]; (6) synthesis of cyclic siloxanes (e.g. **114**) for attenol total synthesis [356]; (7) synthesis of carbohydrate-containing cyclic siloxanes [357]; (8) preparation of cyclic phosphonate esters [358]; (9) preparation of cyclic sulfonamides (e.g. 115) [359]; (10) synthesis of cyclic sulfones via RCM and enyne RCM [360]; (11) synthesis of cyclic sulfonamides (e.g. **115**) [361]; and (12) preparation of cyclic phosphonates [362]. Patents were issued for the synthesis of cyclic phosphamides [363] and cyclic sulfamides [364].

Numerous examples of successful macrocyclic ring closure (formation of rings with $\geq$11 atoms) using the RCM reaction were reported in 2002 (Fig. 11), including: (1) synthesis of macrocyclic lactones (e.g. **117**) for total synthesis of salicylihalamide [365,366]; (2) synthesis

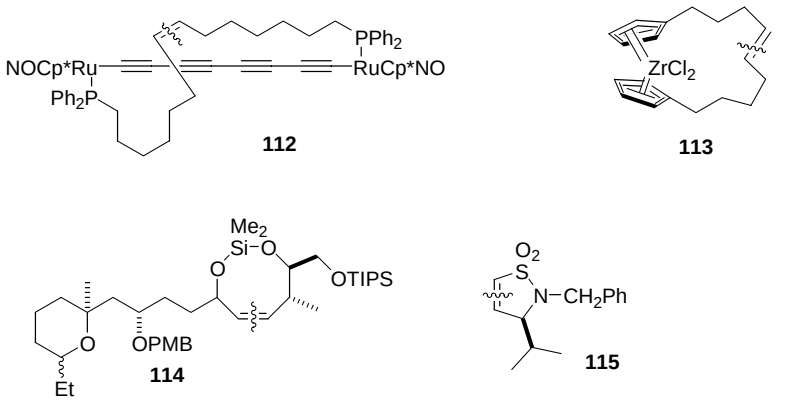


Fig. 10. Representative examples of other heterocycles prepared via the RCM reaction (bond constructed through RCM indicated).

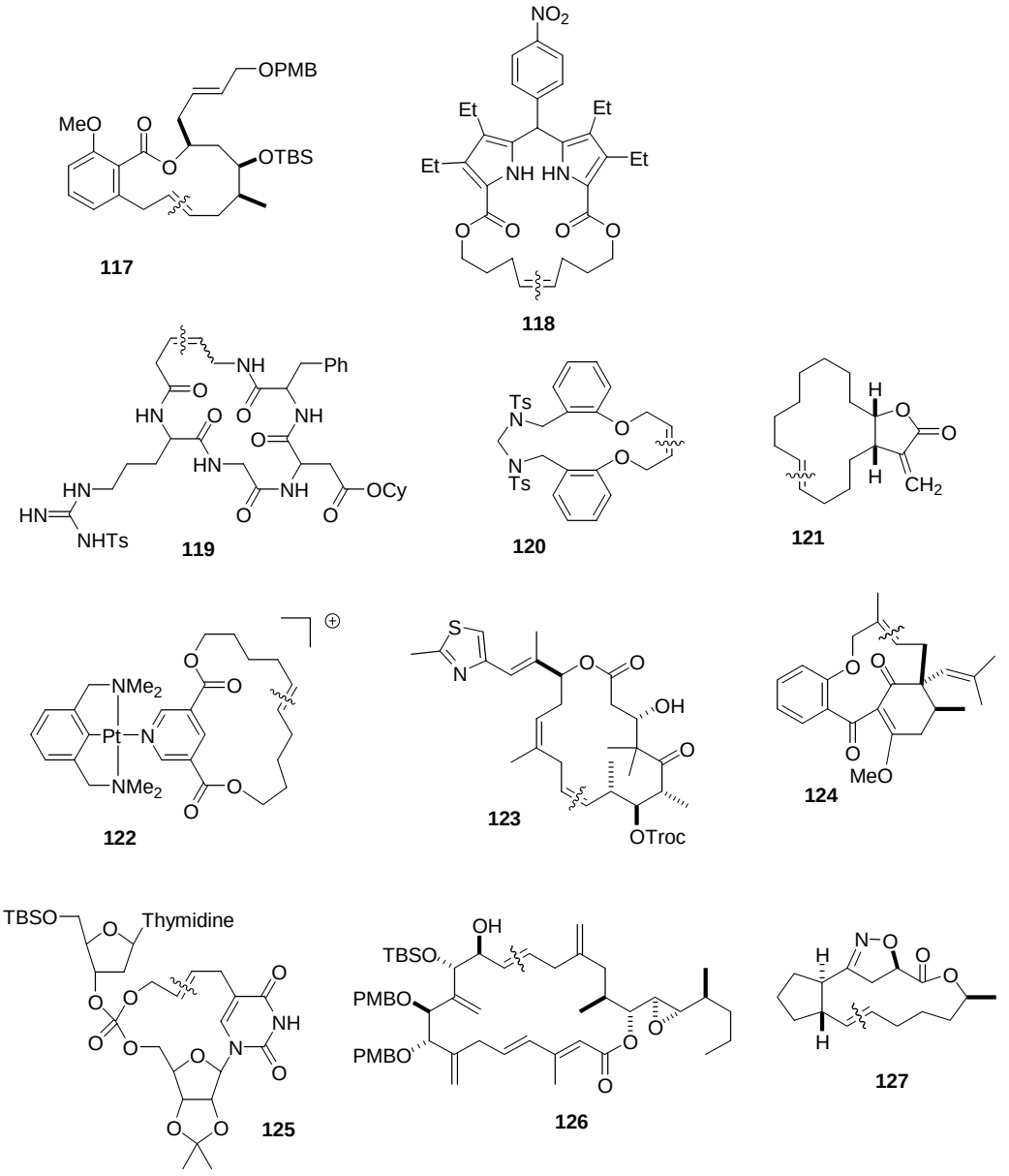


Fig. 11. Representative macrocycles (ring size >10) prepared using the RCM reaction (bond constructed through RCM indicated).

of macrocyclic diesters, esters, and carbocycles featuring ester substituents [367]; (3) formation of macrocyclic lactones [368]; (4) formation of macrocycle-bridged dipyrroles (e.g. **118**) [369]; (5) formation of macrocyclic peptide analogs (e.g. **119**) [370–380]; (6) formation of macrocyclic diazacyclic-diethers (e.g. **120**) [381–383]; (7) formation of macrocyclic lactone-acylamides [384]; (8) formation of macrocyclic carbocyclic rings fused to γ-lactones (e.g. **121**) and the effect of lactone stereochemistry on the macrocyclic RCM [385]; (9) synthesis of macrocyclic diesters of 3,5-pyridinedicarboxylic acid (e.g. **122**) while the pyridine nitrogen is complexed to either palladium or platinum [386]; (10) formation of macrocyclic rings (e.g. **123**) for total synthesis of epothilone and structural analogs [387–390]; (11) formation of a macrocycle-bridged tetrasaccharide derivative [391]; (12) formation of an 11-membered ring (**124**) through RCM of a disubstituted alkene and a trisubstituted alkene [392]; (13) formation of a macrocyclic lactone for amphidinolide T4 total synthesis [393]; (14) establishment of a tethering chain between a phosphate ester and the base of a nucleoside derivative (see e.g. **125**) [394,395]; (15) synthesis of macrocyclic sulfonimine derivatives [396]; (16) synthesis of a macrocyclic lactone from a heptaene derivative (e.g. **126**) [397]; (17) formation of a macrocyclic lactone (e.g. **127** for brefeldin A total synthesis [398]; (18) synthesis of diester-bridged macrocycles [399]; (19) synthesis of chiral diamide-bridged macrocycles [400]; (20) formation of trimeric double-rossette assemblies [401]; (21) synthesis of macrocycle-bridged taxol analogs [402]; (22) cyclization of a polytetrahydrofuran derivative [403]; (23) crosslinking of cored dendrimers [404]; (24) formation of dimeric cyclodextrins by metathesis dimerization followed by macrocyclic RCM [405]; (25) formation of macrocyclic ketones for muscone total synthesis [406]; (26) formation of macrocyclic urethanes [407]; and (27) formation of macrocyclic bis(lactones) [408].

2.2.6. *Alkene metathesis involving alkyne components*

Several examples of the synthesis of conjugated dienes through the intramolecular (enyne RCM) and intermolecular (enyne CM) metathesis of enynes (see Scheme 1) were reported in 2002. Examples of intermolecular enyne metathesis reactions (Fig. 12) include: (1) formation of

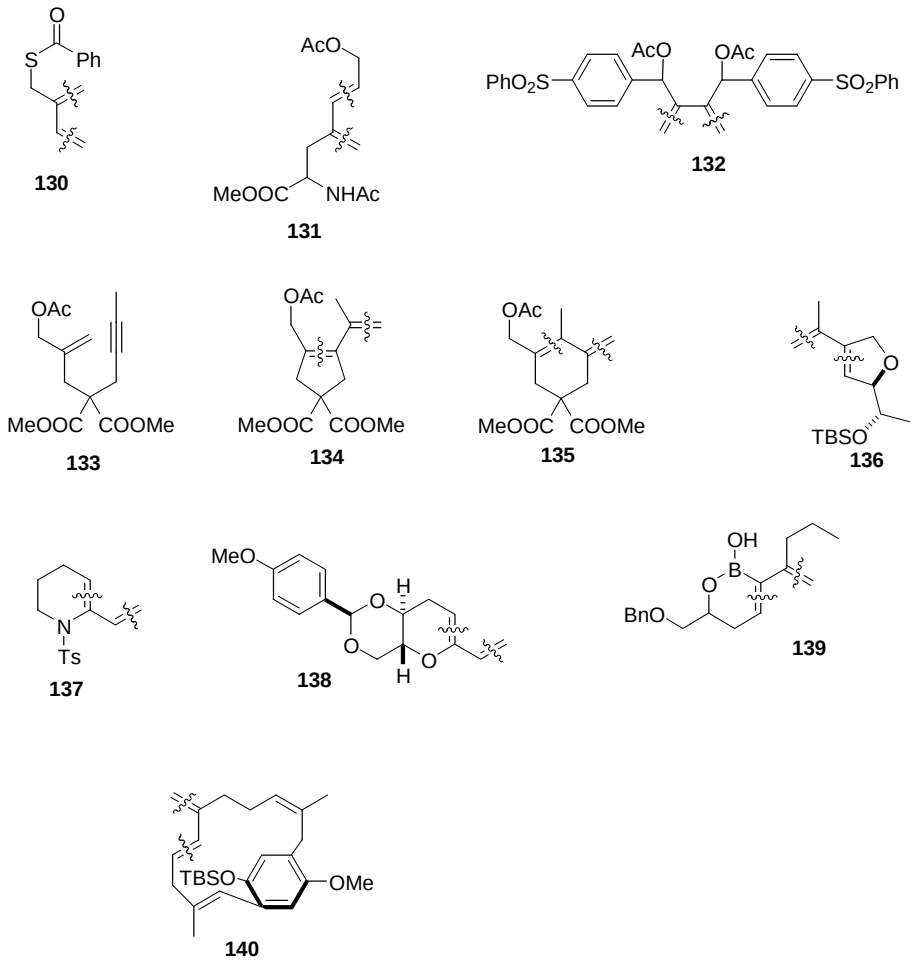


Fig. 12. Representative conjugated dienes prepared using an enyne metathesis reaction (bonds constructed through RCM indicated).

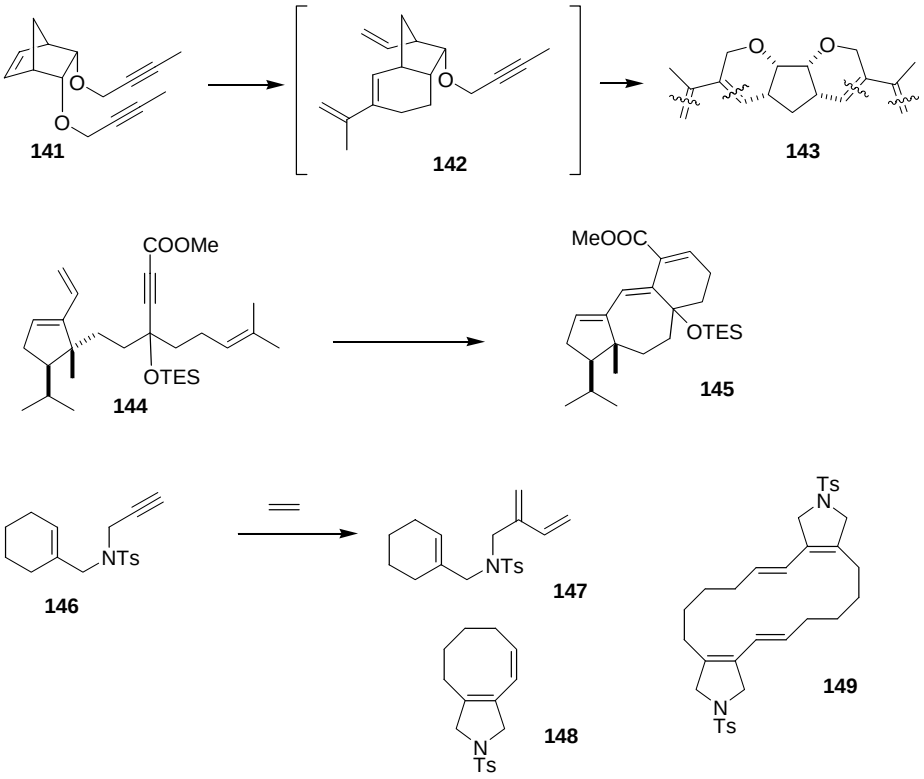
2-(thiomethyl)butadienes (e.g. **130**) through enyne CM of *S*-propargyl thioesters and ethylene [409]; (2) formation of 2-acetoxymethylbutadiene derivatives through enyne CM of propargylic esters and ethylene [410]; (3) formation of diene-amino acid derivatives (e.g. **131**) through enyne CM of ethynylamino acids and allyl acetate [411]; and (4) formation of diene **132** through enyne CM of a 1,4-diacetoxy-2-alkyne derivative and ethylene [412]. Examples of intramolecular enyne metathesis include: (1) competitive five- versus six-membered ring formation (e.g. formation of **135** versus **134** from **133**) in intramolecular enyne metathesis [413]; (2) formation of cyclic ethers (e.g. **136**) via intramolecular enyne metathesis [414]; (3) formation of cyclic enamides (e.g. **137**) via intramolecular enyne metathesis using an ynamide [415]; (4) formation of cyclic ethers present in ciguatoxin and related compounds (e.g. **138**) [416]; (5) in situ formation of a homoallyloxy(alkynyl)borane followed by intramolecular enyne metathesis resulting in cyclic vinylboronates (e.g. **139**) [417]; (6) atropoisomer selective formation of the p-cyclophane-conjugated diene (**140**) for total synthesis of longithorone [418]; (7) formation of six-membered rings fused to the indole ring system [419]; (8) formation of highly oxygenated vinylcyclohexene derivatives [420]; (9) formation of cyclic siloxanes [421]; and (10) comparison of intramolecular enyne metathesis for propargylic alcohols and propargylic ethers [422].

Some more complex examples of enyne metathesis are depicted in Scheme 4. Tricyclic compounds (e.g. **143**) were obtained through double enyne RCM using bis(propargyloxy)norbornene derivatives (e.g. **141**) [423]. Competitive RO-RCM and enyne RCM was observed for analogs of **141** featuring longer alkyne tethers [424]. Other examples of double enyne-RCM include: (1) construction of the tricyclic compound **145** [425]; and (2) preparation of bicyclic amides [426]. Intermolecular enyne metathesis was observed from the room temperature reaction of compound **146** with Grubbs catalyst II in the presence of ethylene [427]. Extended reflux time led to a mixture of intramolecular enyne metathesis product **147** and the corresponding metathesis dimerization product of **147**, tetraene **148**.

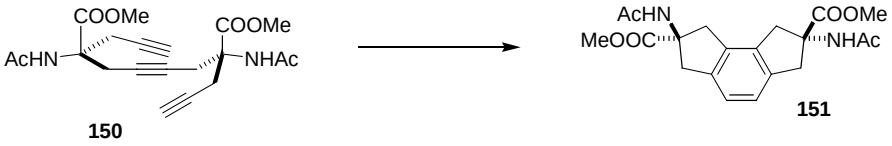
Grubbs catalyst I was an effective alkyne trimerization catalyst. Trialkyne derivative **150** (Scheme 5) was transformed into aromatic compound **151** upon treatment with Grubbs catalyst. [428]. This catalyst was similarly effective in catalyzing intermolecular alkyne trimerization using a propargyloxyglycoside derivative [429].

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

Several processes unrelated to metathesis were also initiated by ruthenium–carbene complex catalysts **1–4** and structurally-related carbene complexes (Scheme 6). Several examples employing ruthenium–carbene complexes to initiate various free-radical reactions were reported in 2002 examples include: (1) initiation of the Kharasch reaction [430] and atom transfer polymerization [431] using carbene complex **9**; and (2) free radical polymerization of acrylate



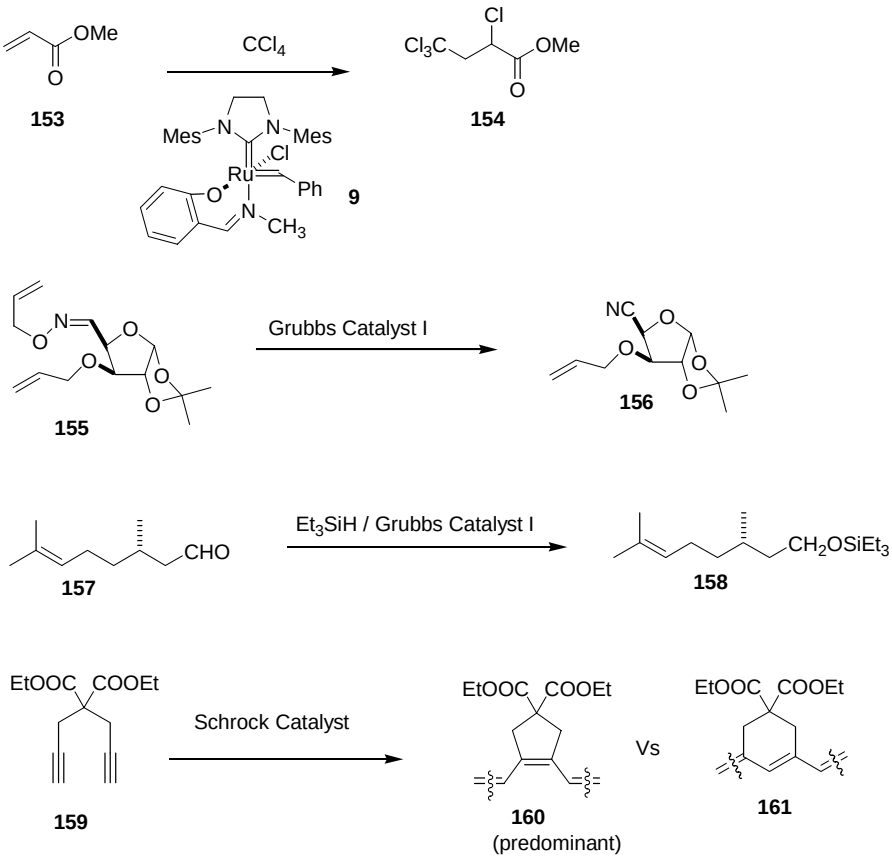
Scheme 4.



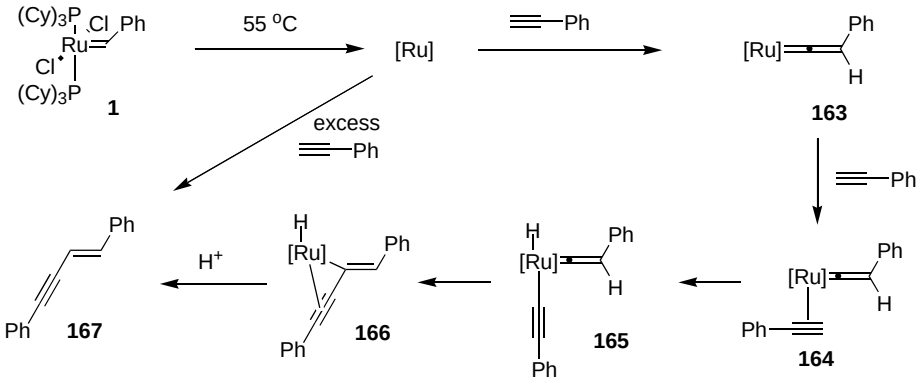
Scheme 5.

esters or vinyl acetate using Grubbs catalyst I or analogs where tricyclohexylphosphine ligands have been replaced by *N*-heterocyclic carbene ligands [432]. Grubbs catalyst II was effective for the isomerization of allylic ethers to enol ethers and of allylic sulfonamides to *N*-sulfonyl enamides [433]. Alkene isomerization is often an unwanted side reaction in alkene metathesis using the Nolan catalyst, however this process can be minimized using the right combination of solvent and temperature [434]. Treatment of *O*-allyl oxime **155** with Grubbs catalyst I led to the nitrile **156** [435]. A similar reaction occurred upon treatment of the simple oxime with Grubbs catalyst I. Catalysis of the hydrosilylation of aldehydes (e.g. conversion of **157** to **158**) or silylation of alcohols by silicon hydrides using Grubbs catalyst I was reported [436]. Use of the Schrock catalyst to initiate alkyne polymerization/cyclization of a dipropargylmalonate derivative (**159**) was reported [437,438]. The cyclization process afforded exclusively the five-membered ring-containing polymer **160** and not the six-membered ring analog **161**.

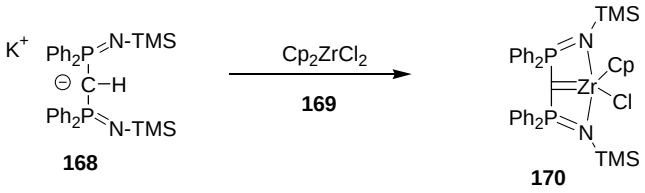
Thermal decomposition of Grubbs catalyst I followed by treatment with two moles of phenylacetylene leads to the vinylidene–ruthenium complex **163** (Scheme 7) [439]. Complex **163** could not be isolated in pure formed but NMR studies support the assignment as a vinylidene complex. The vinylidene complex was a moderately effective catalyst for the RCM of diethyl diallylmalonate. Reaction of the vinylidene complex with additional phenylacetylene led to the enyne **167** in low yield, however the yield was considerable higher when acetic acid was added. The mechanism for formation of **167** involves formation of π-alkyne complex **164** followed by conversion to the alkynyl complex **165**, which undergoes insertion to afford the enynyl complex 166. Protonation affords enyne **167**. Acetic acid accelerates the process through protonation of the enynyl ligand. The Grubbs catalyst I decomposition product ([Ru]) also



Scheme 6.



Scheme 7.



Scheme 8.

catalyzed the addition of carboxylic acids to terminal alkynes [440].

2.3. Individual carbene or alkylidene complexes classified according to metal

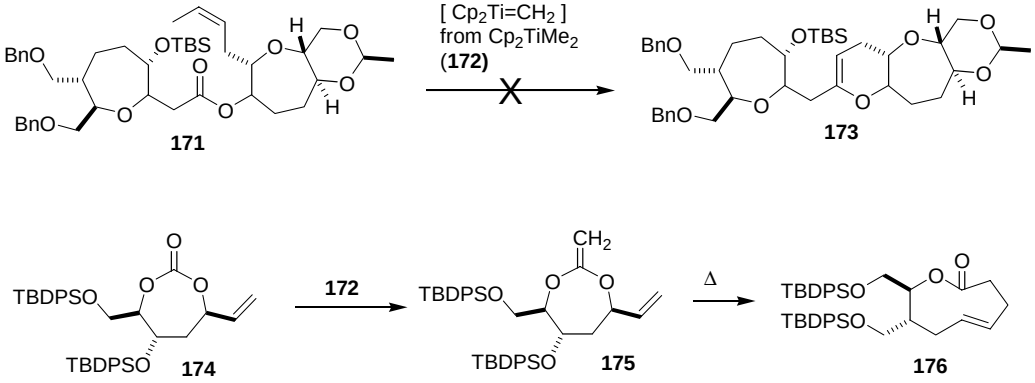
2.3.1. Group IV metal–carbene complexes

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

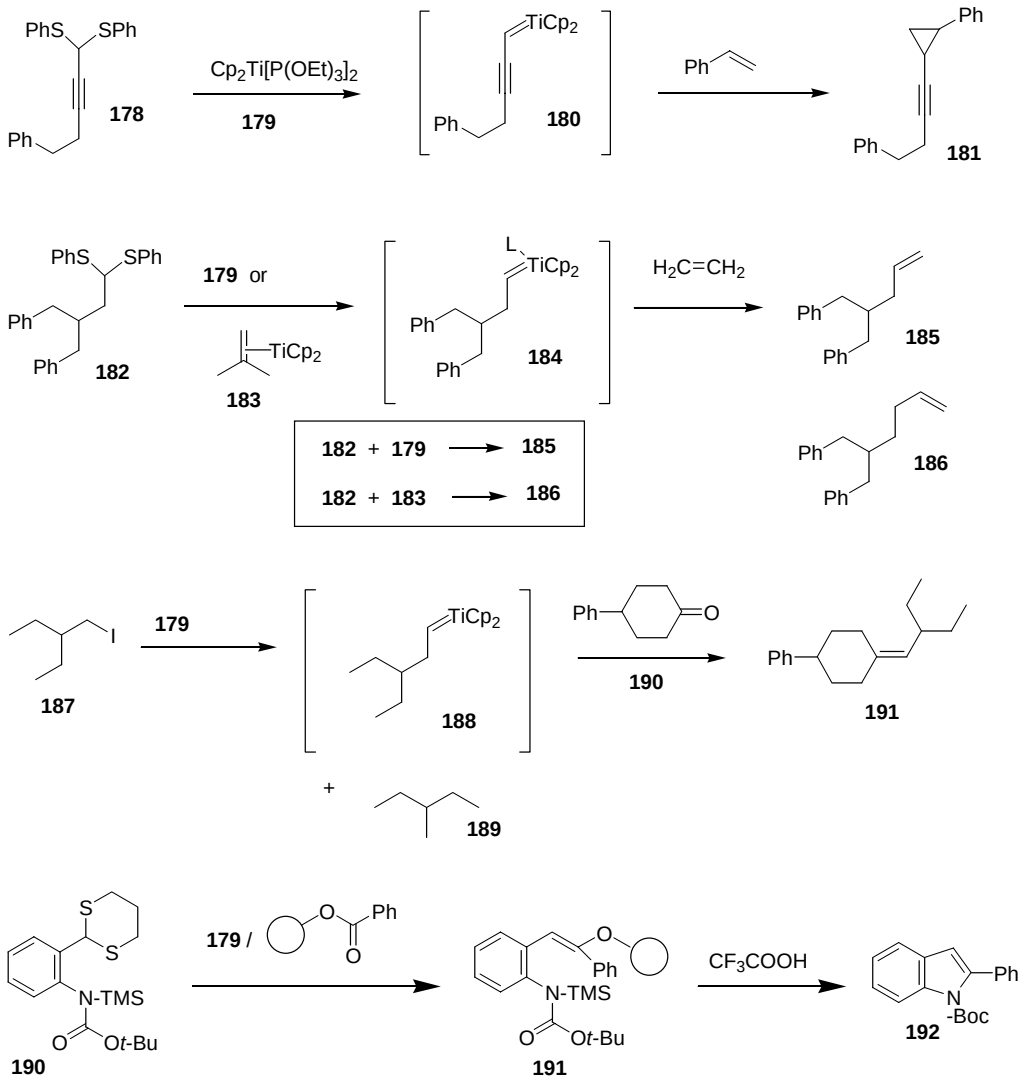
Zirconium-pincer carbene complexes (e.g. **170**, Scheme 8) were prepared by treatment of zirconacene dichloride with anionic pincer ligand **168** [441]. Displacement of chloride by **168** followed by extrusion of cyclopentadiene was proposed. Patents were awarded for the use of titanium pincer carbene complexes as precursors to alkene polymerization catalysts [442,443].

Tandem carbonyl olefination-RCM (e.g. conversion of **171** to **173**, Scheme 9) is a commonly employed method for closure of six-membered ring cyclic ethers present in ciguatoxin and related compounds. Failure of this process was noted for substrate **171** [444]. In another effort to synthesize this class of compounds, tandem carbonyl olefination of **174** followed by Claisen rearrangement was used for formation of one of the nine-membered ring cyclic ethers present in these compounds [445].

Several examples of the generation of titanium alkylidene intermediates (e.g. **178**, Scheme 10) from dithioacetals (**178**) and low-valent titanium (**179**) were reported in 2002. Treatment of propargylic dithioacetal **178** with styrene and titanium complex **179** led to the alkynylcyclopropane derivative **181** [446]. Treatment of dithioacetal **182** with ethylene in the presence of various titanium(II) species was reported [447]. A metathesis product (**185**) derived from the carbene intermediate **184** was observed when titanium complex **179** was employed. Use of titanium(II)–isobutene complex **183** led to the alkene **186** by a mechanism involving [2+2]-cycloaddition from titanium–carbene intermediate **184** followed by β-hydride elimination and reductive elimination. Related titanium carbene complexes were generated from alkyl iodides that contain a sterically hindered β-carbon atom [448]. Coupling of iodide **187** (2 eq.) and ketone **190** in the presence of titanium complex **179** led



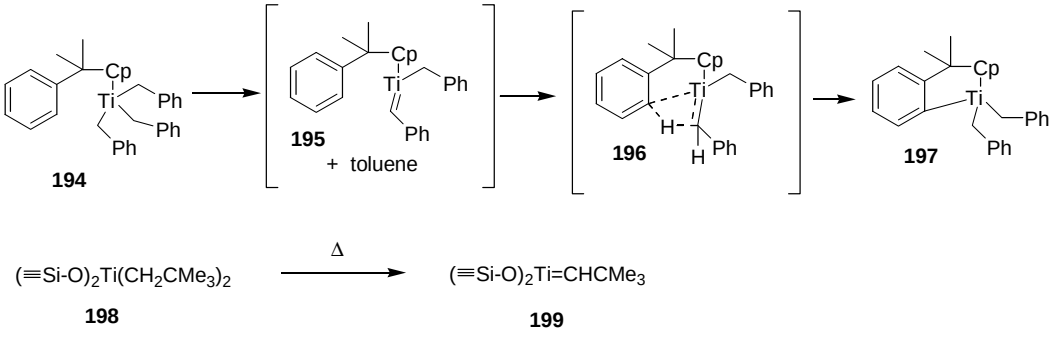
Scheme 9.



Scheme 10.

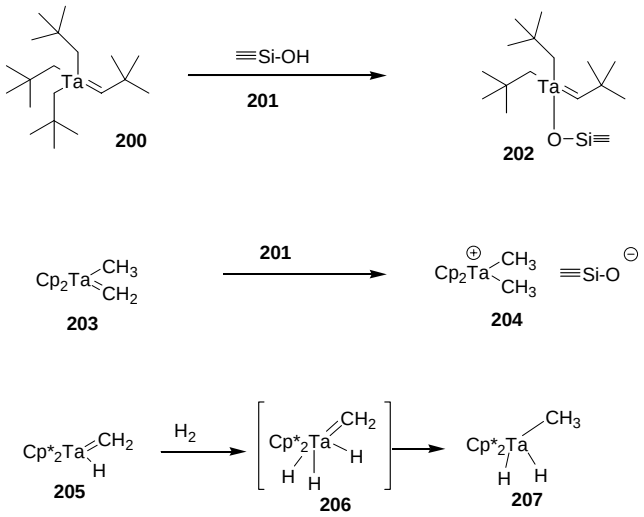
to the alkene **191** via reaction of in situ-generated carbene complex **188** with the ketone. A bulky carbon β- to the iodide was required to suppress β-hydrogen elimination processes; α-hydride elimination is required for formation of carbene complex **188**. A novel solid-phase indole synthesis (conversion of **190** to **191**) was developed using dithioacetal-generated titanium alkylidenes [449].

Titanium–carbenoid species were obtained from the reaction of $(t\text{-Bu}_3\text{PN})_2\text{TiMe}_2$ with trimethylaluminum [450]. Titanium–carbene complexes (e.g. **195**, Scheme 11) were suggested as intermediates in the intramolecular C–H



Scheme 11.

activation processes of titanium alkyls [451]. The observed kinetics and labeling were consistent with the intermediacy of benzylidene complex **195**. Silica-bound metal dialkyl-metal complexes (e.g. **198**) were prepared for titanium, vanadium, and chromium, and their thermal conversion to alkylidene complexes (e.g. **199**) was reported [452]. Thermal elimination of an alkyl group from these complexes occurs readily. A mechanism consistent with α-hydride elimination followed by reductive elimination was proposed and supported through deuterium labeling studies. Signals for the carbene carbon could not be observed by solid-state NMR. Coupling of the alkylidene complexes with acetone led to the expected carbonyl olefination products. The chromium alkylidene complex would polymerize ethylene but would not undergo a metathesis reaction with ethylene.



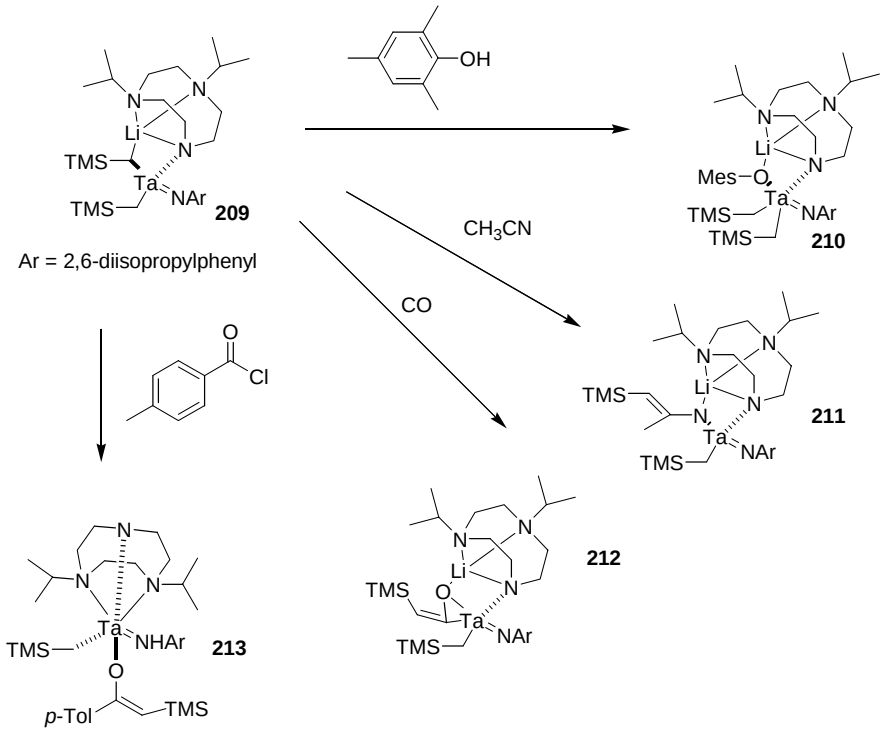
Scheme 12.

2.3.2. Group V metal–carbene complexes

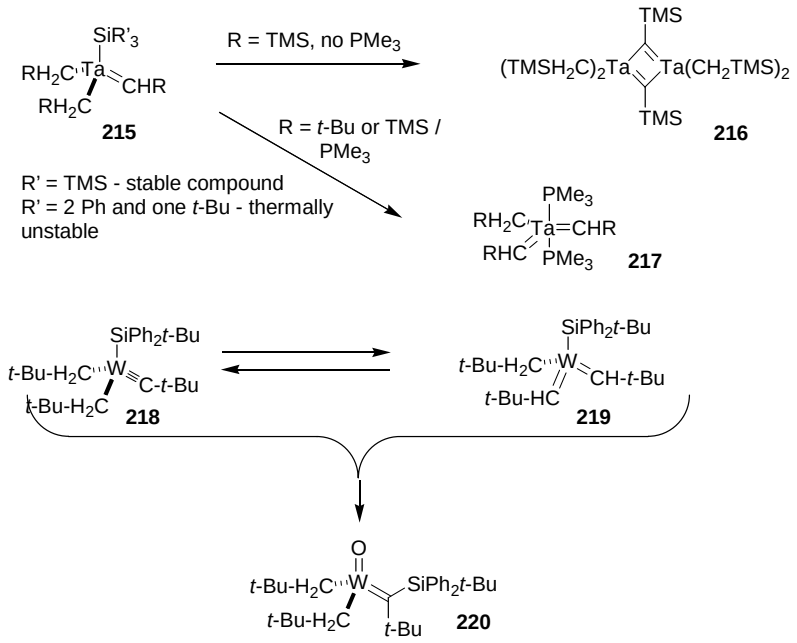
Several papers emphasizing the synthesis and reactivity of group V metal–carbene complexes appeared in 2002.

Binding of tantalum–carbene complexes to siloxane polymers was reported (Scheme 12) [453]. Only non-Cp-containing tantalum–carbene complexes (e.g. **200**) retained the carbene complex functionality upon binding to the polymer. Binding of Cp–carbene complex **203** led to cationic dimethyltantalocene (**204**). The coupling of tantalum–carbene complexes (e.g. **205**) with hydrogen was examined using parahydrogen-induced polarization and carbon-13 labeling [454]. A mechanism involving oxidative addition of dihydrogen to tantalum was favored since the polarized hydrogens are bound to tantalum.

The carbenoid complex **209** (Scheme 13) was treated with a variety of electrophiles [455]. The reactivity profile is very much like that expected for a typical Schrock carbene complex and is depicted in Scheme 13. Reaction with the acid chloride afforded the expected enolate complex **213** and reaction with CO afforded ketene complex **212**. Metalloenamine complex **211** was obtained from reaction with acetonitrile. The dialkyl complex **210** was obtained upon protonation.



Scheme 13.



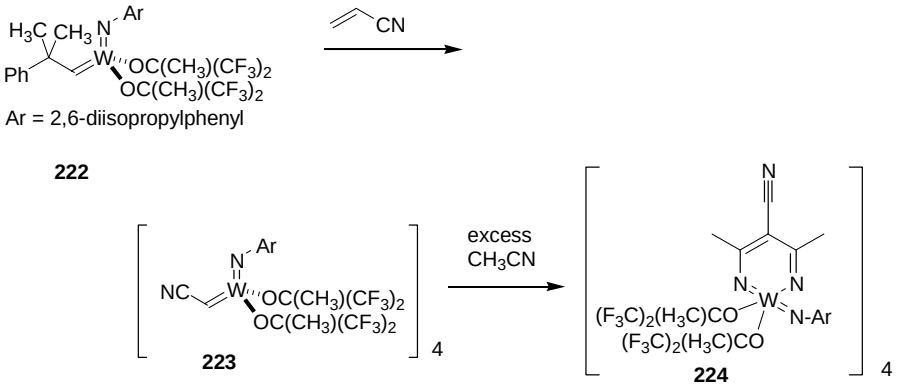
Scheme 14.

Tantalum–carbene complexes were suggested as intermediates in the formation of μ-alkylidene–ditantalum complexes from alkylation of tantalacene dichlorides [456]. A single paper reporting on the synthesis of both silylcarbene–tantalum complexes and silylcarbyne–tungsten complexes appeared in 2002 [457]. Alkylidene complexes [e.g. $(RCH_2)_3Ta(PMe_3)$=CHR and $RCH_2Ta(PMe_3)_2(=CHR)_2$] (Scheme 14) reacted with phenylsilanes [e.g. $H_2SiR'_3$ and $(PhSiH_2)_2CH_2$] to give disilyl-substituted alkylidenes $(Me_3SiCH_2)_3Ta{=}C(SiMe_3)(SiR_3)$ (e.g. **215**). The TMS_3Si derivative of **215** was stable, however the (*t*-Bu)Ph_2Si analog decomposed to the dimetallacyclobutadiene complexes (e.g. **216**). A silyl-substituted alkylidene complex (**220**) was obtained through oxidation of an equilibrium mixture of carbyne complex **218** and carbene complex **219.**

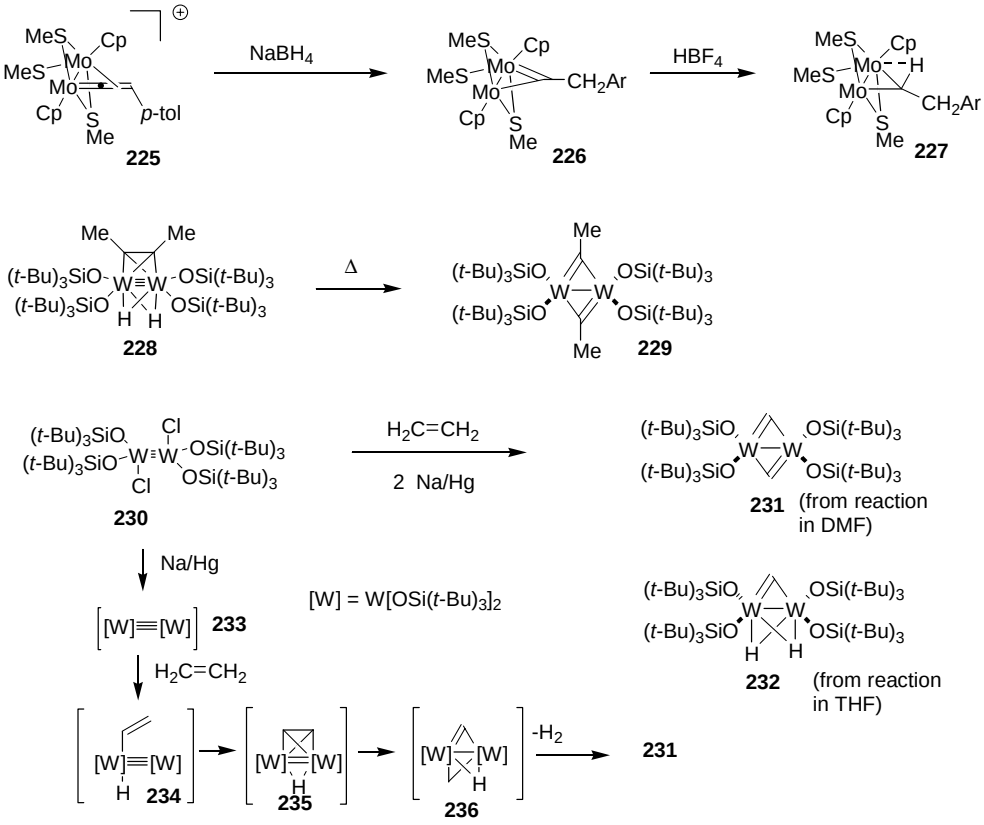
2.3.3. Group VI metal–carbene complexes (further classified according to structure and reaction type)

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

Coupling of a tungsten analog of the Schrock carbene complex (**222**, Scheme 15) with acrylonitrile was examined [458]. Coupling of **222** with acrylonitrile resulted in metathesis followed by aggregation to form cyclic tetrameric carbene complex **223**; aggregation was due to ligation of the nitrile nitrogen to the tungsten of another molecule. Reaction with acetonitrile led to the tetrameric diimine complex **224** via a net insertion of two nitriles into the metal–carbene bond. Aggregation was again due



Scheme 15.



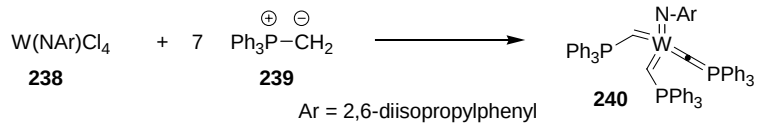
Scheme 16.

to ligation of the nitrile nitrogen to tungsten of another molecule.

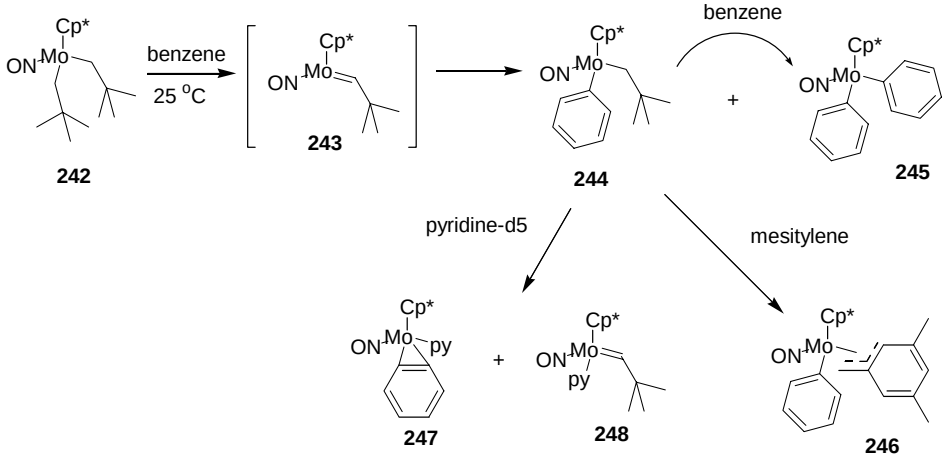
The reaction of dimolybdenum–vinylidene complex **225** (Scheme 16) with sodium borohydride was reported [459]. Reduction afforded a neutral bridging carbyne complex (**226**), which could be protonated at the carbene carbon to afford the cationic bridging carbene complex (**227**). Thermolysis of ditungsten–alkyne complex **228** led to the bridging dicarbyne complex **229** [460]. Similar complexes (e.g. **231** and **232**) could also be prepared through reduction of dichloroditungsten complex **230**. The proposed mechanism for formation of **231** from **230** involves C–H activation to form the vinyl complex **234**, followed by conversion to the bridging η^2-vinyl complex **235,** followed by conversion to the bridging carbene–carbyne hydride **236**, followed by loss of hydrogen to form **231**. A bridging chlorocarbyne–ditungsten complex was formed from the reaction of tungsten(VI) chloride with carbon tetrachloride and arsenic [461].

Multicarbene complexes of general structure **240** (Scheme 17) were produced in the coupling of excess methylenetriphenylphosphorane (**239**) with (imido)WCl_4 derivatives (**238**) [462]. The complex was reported to be sensitive to a variety of ligating substances, including CO, isocyanides, ketenes, CS_2, thiols, and chlorotrimethylsilane.

Molybdenum–carbene complexes (e.g. **243**, Scheme 18) were proposed as intermediates in C–H activation reactions of dialkylmolybdenum complex **242** [463]. Room temperature thermolysis of complex **242** in benzene resulted in both the monophenyl complex **244** and the diphenyl complex **245**. Thermal (25 °C) decomposition of complex **244** resulted in the parallel formation of either benzyne and carbene complex intermediates. A mixture of the alkylidene complex **248** and benzyne complex **247** was produced when the reaction of complex **244** with benzene was conducted in the presence of pyridine. Benzyne complex-derived C–H activation products (e.g. **244** and **245**) were obtained from thermolysis of complex **242** in either benzene or mesitylene. Related



Scheme 17.



Scheme 18.

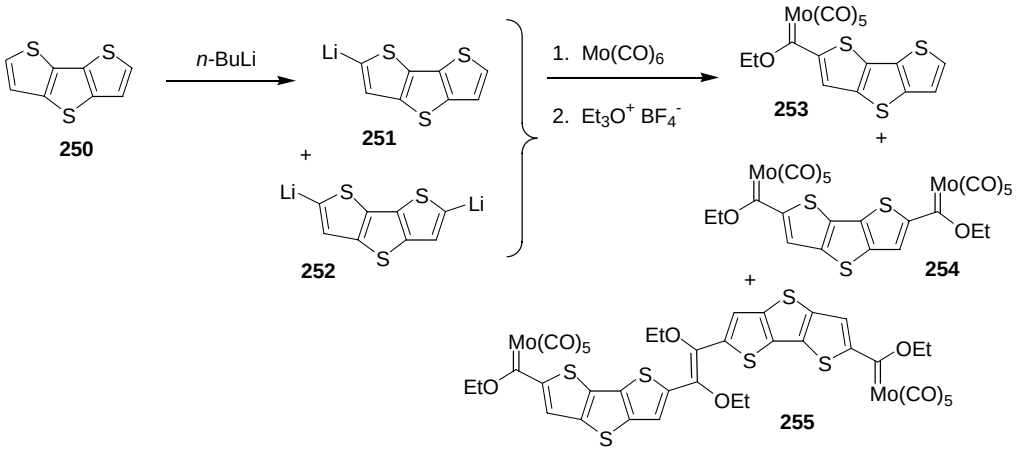
experimental [464] and theoretical [465] studies were reported for analogous tungsten systems.

A chromium(III)–carbene complex was proposed as an intermediate in the chromium-mediated cyclopropanation of styrene by dichloromethane [466].

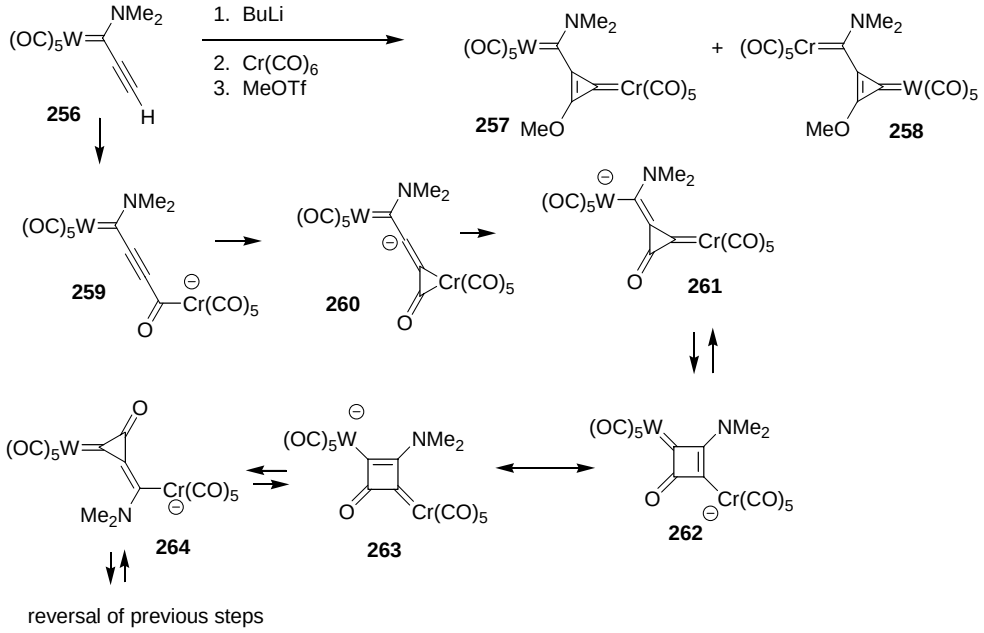
2.3.3.2. Publications focusing on synthesis or formation of Fischer carbene complexes of group VI metals. The most common procedure used for the synthesis of group VI metal–carbene complexes is the Fischer synthesis, which involves coupling of an organolithium reagent with a group VI metal carbonyl derivative, followed by alkylation of the resulting acylate. An example of the Fischer synthesis is depicted in Scheme 19, involving the formation of molybdenum–carbene complexes (e.g. **253–255**) from dithiophene and trithiophene [467]. A sequence involving lithiation of the thiophene ring followed by the Fischer synthesis was employed. The unstable dicarbene complex **254** decomposed through a carbene dimerization process to afford the dicarbene complex **255**.

A series of dicarbene complexes (e.g. **257**, **258**, Scheme 20) was prepared through deprotonation of the ethynylcarbene complex **256** followed by reaction with a group VI metal carbonyl, followed by methyl triflate [468]. When the metals are different, a mixture of the two complexes **257** and **258** were obtained. The ratio was not affected by the method of synthesis. Nucleophilic addition of the anionic metal of the acrylate to the alkyne carbon (i.e. conversion of **259** to **260**) followed by ring closure to **261** followed by ring expansion to **262** was proposed to explain the interconversion. The individual carbene complexes did not interconvert. The preference for occupying the aminocarbene site decreased in the series Mo > W > Cr. A mechanism for the interconversion is depicted in Scheme 20. The reaction using a monophosphine (PMe_3) analog of the alkynylcarbene complex leads predominantly to the product where phosphine ligation is in the aminocarbene site.

Preparation of chromium complexes of Bertrand-type carbene complexes was reported (Scheme 21) [469]. The synthetic route involves addition of the anion **265** to the



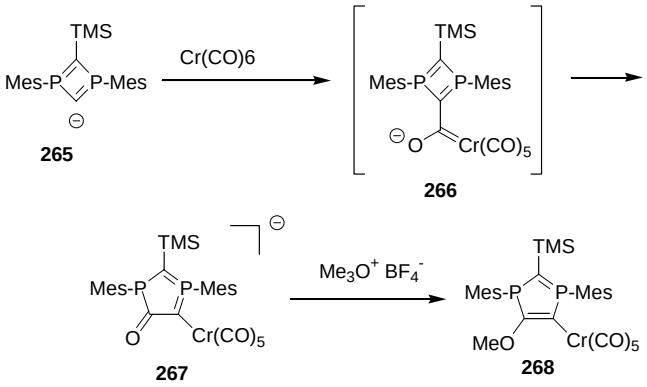
Scheme 19.



Scheme 20.

CO ligand of a metal carbonyl, followed by a ring expansion process. These anionic complexes feature longer Cr–C bonds than typical Fischer carbene complexes, however is shorter than that for diaminocarbene–chromium complexes, suggesting that some degree of π-acceptor ability might exist in these complexes. Neutral complexes (e.g. **268**) were produced through an *O*-alkylation reaction. The Cr–carbene bond length was identical for the neutral and anionic complexes.

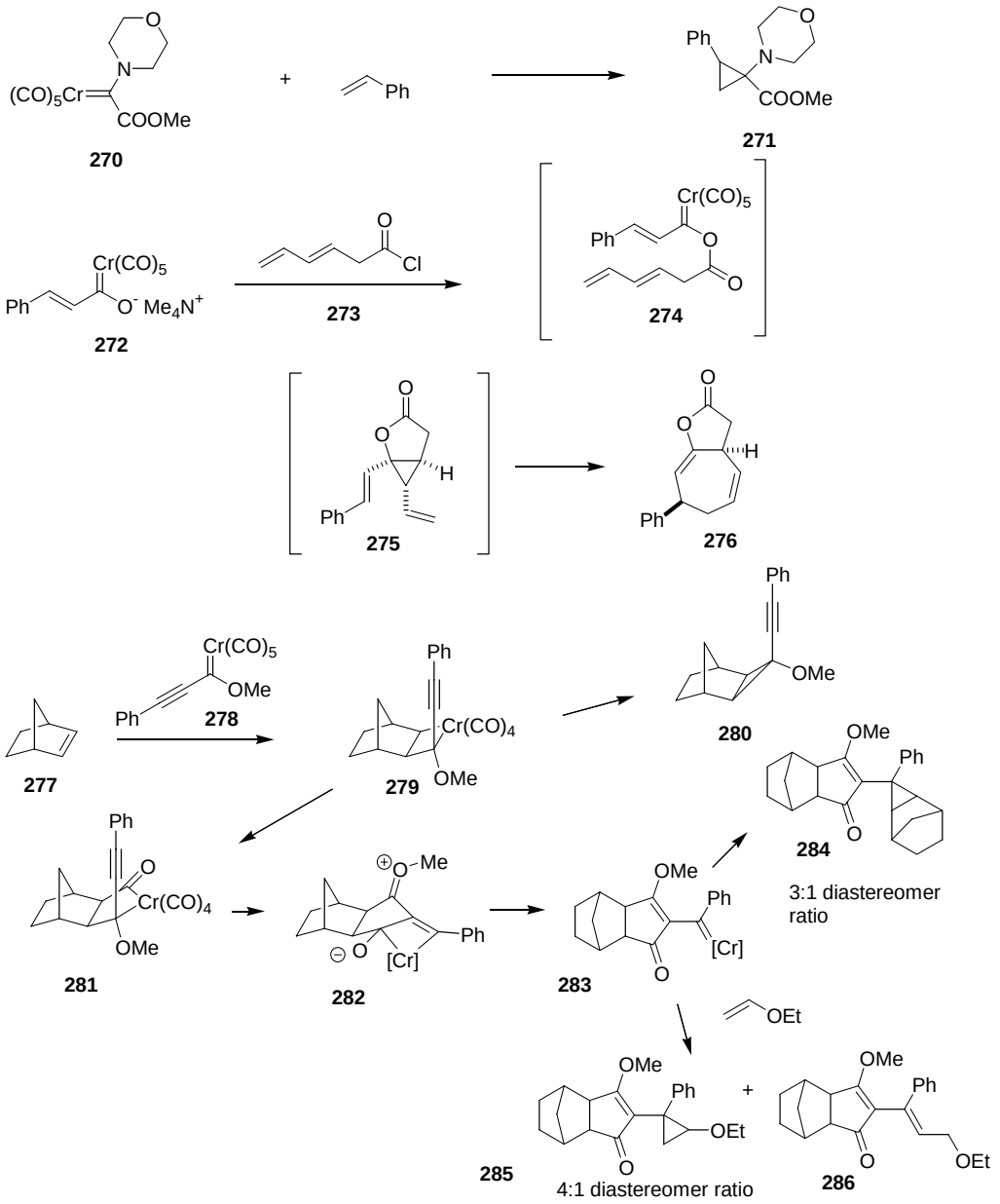
2.3.3.3. Reaction of group VI metal–carbene complexes with alkenes and dienes. This section focuses on reactions of group VI metal–carbene complexes involving coupling with alkenes at the carbene-carbon. Other examples of the coupling of carbene complexes with alkenes where the reactive site is elsewhere can be found ahead under the heading: cycloaddition reactions occurring at the C–C π-bond of α,β-unsaturated metal–carbene complexes (section 2.3.3.3.7).



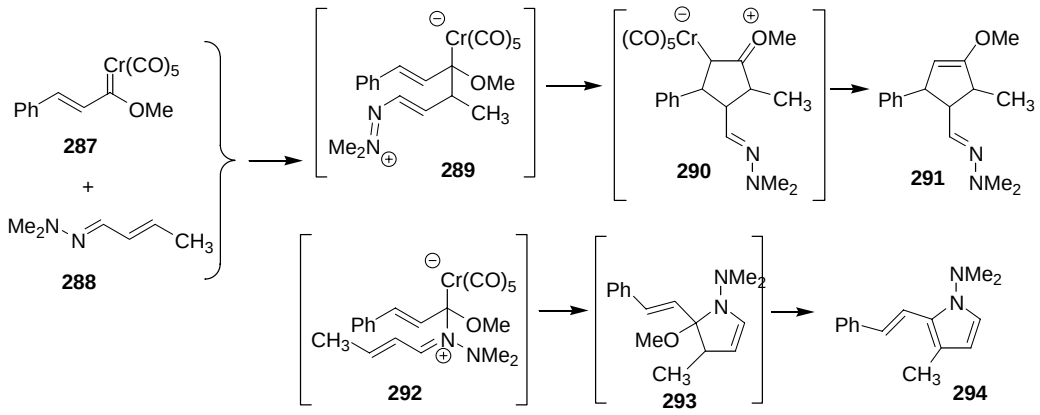
Scheme 21.

Cyclopropanation is a common reaction pathway for the coupling of Fischer carbene complexes with polarized alkenes. Successful cyclopropanation of styrene using aminocarbene complexes that feature an acyl group at the carbene carbon (e.g. **270**, Scheme 22) was reported [470]. Cyclopropanation was observed when chromium carbene acylates were treated with β,γ-unsaturated acid chlorides [471]. Formation of the acyloxycarbene complex (e.g. **274**) followed by intramolecular cyclopropanation was proposed. In the case where an α,β-unsaturated carbene acylate (e.g. **272**) couples with a diene-containing acid chloride (e.g. **273**), the initially-formed cyclopropane (e.g. **275**) underwent a Cope rearrangement to afford the seven-membered ring derivative (e.g. **276**). The coupling of alkynylcarbene–chromium complexes (e.g. **278**) with strained bicyclic alkenes (e.g. norbornene, **277**) was reported [472]. The reaction with norbornene derivatives afforded mixtures of the simple cyclopropanation product **280** and an adduct **284** incorporating CO and two moles of the norbornene. A mechanism involving [2+2]-cycloaddition, CO insertion, and simultaneous 1,3 shift of chromium and carbonyl addition led to intermediate carbene complex **283**, which couples with the starting alkene to provide adduct **284**. Carbene complex intermediate **283** can also couple with electron-rich alkenes to provide cyclopropane derivatives (e.g. **285**) and accompanied by ring-opened products (e.g. **286**).

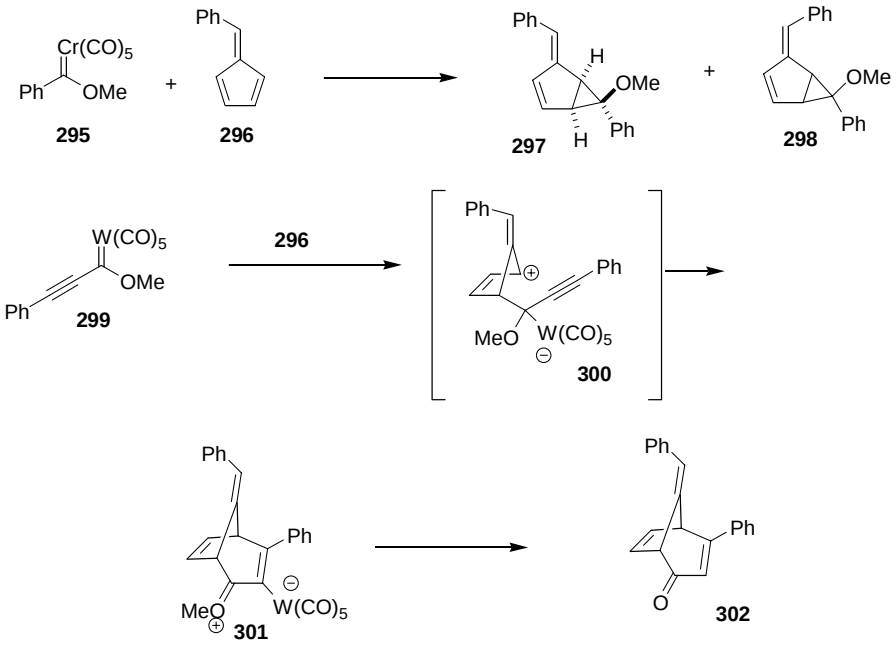
The synthesis of cyclopentenones (e.g. **291**, Scheme 23) from the coupling of α,β-unsaturated Fischer carbene complexes (e.g. **287**) and α,β-unsaturated *N*,*N*-dimethylhydrazones (e.g. **288**) was reported [473]. The pyrrole **294** was a minor product in the reaction. Moderate levels of ee were observed using the chiral alkoxycarbene complexes. Cyclopentenones were produced by nucleophilic addition of



Scheme 22.



Scheme 23.



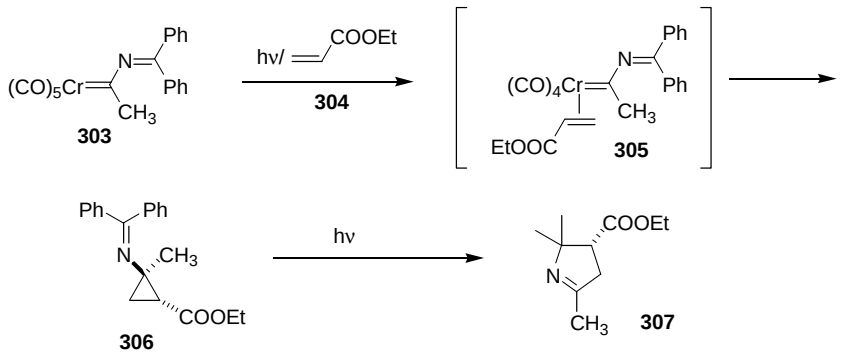
Scheme 24.

the β-carbon of the hydrazone at the carbene carbon followed by addition of the resulting allylmetal group to the hydrazone. The pyrrole was formed through nucleophilic attack of the imine nitrogen to the carbene carbon followed by intramolecular Michael addition of the organochromium compound.

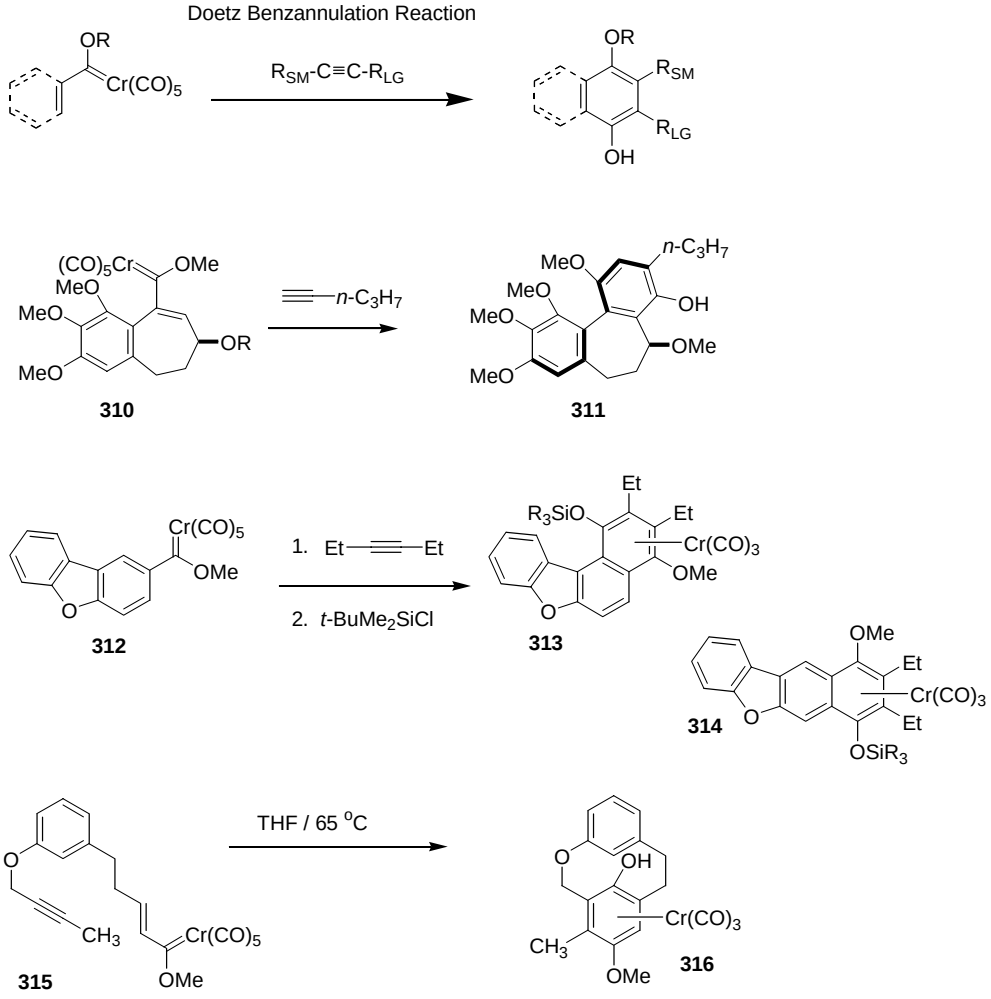
Coupling of carbene complexes with fulvenes was reported (Scheme 24) [474]. Reaction of fulvene **296** with the phenylcarbene complex **295** led to cyclopropanation of an endocyclic double bond with a high degree of stereoselectivity and a moderate degree of regioselectivity (favoring **297** over **298**). Reaction of alkynylcarbene complexes (e.g. **299**) with fulvenes led to [4+3]-cycloadducts (e.g. **302**). A mechanism involving nucleophilic addition of an alkene to the carbene complex, followed by 1,2-migration of tungsten and ring closure was proposed to account for formation of the [4+3]-cycloadducts.

Photolytic coupling of iminocarbene group VI metal complexes (e.g. **303**, Scheme 25) and electron-deficient alkenes (e.g. **304**) led to 1-pyrrolines (e.g. **307**) [475]. In this reaction, a mechanism involving photo-assisted CO dissociation, followed by complexation and cyclopropanation, followed by photochemically-induced transformation of the *N*-cyclopropylimine (**306**) to the 1-pyrroline (**307**) was proposed. The cyclopropylimine derivative **306** could be isolated from the reaction at short reaction times. Related studies involving the reaction of iminocarbene complexes with ketones and azo compounds were also reported [476].

2.3.3.4. Reaction of group VI metal–carbene complexes with alkynes—benzannulation. Many examples of benzannulation using α,β-unsaturated chromium–carbene complexes (Scheme 26) and alkynes (commonly known as the Dötz reaction) were reported in 2002. Examples are



Scheme 25.



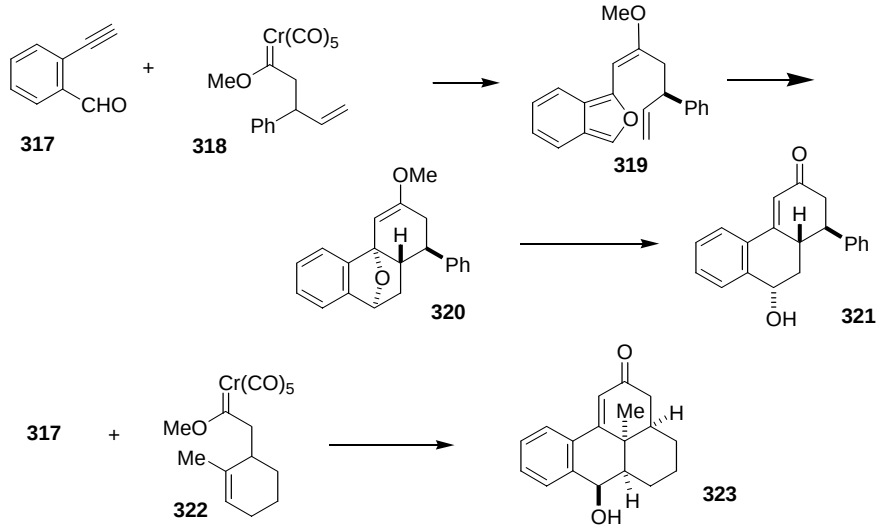
Scheme 26.

depicted in Scheme 26 and include: (1) atropoisomer-selective formation of benzene rings from coupling of carbene complex **310** with 1-pentyne [477]; (2) linear versus angular fusion (formation of **314** versus **313**) in the benzannulation of dibenzofuran–carbene complexes with 3-hexyne [478]; (3) benzannulation resulting from coupling of carbene complexes with diphenylacetylene derivatives that feature an ortho carbonyl group on one of the phenyl rings [479]; (4) benzannulation under microwave irradiation [480]; and (5) intramolecular benzannulation to afford *m*-cyclophane derivatives (e.g. **316**) [481].

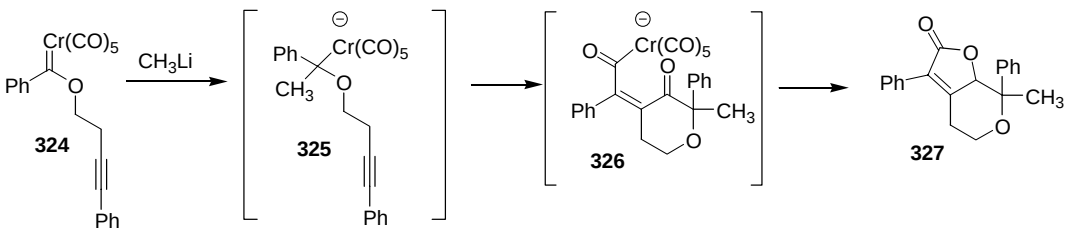
2.3.3.5. Nonbenzannulation reactions of group VI metal–carbene complexes with alkynes. Other processes involving the capture of vinylcarbene complexes generated from the coupling of carbene complexes and functionalized alkynes were reported in 2002 (Scheme 27). Coupling of *o*-alkynylbenzaldehyde derivatives (e.g. **317**) with γ,δ-unsaturated carbene complexes (e.g. **318**) led to the generation of isobenzofurans (e.g. **319**), which were captured via an intramolecular Diels–Alder reaction [482]. The reaction was highly stereoselective when complexes that feature a chiral atom in the tethering chain were employed. The direction of stereoinduction was opposite for systems that feature the chiral carbon and the alkene in the same ring (e.g. **322**) relative to systems where the chiral carbon is either acyclic (e.g. **318**) or in a ring that does not contain the alkene.

Treatment of alkyne–carbene complexes (e.g. **324**, Scheme 28) with organolithium derivatives led to the bicyclic derivatives (e.g. **327**) [483]. This process incorporates three of the carbon monoxide molecules originating from chromium hexacarbonyl. A mechanism was proposed involving nucleophilic addition to the carbene ligand, followed by CO insertion, alkyne insertion, and a second CO insertion, followed by intramolecular attack of the ketone on the metal acyl of intermediate **326**.

Coupling of carbene complexes (e.g. **329**, **330**, Scheme 29) with furan and thiophenes featuring an ortho arrangement of alkyne and carbonyl groups (e.g. **328**, **334**) was reported [484]. Reaction employing simple carbene complexes led to the *o*-quinoidal-like pyrone ring systems (e.g. **331**). The reaction employing γ,δ-unsaturated carbene complexes (e.g. **330**) led to the intramolecular Diels–Alder adducts (e.g.



Scheme 27.

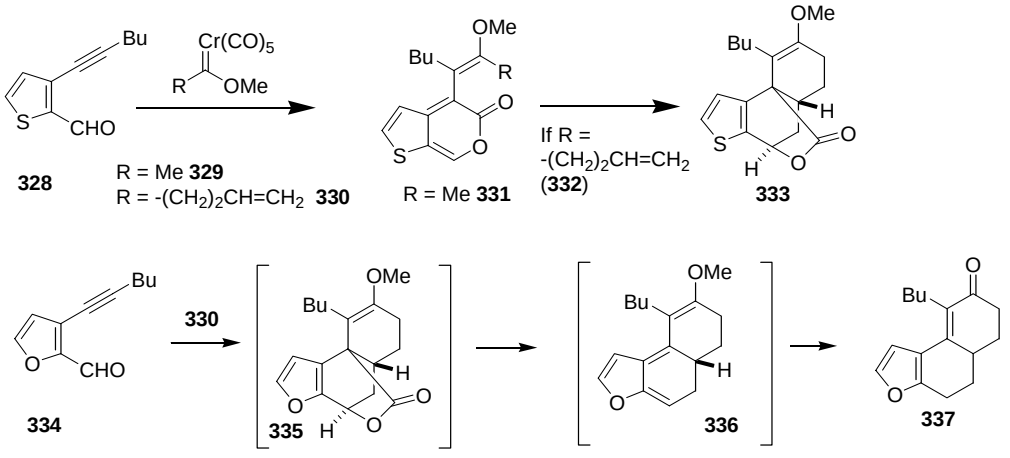


Scheme 28.

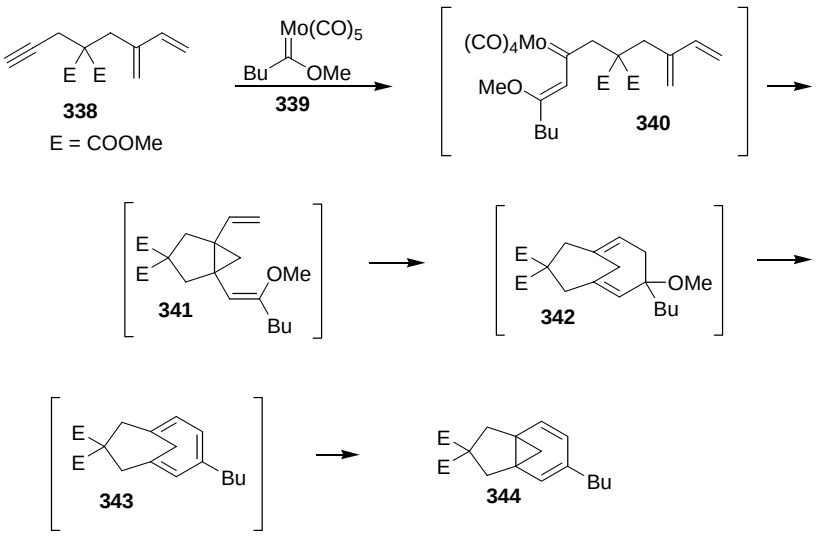
332). Furan derivatives undergo a further loss of CO_2 leading to simpler tricyclic ring systems (e.g. **337**); this process was used as the cornerstone for a total synthesis of cadinene natural products.

The coupling of molybdenum carbene complexes (e.g. **339**, Scheme 30) with dienynes where the diene and alkyne functionalities are spaced by at least three carbon atoms (e.g. **338**) was reported [485]. Coupling of alkyne **338** with carbene complex **339** resulted in tricyclic compound **344**. A mechanism involving alkyne insertion to afford vinylcarbene complex **340** followed by intramolecular cyclopropanation was proposed. Divinylcyclopropane **341** then undergoes a Cope rearrangement, followed by methanol loss, followed by electrocyclic ring opening to afford **344**.

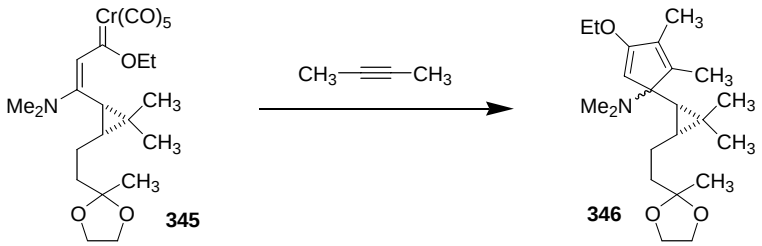
Use of the cyclopentannulation reactions (e.g. conversion of **345** to **346**, Scheme 31) of β-aminoalkenylcarbene–chromium complexes (e.g. **345**) for synthesis of angularly-fused triquinanes was reported [486].



Scheme 29.



Scheme 30.

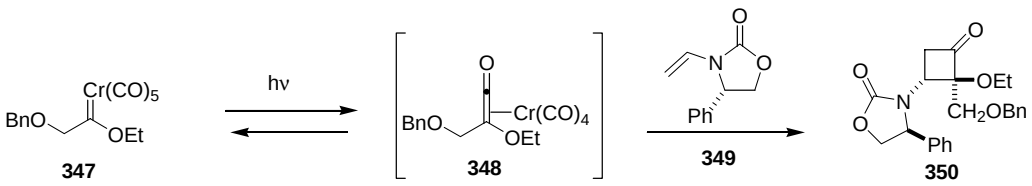


Scheme 31.

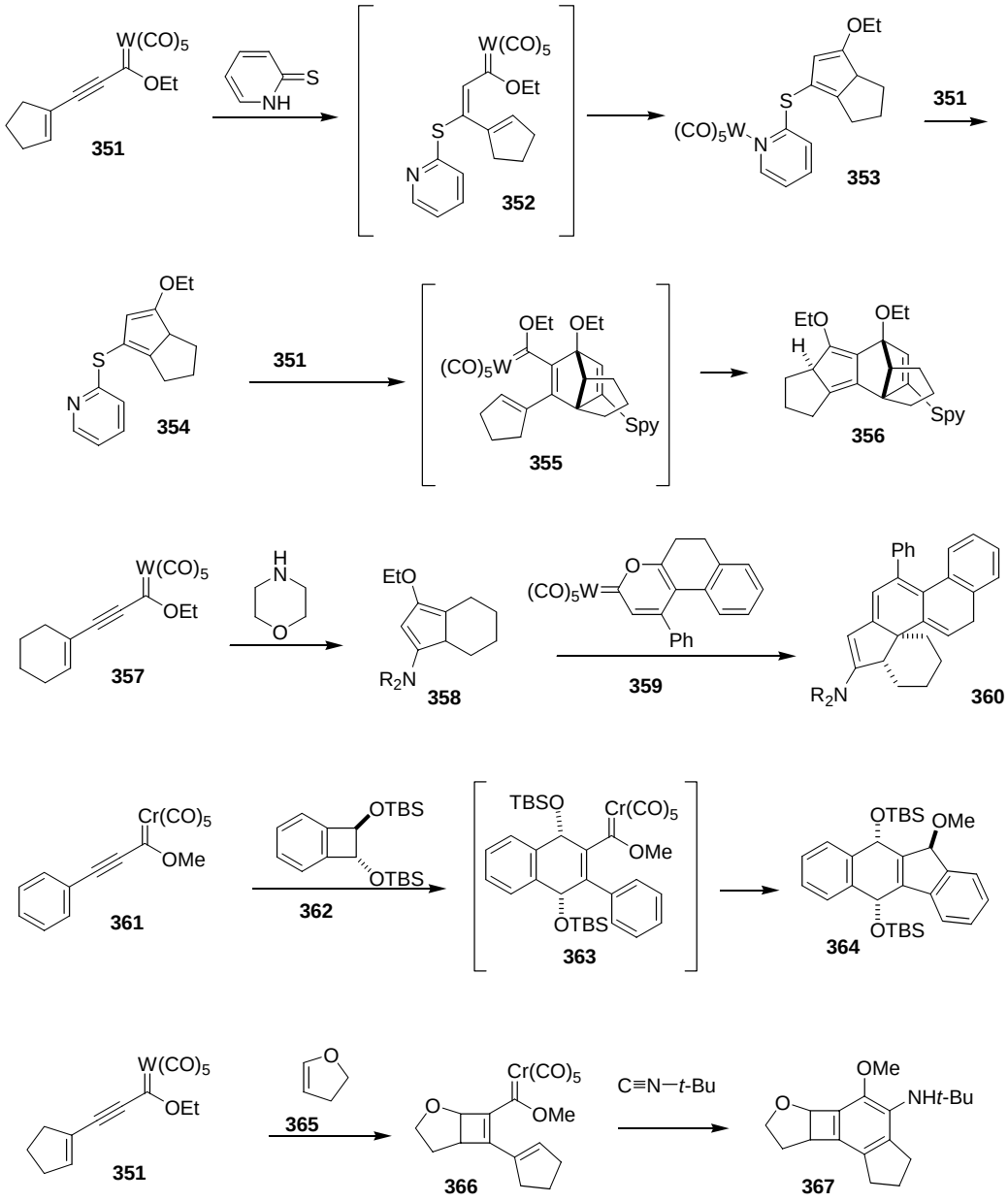
2.3.3.6. Photolytic generation of ketenes from group VI metal–carbene complexes. The formation of chromium ketene complexes (e.g. **348**, Scheme 32) through photolysis of Fischer carbene–chromium complexes was reported. Chromium carbene-derived optically pure cyclobutenones or β-lactams were used as starting materials for the synthesis of several C-nucleoside derivatives [487].

2.3.3.7. Reactions occurring at the conjugated C–C π-bond of α,β-unsaturated group VI metal–carbene complexes. Numerous reaction processes were reported in 2002 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").

In numerous cases, either nucleophilic addition or cycloaddition to the triple bond of an enynylcarbene complex (e.g. **351**, Scheme 33) or arylalkynylcarbene complex is followed by a secondary cyclization process of the resulting α,β,γ,δ-unsaturated carbene complex (e.g. **352**) (or 1-metalla-1,3,5-hexatriene); several examples are depicted in Scheme 33. Nucleophilic addition of thioamides to enynylcarbene complexes (e.g. **351**) led to the α,β,γ,δ-unsaturated carbene complex (e.g. **352**), which rapidly cyclized to a cyclopentadiene derivative (e.g. **353**) [488]. After decomplexation of tungsten to afford **354**, an additional mole of enynylcarbene complex could be incorporated through a Diels–Alder reaction followed by cyclization to afford a complex ring system (e.g. **356**). The coupling of enynylcarbene complex **357** with amines led to formation of the aminocyclopentadienes (e.g. **358**) which react with the pyranylidene–group VI metal complex **359** to afford angularly fused tricyclic ring systems (e.g. **360**) [489]. Formation of **360** involves Diels–Alder reaction between the pyranylidene and the enol ether of **358**, followed by expulsion of



Scheme 32.

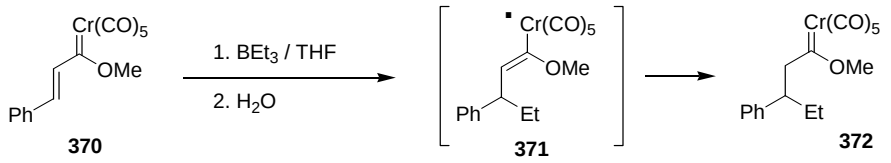


Scheme 33.

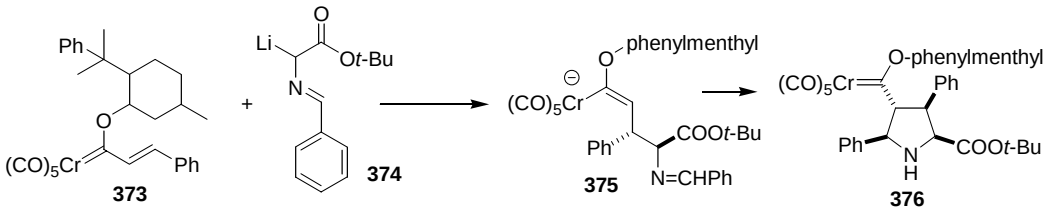
$W(CO)_6$ in a retro Diels–Alder reaction followed by loss of ethanol. Tandem Diels–Alder-cyclopentannulation reactions were reported in the coupling of phenylethynylcarbene complexes (e.g. **361**) with *o*-quinonedimethane precursors (e.g. **362**) [490]. Reaction of **362** with simple enynylcarbene complexes (e.g. **351**, **357**) afforded products where Diels–Alder reaction preferentially occurs at the alkene substituent. A tandem reaction sequence was reported involving [2+2]-cycloaddition of enol ethers (e.g. **365**) and enynylcarbene complexes (e.g. **351**), followed by cyclization of the resulting alkenylcyclobutenylcarbene complexes to cyclobutane-fused anilines (e.g. **367**) [491].

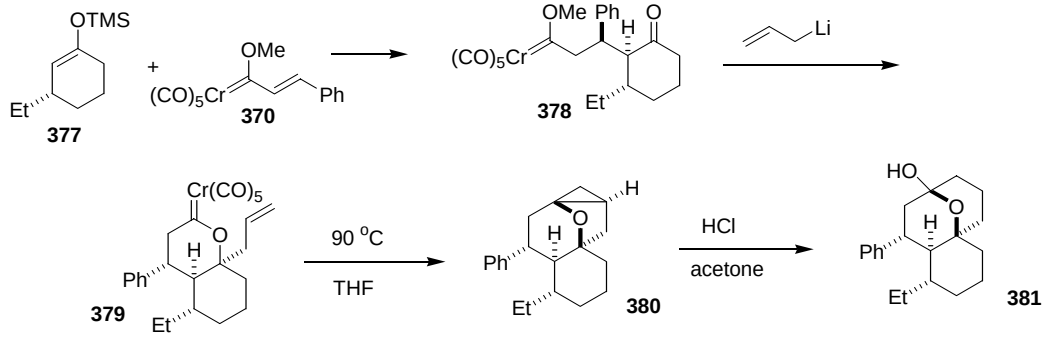
The addition of radical reagents (e.g. triethylborane/oxygen, Scheme 34) to α,β-unsaturated carbene complexes was examined [492]. Reaction of carbene complex **370** with triethylborane followed by water led to the net Michael addition products (e.g. **372**). The proposed mechanism involves the addition of ethyl radical to the double bond to afford a chromium–carbene stabilized radical (e.g. **371**), followed by hydrogen abstraction to form the net Michael addition product. Related processes were observed for alkynylcarbene complexes.

Pyrrolidine derivatives (e.g. **376**, Scheme 35) were prepared through the coupling of chiral and optically pure α,β-unsaturated carbene complexes (e.g. **373**) with imido-enolate derivatives (e.g. **374**) [493]. A mechanism involving stereocontrolled Michael addition followed by addition of the resulting anion to the imine was proposed. A



Scheme 34.



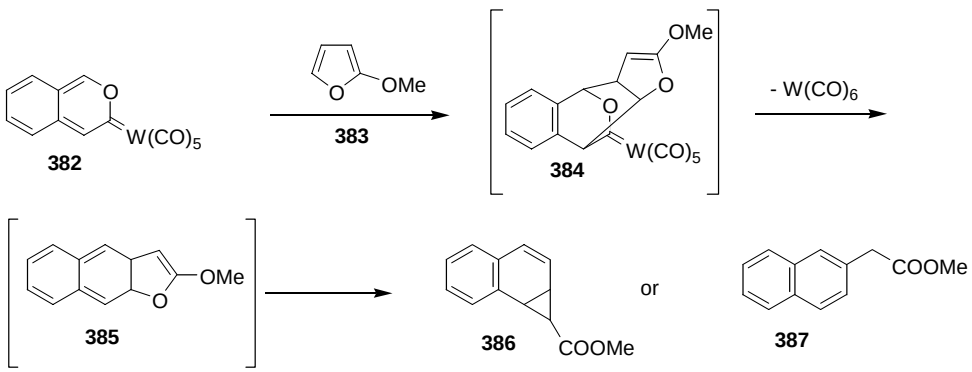


Scheme 35.

novel eight-membered ring synthesis (e.g. formation of **381** from carbene complex **370**) involving the one-pot sequential coupling depicted in Scheme 35 was reported [494]. The reaction sequence proceeds through Michael addition of a silyl enol ether to a carbene complex, followed by allylation of the ketone in **378** to form **379** after alkoxide metathesis, followed intramolecular cyclopropanation and ring opening.

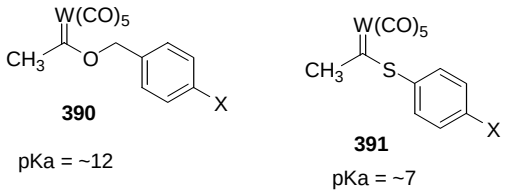
The Diels–Alder coupling of benzopyrylidene–tungsten complexes (e.g. **382**, Scheme 36) with electron-rich alkenes was reported [495]. Coupling with 2-methoxyfuran (**383**) led to cyclopropane **386** under neutral or basic conditions, and to naphthalene **387** under acidic conditions. A mechanism involving Diels–Alder reaction, followed by retro Diels–Alder reaction and expulsion of $W(CO)_6$ to afford dihydrofuran intermediate **385** was proposed. Concerted formation of cyclopropane **386** from **385** occurs under neutral conditions. Protonation of the enol ether double bond of **385** followed by aromatization/elimination was proposed for formation of the naphthalene **387**.

2.3.3.8. Physical organic chemistry of group VI Fischer carbene complexes. The pK_a was determined for several arylmethylcarbene complex derivatives [*p*-$XArCH_2C(OMe)$=$Cr(CO)_5$] and was found to vary from 10.4 (X = H) to 10.68



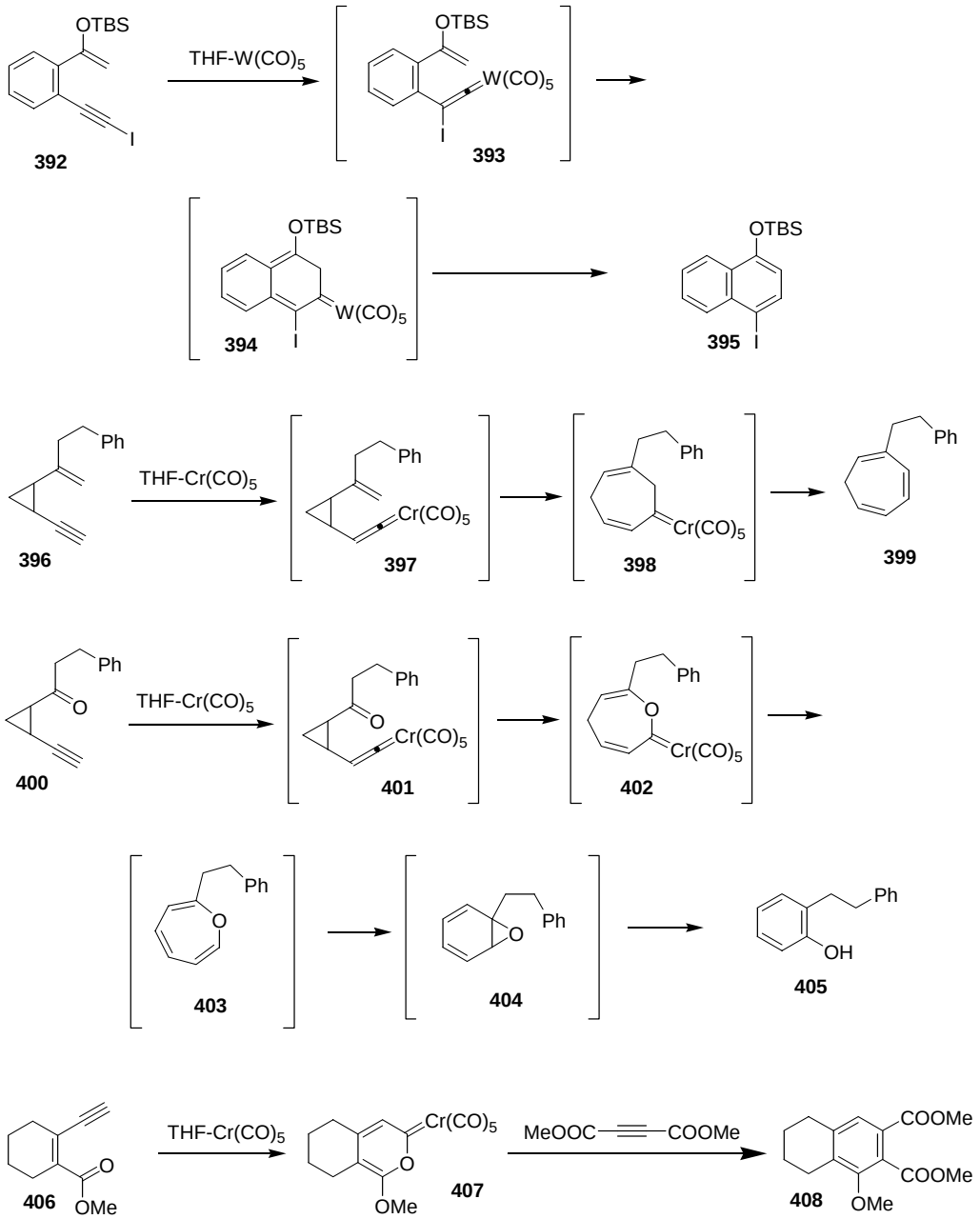
Scheme 36.

(X = OMe) [496]. A kinetic study of the reversible deprotonation of carbene complexes of general structures **390** and **391** (Scheme 37) by primary and secondary amines in 1:1, water:acetonitrile was reported [497]. The pK_a of alkoxycarbene complexes was determined to be approximately 12, while that of thiocarbene complexes is approximately 7. The acidity difference was attributed to stabilization of the alkoxycarbene complexes through electron donation by oxygen and the greater inductive affect emanating from the directly-attached aromatic ring in the thiocarbene complexes studied. Electron withdrawing X-groups enhance the acidity for both complexes.



Scheme 37.

2.3.3.9. Synthesis and reactivity of group VI metal–vinylidene complexes, and reactions that involve vinylidene–metal complexes as intermediates. Several papers in 2002

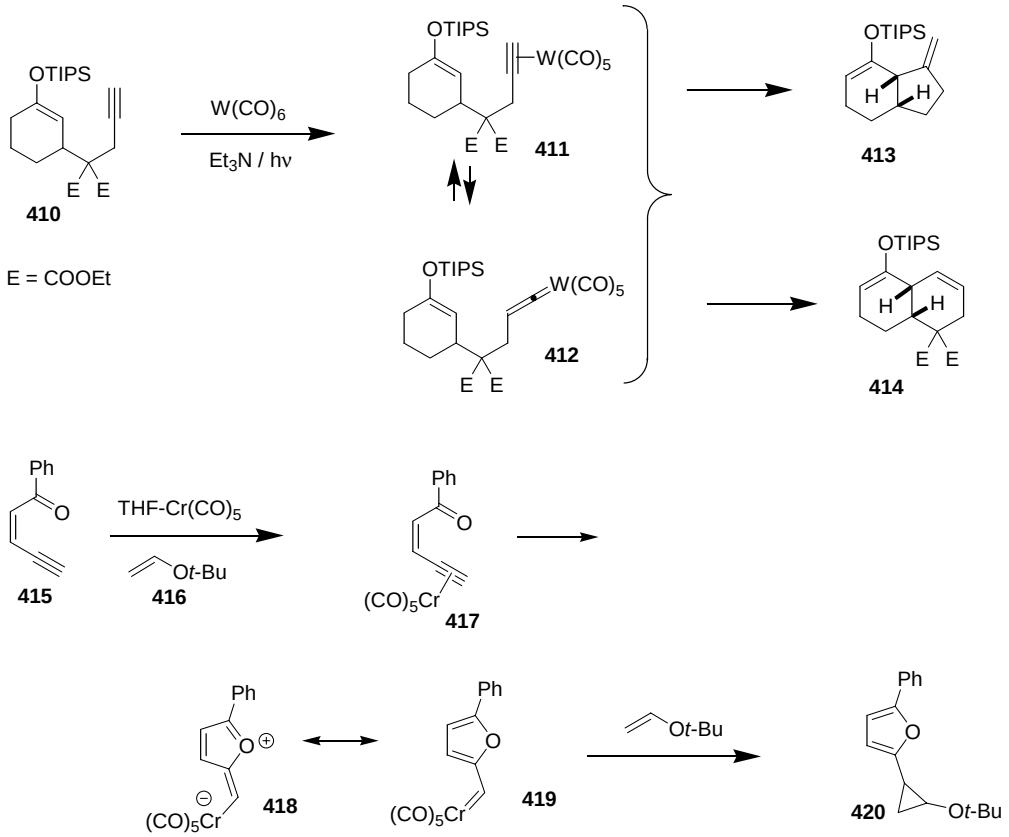


Scheme 38.

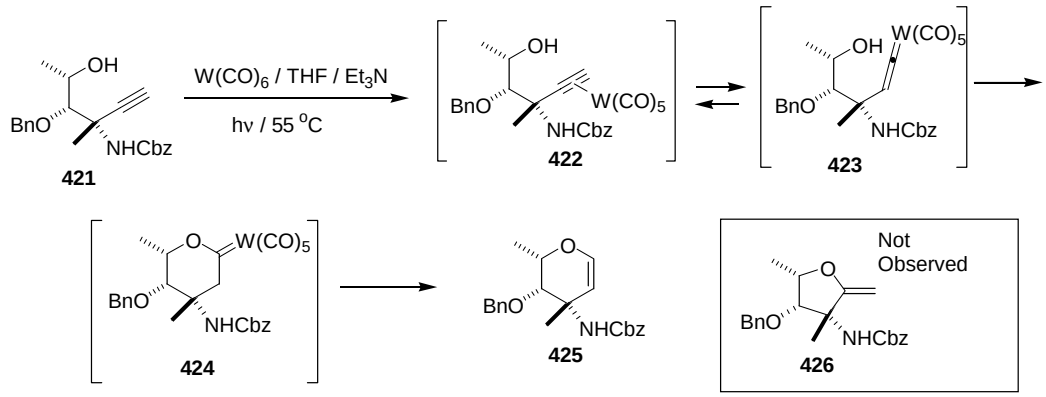
report on the generation of group VI metal–vinylidene complexes for the purpose of initiating a pericyclic reaction (Scheme 38). Naphthalene formation was effected by reaction of iodoalkyne derivatives (e.g. **392**) with tungsten–pentacarbonyl sources [498]. Formation of a β-iodovinylidene (e.g. **393**) followed by electrocyclic ring closure was proposed. Capture of iodoalkyne-derived β-iodovinylidene-tungsten complexes by enol ether nucleophiles was also reported. Formation of cycloheptatrienes (e.g. **399**) from reaction of alkenylcyclopropylacetyenes (e.g. **396**) with chromium pentacarbonyl sources was reported [499]. A mechanism involving formation of a vinylidene (e.g. **397**) followed by Cope rearrangement and conversion of the carbene complex to an alkene was proposed. Ketone analogs (e.g. **400**) afforded phenol derivatives (e.g. **405**). A mechanism involving vinylidene formation, followed by Cope rearrangement, followed by conversion to the oxepin derivative (e.g. **403**), followed by electrocyclic ring closure and opening of the resulting epoxide was proposed. The coupling of enyne–ketones, esters, and amides with chromium pentacarbonyl sources was reported [500]. Pyranylidene–chromium complexes (e.g. **407**) were formed from enyne–esters- and amides via formation of the vinylidene complex followed by electrocyclic ring closure. Treatment of the complexes with dimethyl acetylenedicarboxylate led to the aromatic rings (e.g. **408**) via Diels–Alder reaction followed by elimination of $Cr(CO)_6$.

Trapping of tungsten–vinylidene intermediates through intramolecular reaction with enol ethers was reported [501]. Reaction of enol ether–alkynes (e.g. **410**, Scheme 39) with tungsten hexacarbonyl and triethylamine under photolysis conditions led to mixtures of five- and six-membered ring-containing compounds (e.g. **413** and **414**). The five-membered ring product was derived via nucleophilic attack of the enol ether on an intermediate tungsten–alkyne complex (e.g. **411**). The six-membered ring was derived from nucleophilic attack of the enol ether at the carbene carbon of an intermediate vinylidene complex (e.g. **412**). Similar studies were reported for homologues featuring one less carbon in the tethering chain [502], which proceeded through the vinylidene intermediate leading to five-membered ring formation. Formation of furanylcyclopropane derivatives (e.g. **420**) from the coupling of enyne ketones (e.g. **415**) with enol ethers (e.g. **416**) in the presence of chromium pentacarbonyl sources was reported [503]. A mechanism involving formation of the furanylcarbene complex (**419**) via nucleophilic addition of the carbonyl oxygen to the π-alkyne complex, followed by cyclopropanation was proposed.

Several examples of the formation of cyclic enol ethers (e.g. **425**, Scheme 40) from coupling of tungsten–pentacarbonyl sources with precursors that contain terminal alkyne and alcohol functionalities were reported. These reactions involve formation of a tungsten–vinylidene (e.g. **423**).



Scheme 39.

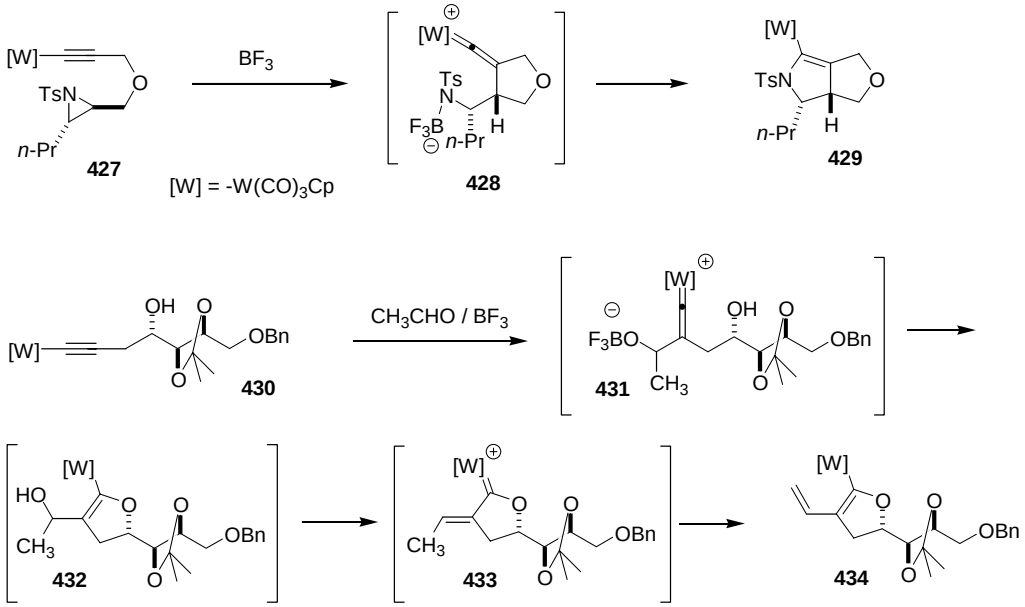


Scheme 40.

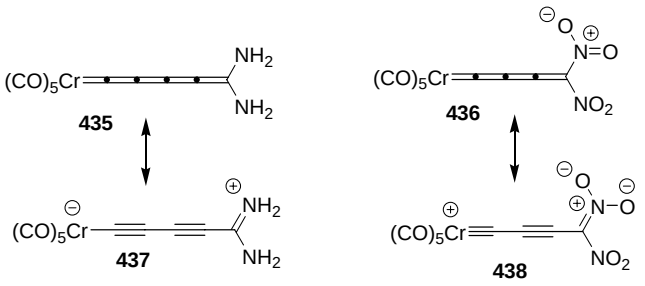
Under the combined thermal/photochemical conditions the reaction is catalytic in tungsten. Reaction of alcohol **421** with catalytic tungsten hexacarbonyl under combined thermal/photolytic conditions led to aminosaccharide precursor **425** [504]. This reaction is also the key reaction used for an iterative oligosaccharide synthesis [505]. Formation of cyclic ethers from hydroxy terminal alkynes and tungsten–pentacarbonyl sources was also studied computationally [506]. The study was concerned with energetics of the individual steps and delineation of the factors involved in six-membered ring formation versus the unobserved formation of isomeric exo-methylene five-membered rings (e.g. **426**). The rate-determining step was determined to be the conversion of the η^2-alkyne complex (e.g. **422**) to the corresponding vinylidene complex (e.g. **423**). An in situ-generated tungsten–vinylidene–tungsten complex was an effective catalyst for the polymerization of ferrocenylacetylene [507].

Coupling of tungsten acetylides that contain aziridine functionality (e.g. **427**, Scheme 41) with Lewis acids was reported [508]. This reaction afforded dihydropyrrole derivatives (e.g. **429**) via a mechanism involving nucleophilic attack of the acetylide at the Lewis acid-complexed aziridine to afford the tungsten–vinylidene intermediate (**428**), followed by nucleophilic attack of the nitrogen at the carbene carbon to generate the dihydropyrrole ring. Coupling of tungsten acetylides that contain alcohol functionality (e.g. **430**) with aldehydes and Lewis acids led to dihydrofuryl–tungsten derivatives (e.g. **434**) [509]. A mechanism involving formation of a cationic vinylidene (**431**) through coupling of the tungsten acetylide and aldehyde–Lewis acid complex, followed by nucleophilic attack by the alcohol to form an alkenyltungsten complex (**432**), followed by elimination of water to form a cationic Fischer carbene complex (**433**), followed by deprotonation was proposed. Deprotonation of a neutral tungsten(0)–vinylidene complex afforded an anionic alkynyltungsten complex [510].

Various metallacumulene–chromium complexes (e.g. **435-438**, Scheme 42) were studied by DFT [511]. The



Scheme 41.



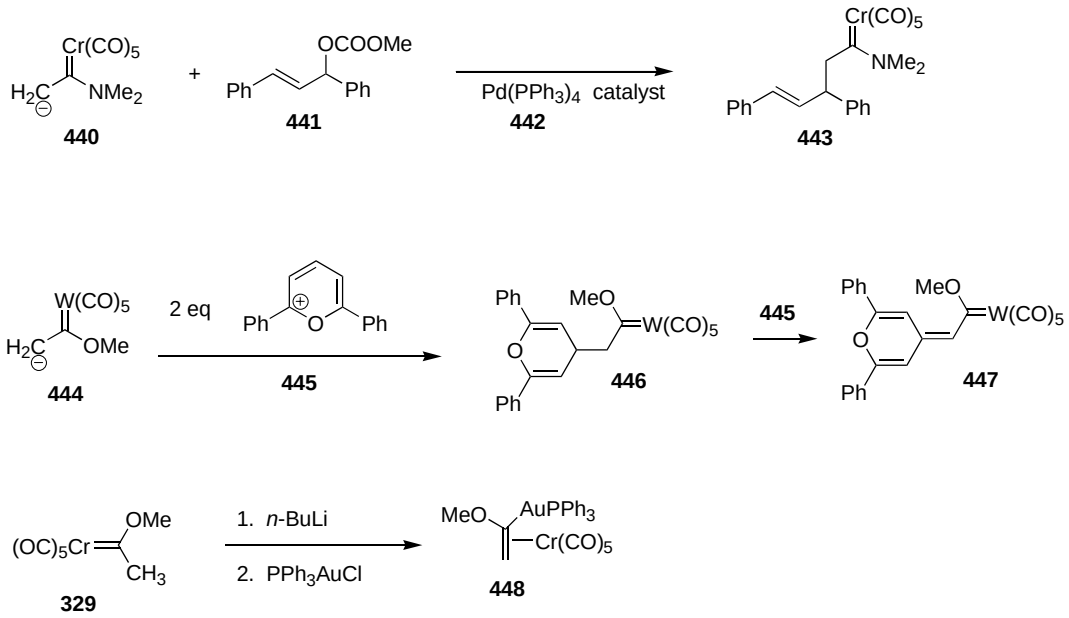
Scheme 42.

strongly electron-donating group NH_2 leads to a decrease in the metal–cumulene bond dissociation energy while the electron-withdrawing nitro group leads to an increase. The electron-donor effect was more pronounced for cumulenes containing an odd number of carbons, while the effect of the electron-withdrawing group was more pronounced for cumulenes containing an even number of carbons. The observed results are consistent with resonance arguments.

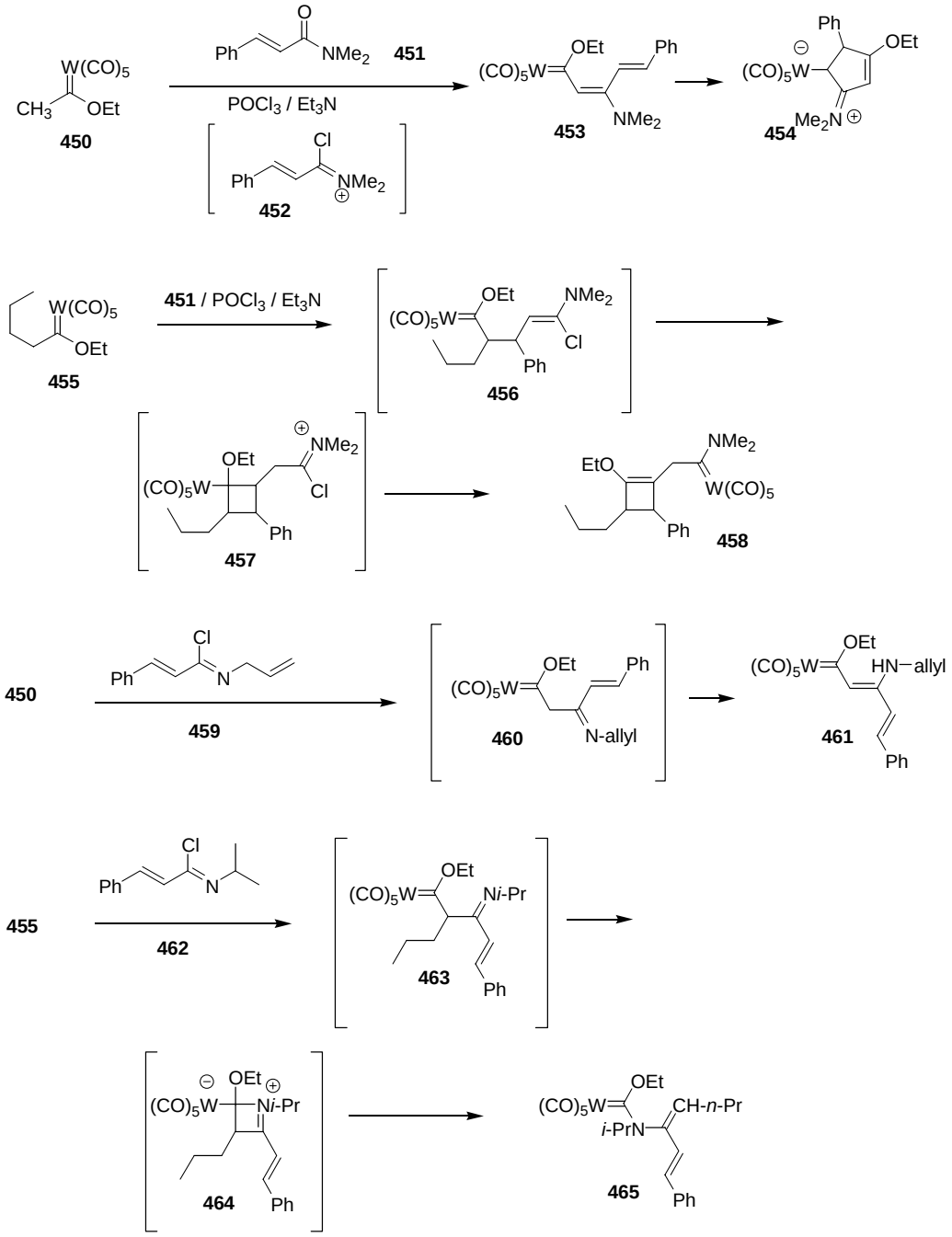
2.3.3.10. Reactions involving carbanions derived from deprotonation of group VI metal–carbene complexes. Several examples of reactions that involve deprotonation of a group VI Fischer carbene complex at the α-position, followed by reaction with an electrophile were reported in 2002. Successful palladium-catalyzed allylic alkylation was reported for carbanions derived from aminocarbene complexes (e.g. **440**, Scheme 43) [512]. Reaction of anions derived from tungsten–carbene complexes (e.g. **444**) with pyrilium salts (e.g. **445**) was reported [513]. The alkoxycarbene complex afforded the alkylidenepyrone derivative **447** upon reaction with *n*-butyllithium followed by 2 eq. of the pyrilium salt. Reaction with 1 eq. of the pyriyium salt led to some of the simple alkylation product **446**; the excess pyrylium salt apparently serves as an oxidant. Reactions using aminocarbene complexes generally led to compounds analogous to **446**. Dimerization of carbene complex **447** and analogs featuring additional –CH=CH– carbene/pyrone spacer units was also reported [514]. These complexes were studied by cyclic voltammetry and DFT. Reaction of carbene complex-derived anions with PPh_3Au^+ led to the vinylaurate complexes (e.g. **448**) [515].

Several examples of the coupling of carbene complexes with chloroiminium salts were reported in 2002 (Scheme 44). Reaction of carbene complex-derived anions with in situ-generated chloroiminium salt derivatives (e.g. **452**) was reported [516]. Reaction of **452** with methylcarbene–tungsten complex **450** initially affords mainly the β-aminocarbene complex (**453**) via 1,2-addition to the chloroiminium carbon. The β-aminocarbene complex decomposes at room temperature to afford five-membered ring species (**454**). A minor reaction pathway results in products from double Michael addition. Higher homologs of complex **450** (e.g. butylcarbene complex **455**) afforded a four-membered ring derivative (e.g. **458**) in a process involving Michael addition followed by intramolecular reaction of the resulting enamine (**456**) with the carbene complex. Analogous reaction of neutral iminoyl chlorides (e.g. **459**) led to β-aminocarbene complexes (e.g. **461**) for the methylcarbene complexes and to a dienylaminocarbene complexes (e.g. **465**) for higher homologues [517]. Formation of dienylaminocarbene complex **465** was proposed to occur through intramolecular nucleophilic addition of nitrogen to the carbene carbon followed by electrocyclic ring opening.

2.3.3.11. Reactions Involving the addition of nucleophiles to the carbene carbon of Group VI metal-carbene complexes. The coupling of carbene complexes with



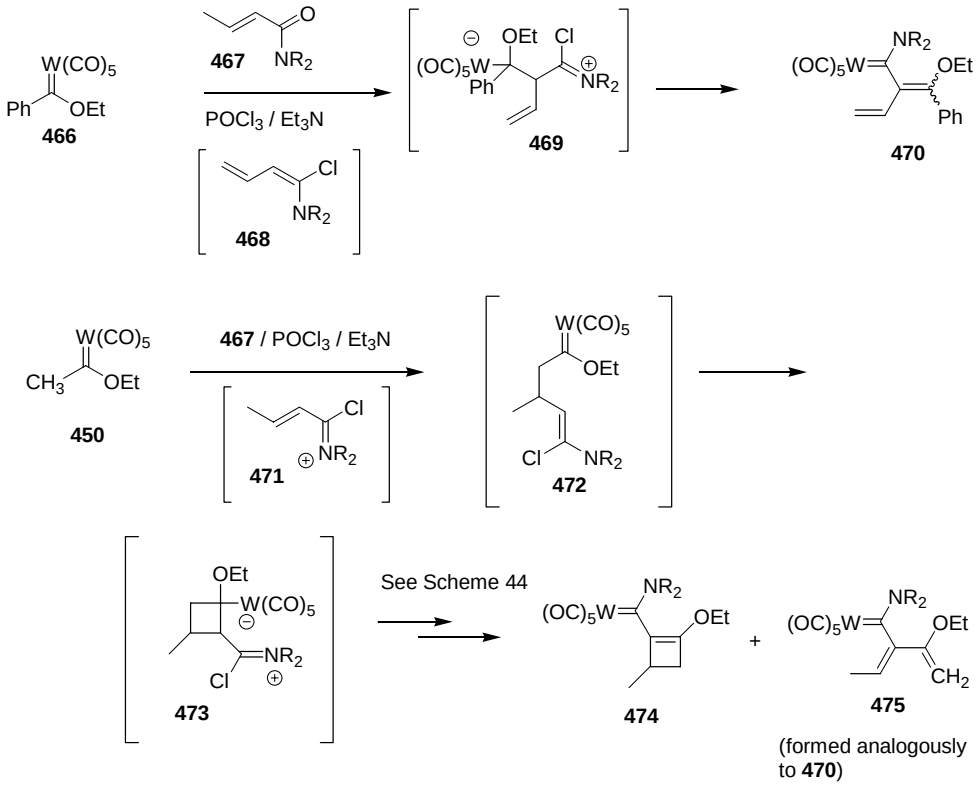
Scheme 43.



Scheme 44.

α,β-unsaturated amides that feature an acidic γ-hydrogen (i.e. **467**, Scheme 45) in the presence of $POCl_3$ was examined [518]. This publication differs from the studies in Scheme 44 in that the acidic γ-hydrogen allows formation of the dienamine intermediate **468**. The reaction employing carbene complexes devoid of α-hydrogens (e.g. **466**) led to dienylcarbene complexes (e.g. **470**) accompanied by the enol ether hydrolysis products. The reaction employing carbene complexes that have α-hydrogens (e.g. **450**) led to mixtures of compounds analogous to **468** (e.g. **475**) accompanied by compounds derived from Michael addition of carbene complex-stabilized anions to the iminium salts (e.g. **474**) (as in Scheme 44).

2.3.3.12. Other reactions of group VI metal–carbene complexes. Condensation of aminocarbene complexes (e.g. **478**, Scheme 46) with α,β-unsaturated amides in the presence of $POCl_3$ was reported [519]. The reaction initially affords iminocarbene complexes (e.g. **479**). Upon thermolysis, iminocarbene complexes cyclize to pyrrole derivatives (e.g. **480**).

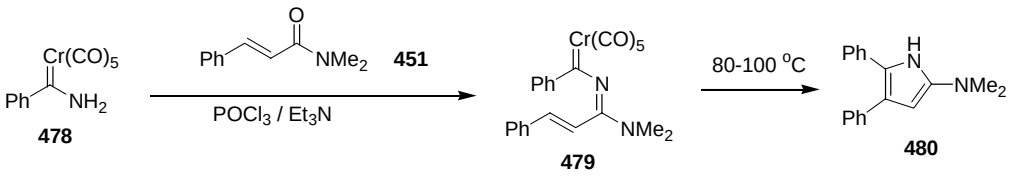


Scheme 45.

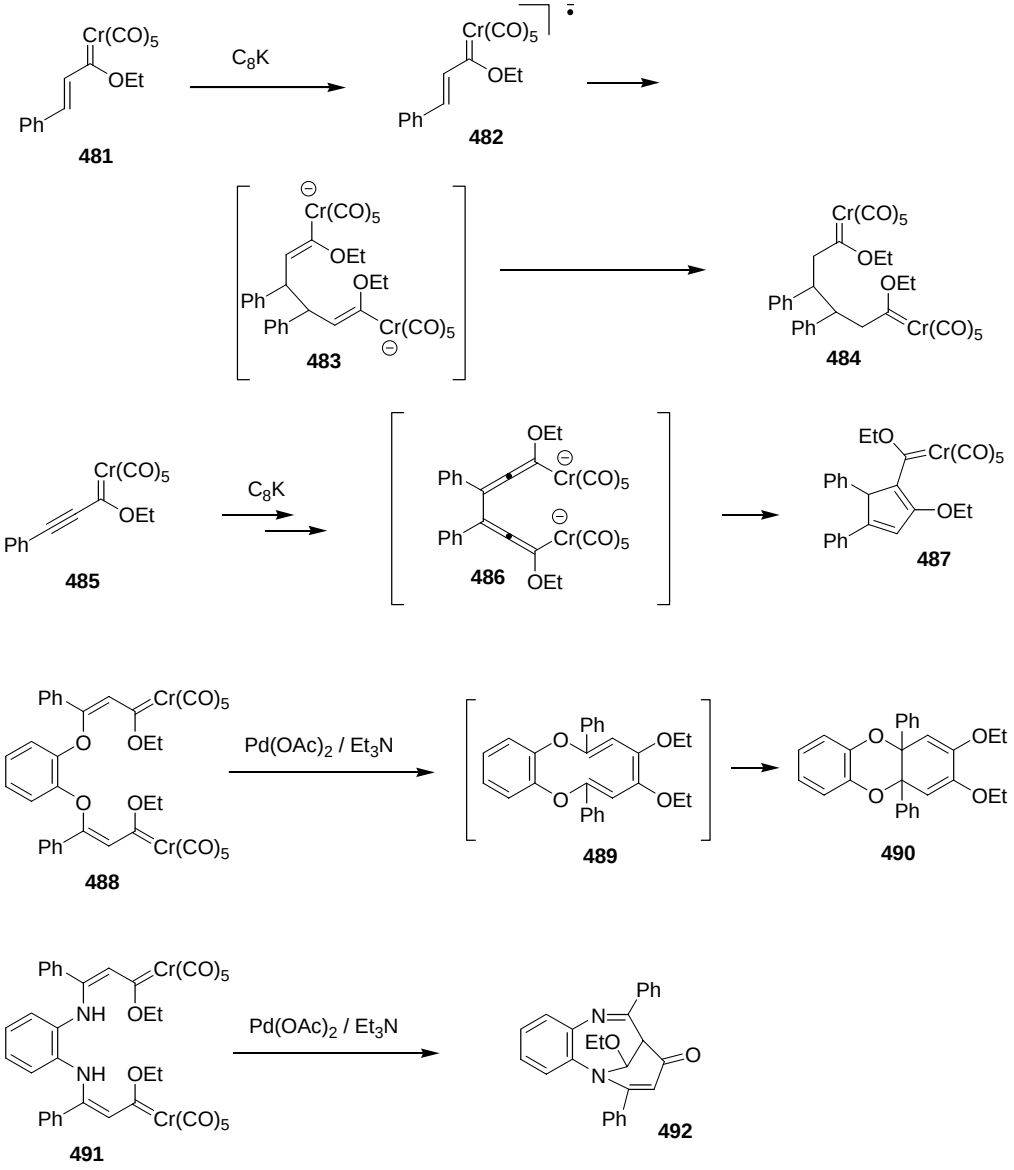
Reductive dimerization of alkenyl- and alkynylcarbene–chromium complexes (e.g. **481**, **485**, Scheme 47) was reported [520]. Coupling at the β-position occurred upon treatment of α,β-unsaturated carbene complex **481** with potassium/graphite, and afforded dimeric species **484** upon protonation. A mechanism involving formation of a radical anion (**482**), followed by coupling, followed by protonation of the resulting dianion was proposed. The analogous reaction of the alkynylcarbene complex **485** led to the cyclopentadienylcarbene complex **487**. In this reaction, formation of a radical anion followed by coupling gives dianionic complex **486**, which undergoes monoprotonation followed by attack of the resulting vinylchromium anion at the neutral carbene complex to effect five-membered ring formation. Related dimeric carbene complexes (e.g. **488**, **491**) were subjected to reaction with palladium complexes [521]. Reaction of the β-alkoxy-bridged complexes (e.g. **488**) led to the cyclohexadiene derivatives (e.g. **490**) in a reaction sequence involving carbene transfer to palladium, followed by intramolecular carbene coupling, followed by electrocyclic ring closure. The corresponding complex bridged by a binaphthyl group afforded a product analogous to **490** without further rearrangement. Analogous β-amino-bridged complexes (e.g. **491**) led to the bridged complexes (e.g. **492**) in a sequence involving carbene transfer to palladium, followed by intramolecular nucleophilic attack to afford **492**. Isolation and X-ray structure determination was reported for a palladium–carbene complex prepared through transfer of a carbene ligand from chromium [522].

Allylic amines (e.g. **496**, Scheme 48) were formed from thermal coupling of simple carbene complexes (e.g. **329**) with *N*-tosyl imines (e.g. **493**) [523]. A mechanism involving [2+2]-cycloaddition, followed by β-hydride elimination, followed by reductive elimination was proposed.

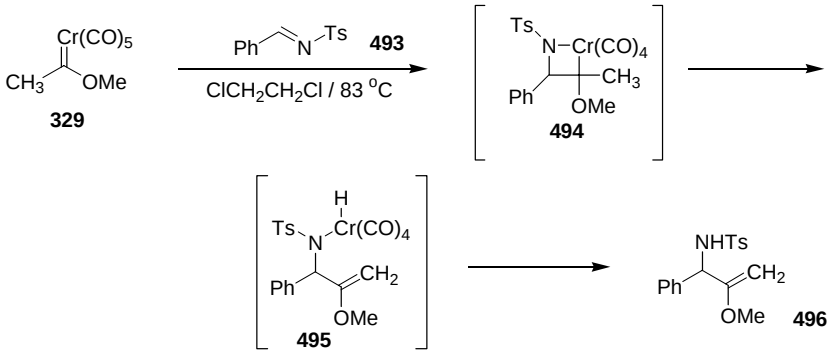
A new procedure for the oxidation of Fischer carbene complexes (e.g. **497**, Scheme 49) to the corresponding organic carbonyl compounds (e.g. **498**) was reported [524]. Reaction of chelated hydrazinocarbene complexes with calcium hypochlorite led to the corresponding amides. An alternative procedure involving the in situ-generation of



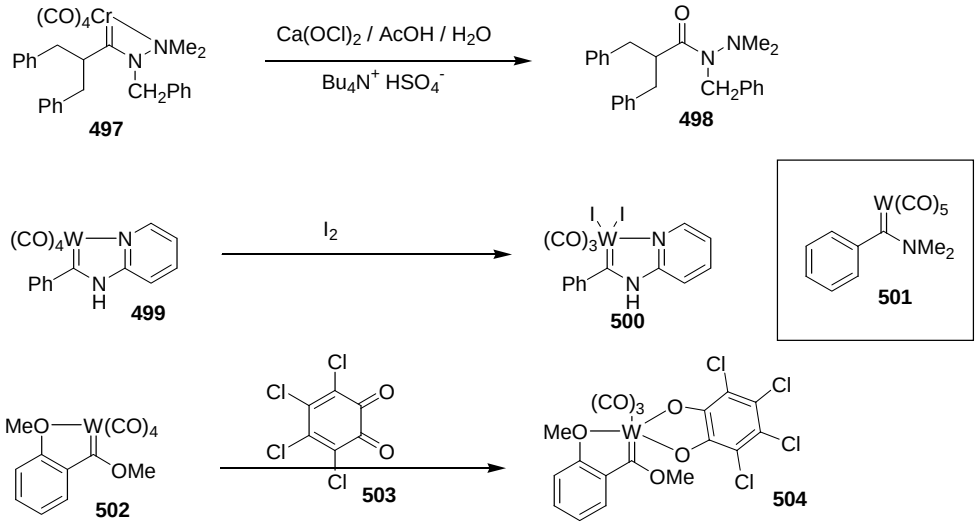
Scheme 46.



Scheme 47.



Scheme 48.



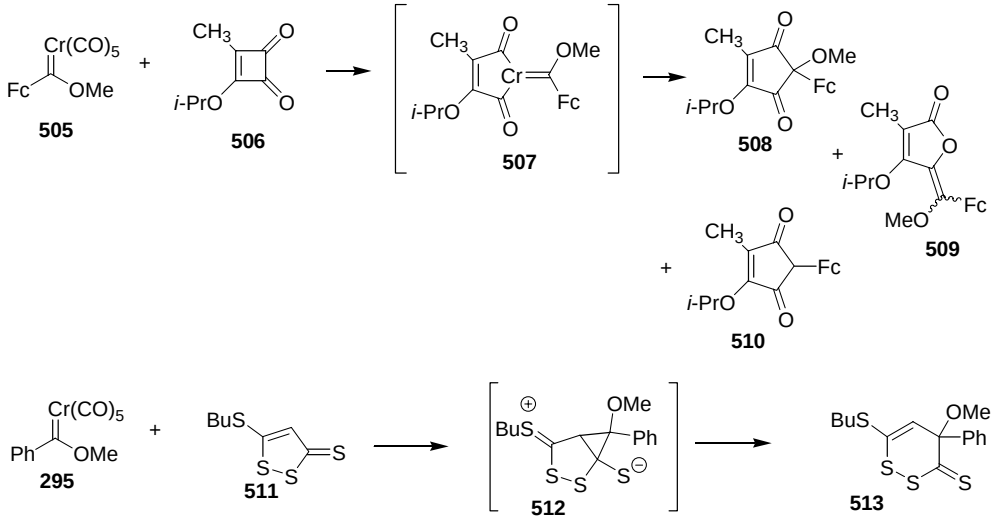
Scheme 49.

iodine from sodium perborate and potassium iodide was also reported. The oxidation of Fischer carbene tungsten complexes (e.g. **499**) to the corresponding tungsten(II) carbene complexes (e.g. **500**) was reported [525]. The reaction was restricted to compounds possessing a high lying HOMO. The simple aminocarbene complex **501** could not be transformed to a tungsten(II) complex using bromine or $SnBr_4$. A similar complex was generated from an alkene chelate complex however it could not be characterized due to decomposition at low temperature. The alkoxy chelate complex **502** could be transformed to a tungsten(II) complex (**504**) by reaction with tetrachloro-*o*-benzoquinone (**503**).

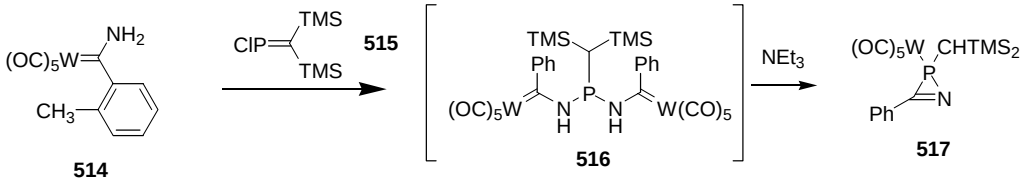
The coupling of ferrocenylcarbene complex **505** (Scheme 50) with cyclobutenediones (e.g. **506**) was reported [526]. The reaction led to a mixture of alkylidenefuranones (e.g. **509**), cyclopentenediones (e.g. **508**, **510**), and acetylferrocene. The product distribution was highly dependent of the structure of the cyclobutenedione. A net insertion of carbene complex unit into the C–C bonds of sulfur heterocycle **511** was also reported [527]. A mechanism involving cyclopropanation (resulting in intermediate **512**) followed by rearrangement to **513** was proposed.

The reactions of alkoxy- and aminocarbene–tungsten complexes featuring ortho groups (e.g. **514**, Scheme 51) with chlorophosphane **515** were reported [528]. These reactions led initially to diaminophosphine–dicarbene derivatives (e.g. **516**), which could be isolated, accompanied by tungsten–azaphosphirene complexes (e.g. **517**). Further treatment of **516** with triethylamine led to azaphosphirene complex **517**. Complex **517** was formed in high yield directly from the reaction of **514** with **515** in the presence of triethylamine.

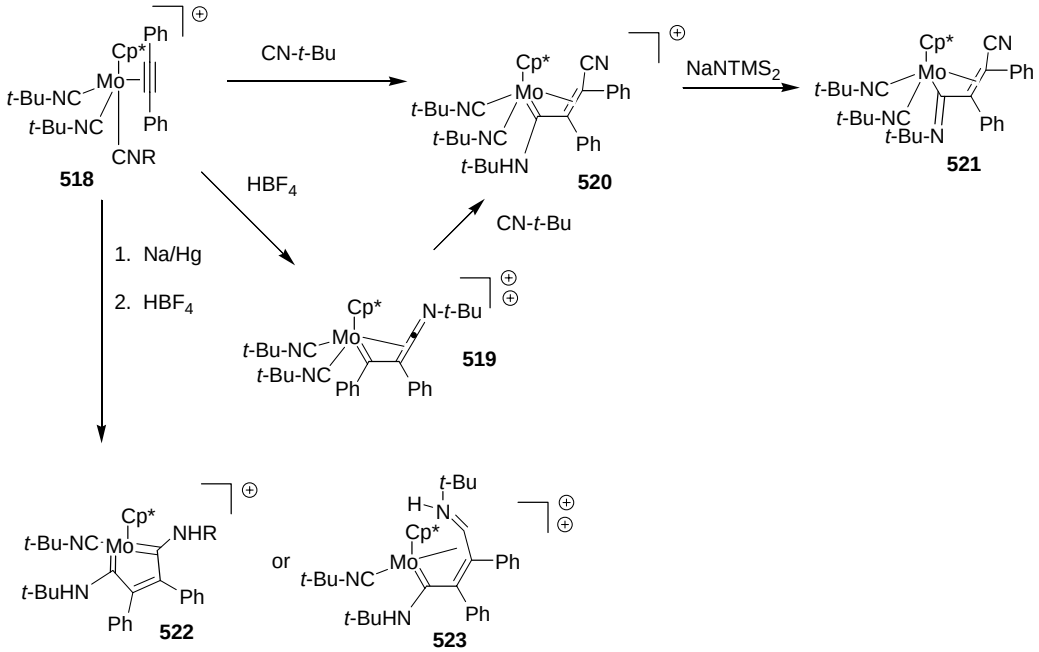
A variety of carbene complexes were prepared from molybdenum–alkyne–isonitrile complexes (e.g. **518**, Scheme 52) [529]. Coupling of complex **518** with an additional molecule of isocyanide led to the carbene complex



Scheme 50.



Scheme 51.

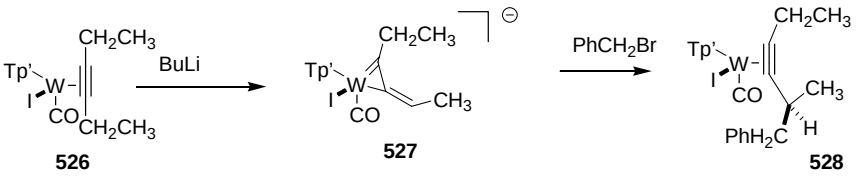


Scheme 52.

520, which afforded the neutral acylimine complex **521** upon treatment with base. Reaction with HBF_4 resulted in the internally-coordinated carbene complex **519**, which transforms to the complex **520** upon treatment with a molecule of isocyanide. A phosphite-substituted analog of **520** was obtained if dicationic complex **519** was treated with trimethyl phosphite. Reduction of complex **518** followed by treatment with HBF_4 led to the dicarbene complex **522** when the reaction was conducted in ether or to the iminium complex **523** when the protonation step was conducted in THF.

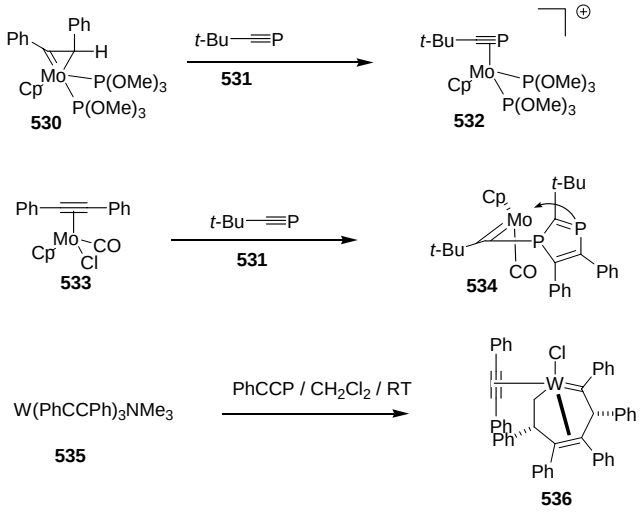
Structural elaboration of various η^2-alkyne–tungsten complexes (e.g. **526**, Scheme 53) via deprotonation followed by alkylation was reported [530]. Deprotonation affords a propargyl anion complex which is best represented as the η^2-alkenyl complex (e.g. **527**). The high stereoselectivity in the electrophilic addition step is attributed to attack from the direction opposite the bulky Tp' (hydridotris(3,5-dimethylpyrazoyl)borate) ligand.

The coupling of η^2-alkenylmolybdenum complex **530** (Scheme 54) with the phosphaalkyne derivative **531** led to the phosphaalkyne complex **532** [531]. The carbene complex **534** was produced when the alkyne complex **533** was treated with the phosphaalkyne **531**. The coupling of trialkyne complex **535** with diphenylacetylene led to the metallacycloheptadiene complex **536** [532].



Tp' = hydridotris(3,5-dimethylpyrazoyl)borate)

Scheme 53.

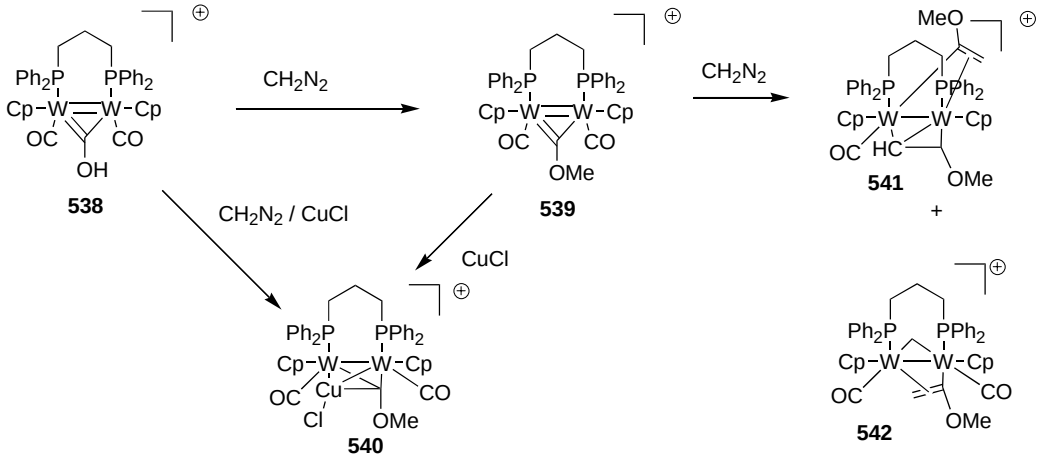


Scheme 54.

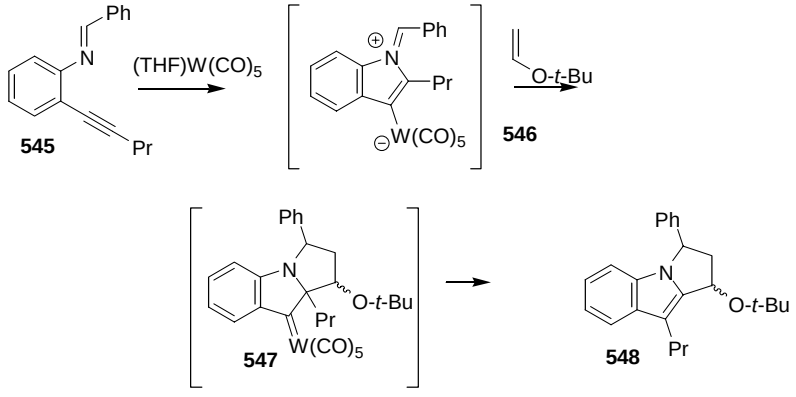
The reaction of bridging hydroxycarbyne complex **538** (Scheme 55) with diazomethane was examined under a variety of conditions [533]. Reaction with 1 eq. of diazomethane led to the corresponding methoxycarbyne complex **539**. Subsequent reaction with cuprous chloride led to the μ^3-carbyne complex **540**. The came complex could be accessed through direct reaction of hydroxycarbyne-ditungsten complex **538** with diazomethane/CuCl. Reaction of original complex **538** with excess diazomethane led to a mixture of complexes **541** and **542**. Formation of **541** was proposed to occur via formation of ketene complex through CO insertion followed by methylation.

Tungsten–carbene complexes (e.g. **547**, Scheme 56) were proposed as intermediates in the tungsten carbonyl-catalyzed conversion of *N*-(2-alkynylaryl)imines (e.g. **545**) to alkyl-shifted indole derivatives (e.g. **548**). Formation of an azomethine ylides (e.g. **546**) followed by cycloaddition, followed by 1,2-alkyl shift and loss of tungsten to afford polycyclic indole derivatives (e.g. **548**) was proposed [534].

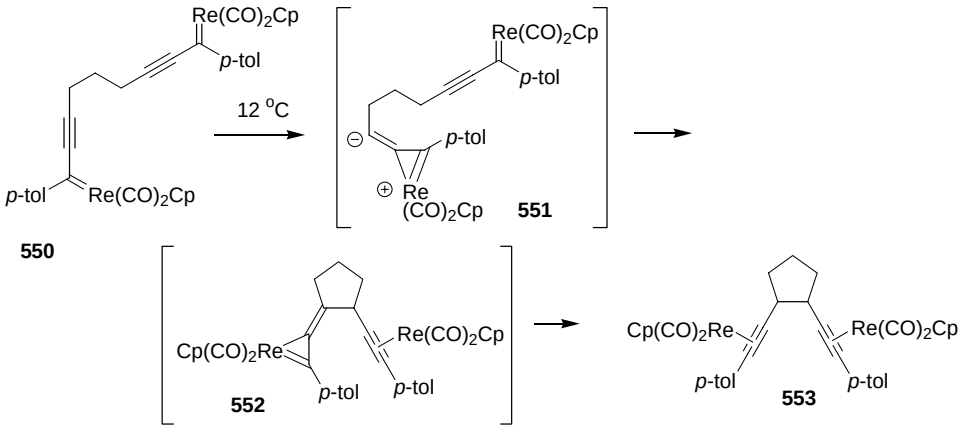
A theoretical study of the structure and bonding in Fischer carbene–chromium complexes was conducted [535]. The emphasis of this study is on the effect of the X and R groups (R: H, Me, vinyl, phenyl, ethynyl and X: OMe, OH, NHMe, NH_2, H). For complexes of general structure $(CO)_5Cr{=}C(X)R$ it was noted that stronger π-electron donors lead to larger $Cr–C_{carbene}$ bond lengths, shorter $Cr–CO_{trans}$ and longer $C{=}O_{trans}$ bond lengths and smaller



Scheme 55.



Scheme 56.



Scheme 57.

Cr–carbene bond dissociation energies. In all of the complexes forward donation is stronger than back donation, however back donation correlates more strongly with most of the observed geometrical and electronic effects. The X substituent has a larger effect on the Cr–$C_{carbene}$ bonding than does the R group.

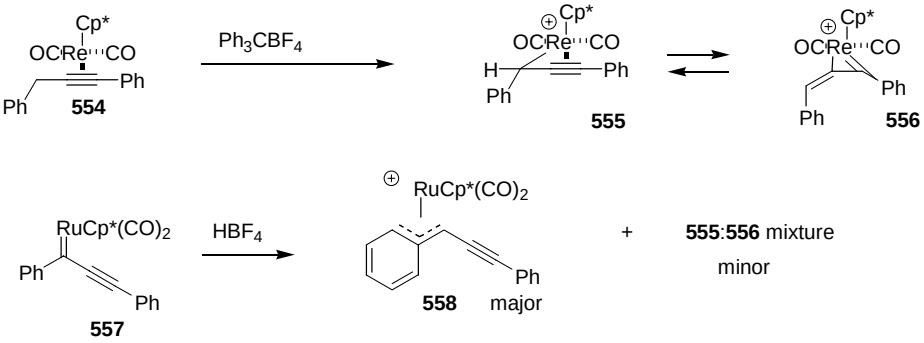
2.3.4. Group VII metal–carbene complexes

Thermolysis of bis(alkynylcarbene-rhenium) complex **550** (Scheme 57) led to cyclization product **553** upon warming to 12 °C [536]. A mechanism involving a 1,1.5-shift of rhenium to afford the rhenametallacyclopropane derivative **551**, followed by intramolecular Michael addition, followed by ring opening was proposed to account for formation of the cyclization product.

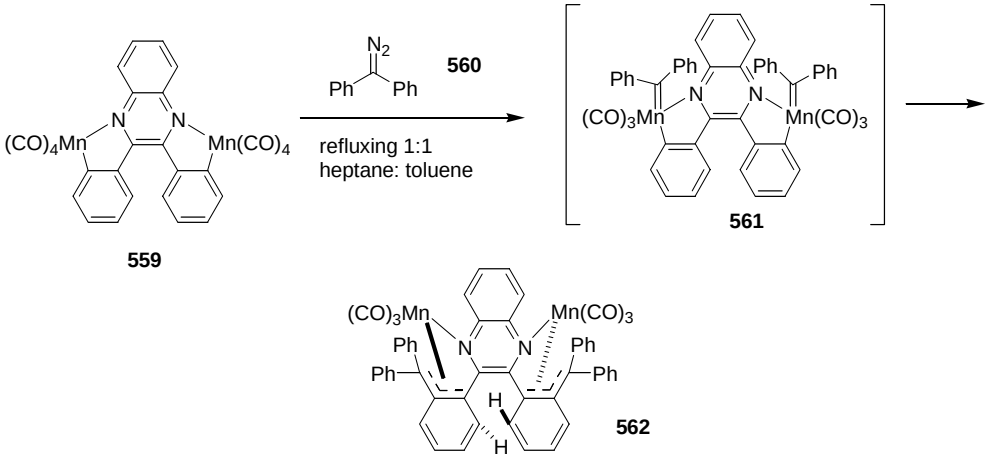
Propargyl hydride abstraction from various rhenium– and molybdenum–alkyne complexes (e.g. **554**, Scheme 58) was reported [537]. The abstraction process affords a mixture of two compounds in equilibrium, the η^3-propargyl complex **555** and the 1-rhena(methylene)cyclopropene complex **556**. If the phenyls were replaced by *p*-tolyl groups, the proportion of metallacyclopropene structure **556** was enhanced. Replacement by *p*-trifluoromethylphenyl groups led to an enhancement in the proportion of **555**. The same complexes were generated as minor products from protonation of alkynylcarbene complex **557**. The formation of 1-rhenacyclopropenes through protonation of η^2-enyne–rhenium complex (coordination to the alkyne) was also reported [538].

The coupling of various cyclomanganated pyridine derivatives (e.g. **559**, Scheme 59) with various diaryldiazomethane derivatives (e.g. **560**) was reported [539]. The process involves formation of a carbene complex (e.g. **561**), which undergoes an insertion to form the observed product **562**. Manganese carbene complexes are likely intermediates in the synthesis of manganese–fluorene complexes from diazofluorene [540].

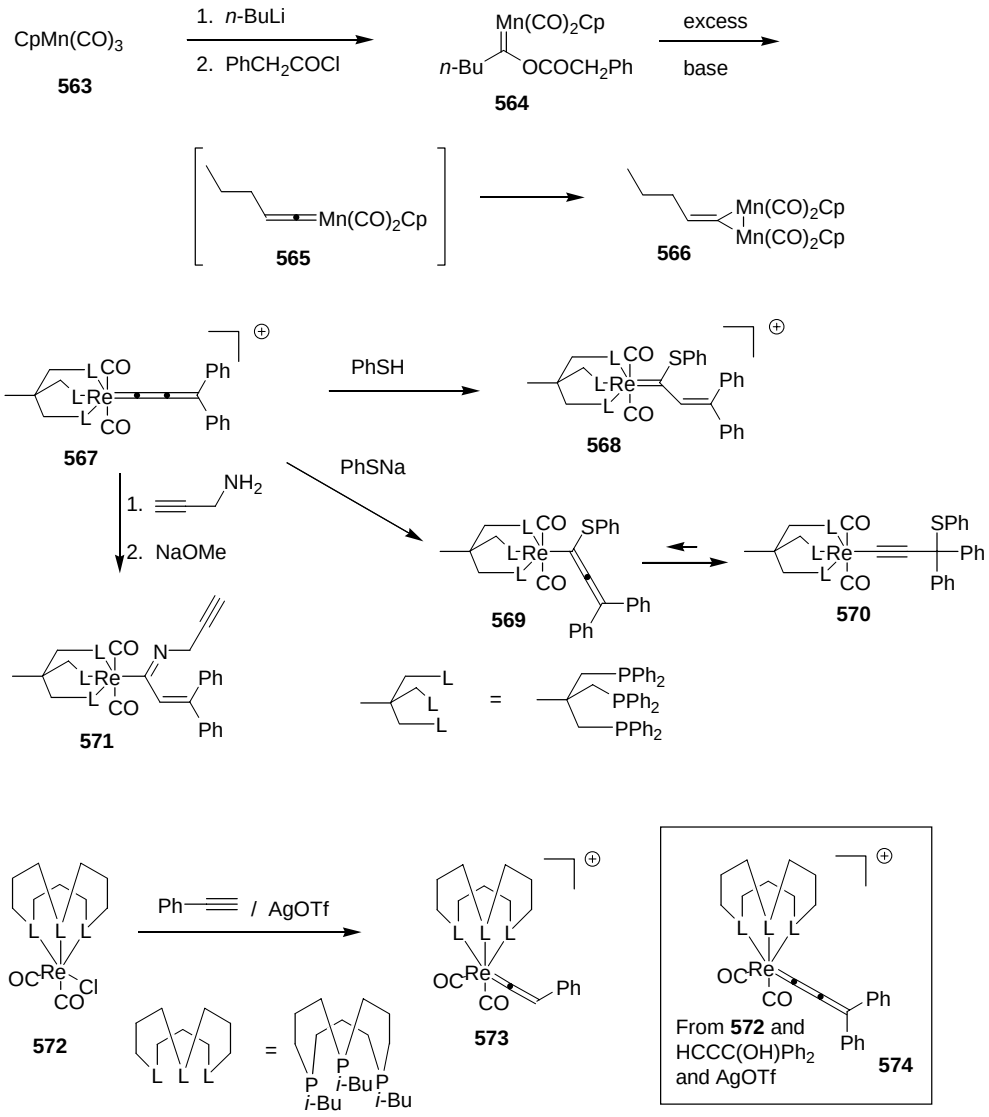
Several examples of group VII metal–cumulene complexes were reported in 2002. An acyloxycarbene–manganese complex (**564**, Scheme 60) was produced in the coupling $CpMn(CO)_3$ with *n*-butyllithium followed by phenylacetyl chloride [541]. Treatment of the acyloxycarbene complex with excess base led to the vinylidene complex **565**, which decomposed to afford the bridging vinylidene-dimanganese complex **566**. The reaction of rhenium allenylidene complex **567** with a variety of nucleophilic substances was reported [542]. In most cases, the reaction proceeded by nucleophilic addition at the α-position followed by protonation at the β-position to afford the alkenylcarbene complex (e.g. formation of **568**). Under basic conditions, the initially-formed allenyl complex **569** isomerized to the alkynyl complex **570**. Formation of cyclic alkoxycarbene complexes through



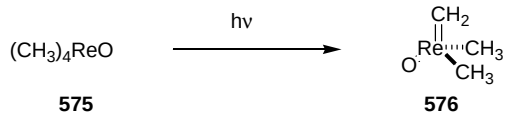
Scheme 58.



Scheme 59.



Scheme 60.



Scheme 61.

reaction of rhenium carbonyl species with alkyne–alcohols was also reported [543]. Rhenium vinylidene complexes (e.g. **573**) or rhenium allenylidene complexes (e.g. **574**) were formed in the reaction of rhenium halide **572** with either simple terminal alkynes or propargyl alcohols [544]. Oxidative dimerization of manganese–vinylidene complexes [e.g. $Cp^*(CO)_2Mn{=}C{=}CHPh$] to the conjugated carbon-linked dimanganese complexes [e.g. $Cp^*(CO)_2Mn{=}C{=}C(Ph)C(Ph){=}C{=}Mn(CO)_2Cp^*$] was reported [545]. A computational study of the conversion of $(\eta^2\text{-}HC{\equiv}CH)Mn(CO)_2Cp$ to the corresponding vinylidene complexes was reported [546]. The most energetically reasonable process involves formation of an agnostic C–H bond followed by 1,2-migration of the H-atom.

Rhenium carbene complexes (e.g. **576**, Scheme 61) were generated from low-temperature matrix photolysis of either tetramethyloxorhenium (**575**) or trimethyldioxorhenium [547,548]. The methylidene complex was determined to be the primary photoproduct and was assigned on the basis of its infrared spectrum in comparison with the vibrational spectrum calculated by DFT. Continued photolysis of trimethyldioxorhenium resulted in a bis(methylidene) derivative.

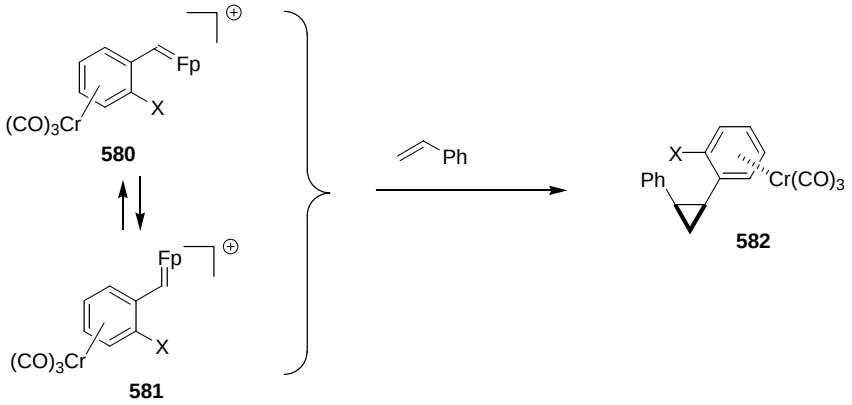
2.3.5. Group VIII metal–carbene complexes

2.3.5.1. Cationic metal–carbene complexes that are not cumulenes. Conformational preferences for chiral iron–carbene complexes (e.g. **580**, **581**, Scheme 62) were examined [549]. Conformational preferences were attributed to a balance of steric and electronic effects. Conformer **581** is favored when $X = CH_3$ due to steric interactions between X and the iron group. When X = OMe, both conformers are present in equal amounts; complex **580** (X = OMe) is stabilized by a favorable electrostatic attraction of the oxygen lone pair and the positively charged iron. Much higher ee's were observed for cyclopropanation reactions when carbene complexes favoring one conformation (i.e. in the case where $X = CH_3$) were involved.

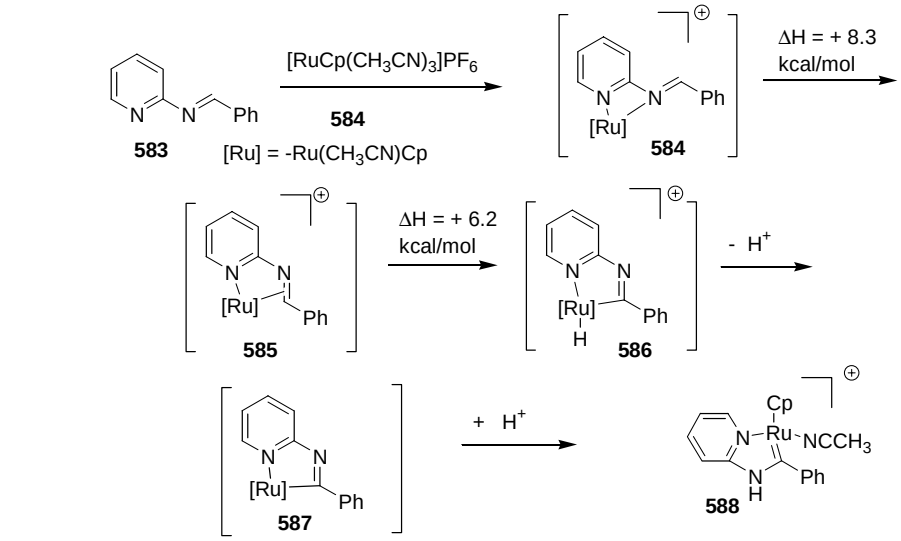
Cationic ruthenium–carbene complexes (e.g. **588**, Scheme 63) were prepared through a C–H activation reaction using imine **583** and ruthenium complex **584** [550]. The mechanism depicted in Scheme 63 has been proposed to account for carbene complex formation. The reaction process was evaluated computationally and found to be exothermic by 8.0 kcal/mol. Conversion of the dintrogen chelate (**585**) to the *N*-π-imine chelate (**586**) was the most endothermic step (+8.3 kcal/mol). Similar carbene complexes were prepared by reaction of aminopyridines with terminal alkynes in the presence of ruthenium halides [551].

Additional studies of this class of compounds are depicted in Scheme 64. Ruthenium–carbene complex **591** was generated through protonation of the alkenylruthenium complex **590** [552]. The carbene complex was converted back into the neutral alkenylruthenium complex by treatment with KO-*t*-Bu. A cationic bridging carbyne complex (**593**) was generated from bridging carbene complex **592** using HBF_4 [553]. Reaction with $LiN(TMS)_2$ led to the cyclooctylamine derivative **594**. Reaction with $LiNEt_2$ led to the ring-opened bridging carbene complex **595**. Reaction of cationic bridging carbyne-iron complexes with metal carbonyl anions was also reported [554]. A dicationic ruthenium–carbene complex (**597**) was generated from the electrochemical oxidation of polyene-bridged diruthenium complex (**596**) [555]. Cationic carbene complexes (e.g. **598**) were formed upon protonation of vinylruthenium complexes (e.g. **599**) [556] or dienylruthenium complexes [557].

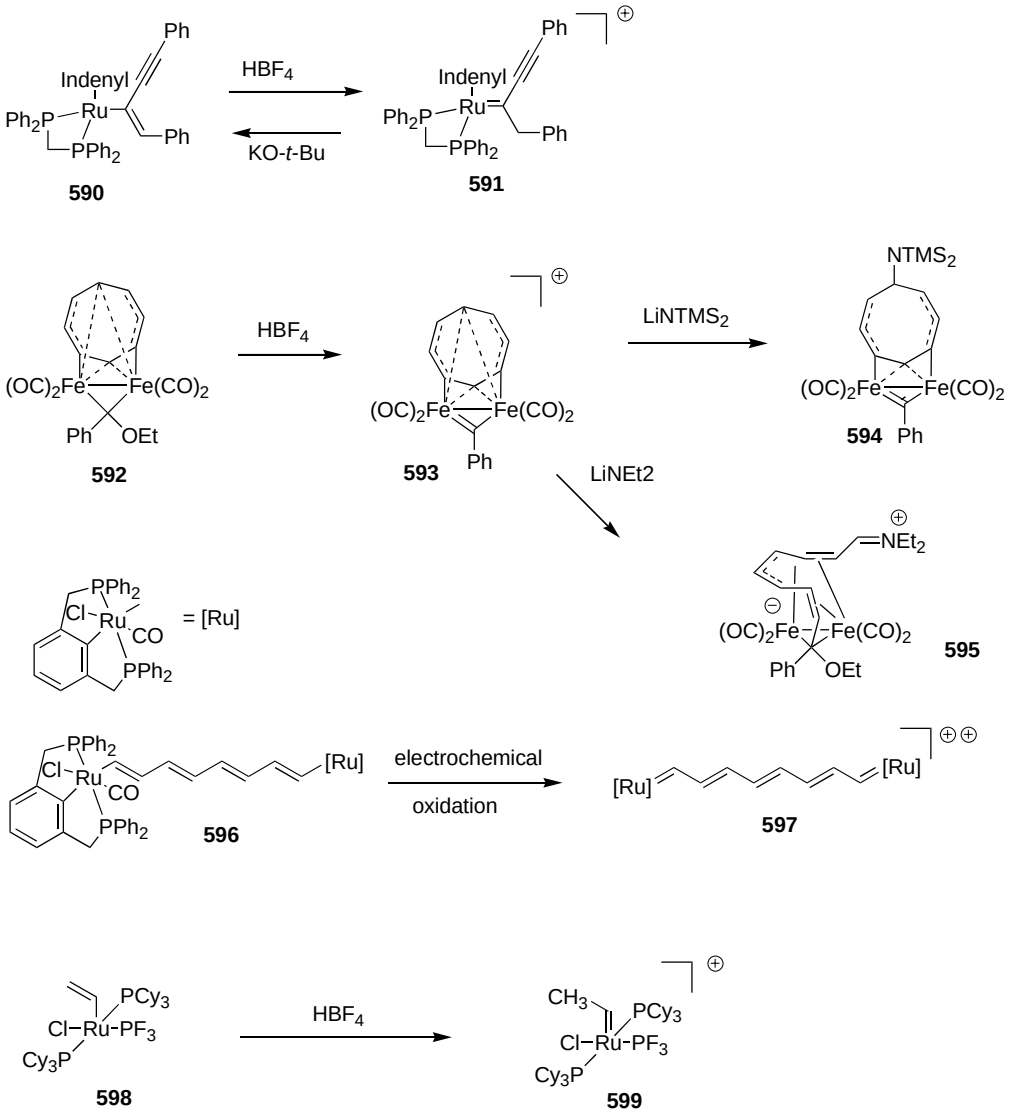
Osmium carbene complexes were considered as intermediates in the H–D isomerization for cationic $Os(D)CH_3$ complexes [558], however this mechanism event was not favored since the requirement for phosphine dissociation was inconsistent with the observed kinetics.



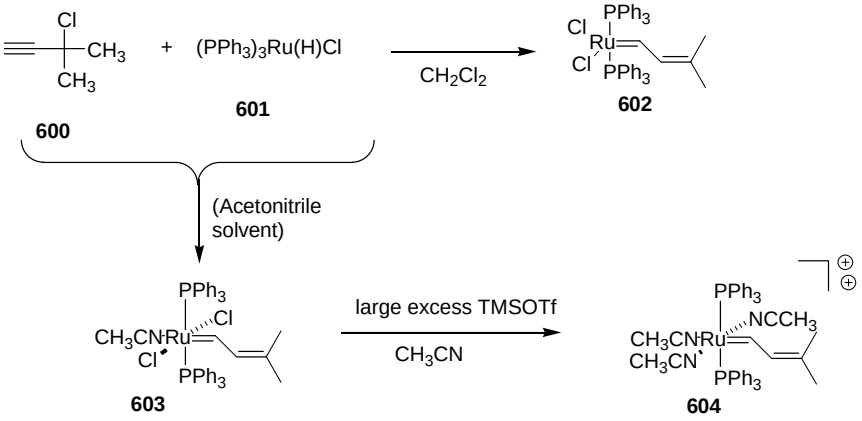
Scheme 62.



Scheme 63.



Scheme 64.



Scheme 65.

2.3.5.2. 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 catalyst falls into this classification.

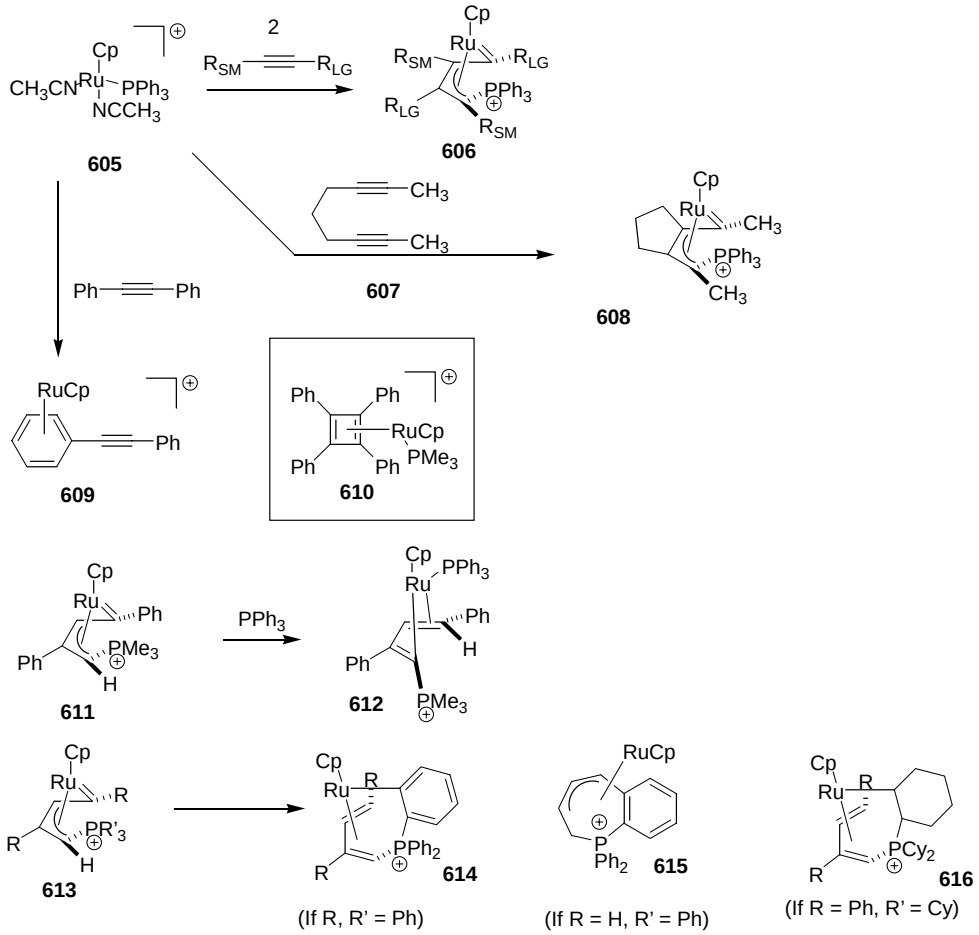
Alkenylcarbene–ruthenium complexes were prepared through the reaction of ruthenium hydride complex $(PPh_3)_3$ Ru(H)Cl (**601**, Scheme 65) with 3-chloro-3-methyl-1-butyne (**600**) [559,560]. A related complex was formed using 3-chloro-1,1-diphenyl-1,3-propadiene. An acetonitrile-coordinated complex (**603**) was produced when the synthesis was conducted in acetonitrile. Treatment of **603** with a large excess TMSOTf led to formation of dicationic carbene complex **604**. A variety of ligand substitution processes were reported for these complexes.

Various π-allyl(carbene)ruthenium complexes (e.g. **606**, Scheme 66) were prepared through the coupling of two moles of an alkyne (or a diyne) with ruthenium complex **605** [561]. The reaction was completely regioselective with terminal alkynes. Unsymmetrical internal alkynes formed mixtures favoring the isomer depicted by structure **606**. Reaction of complex **605** with diynes (e.g. **607**) led to cyclized complexes (e.g. **608**). Reaction with diphenylacetylene afforded arene complex **609**; the reaction using the trimethylphosphine analog of **605** led to cyclobutadiene complex **610**. Formation of vinylidene complexes occurred when trimethylsilylacetylene or ethynylferrocene was treated with ruthenium complex **605**. Proposed mechanisms for formation of these complexes were evaluated by DFT calculations. Intramolecular C–H activation reactions of π-allylcarbene–ruthenium complexes were also reported [562]. Coupling of the π-allyl complex **611** with PPh_3 led to the butadienyl complex **612**. Coordination of triphenylphosphine occurs along with migration of a hydride ligand. Complexes of general structure **613** decompose to form intramolecular C–H activation products **614–616**. Studies of the synthesis and reactivity of π-allyl(carbene) iron complexes were also reported [563].

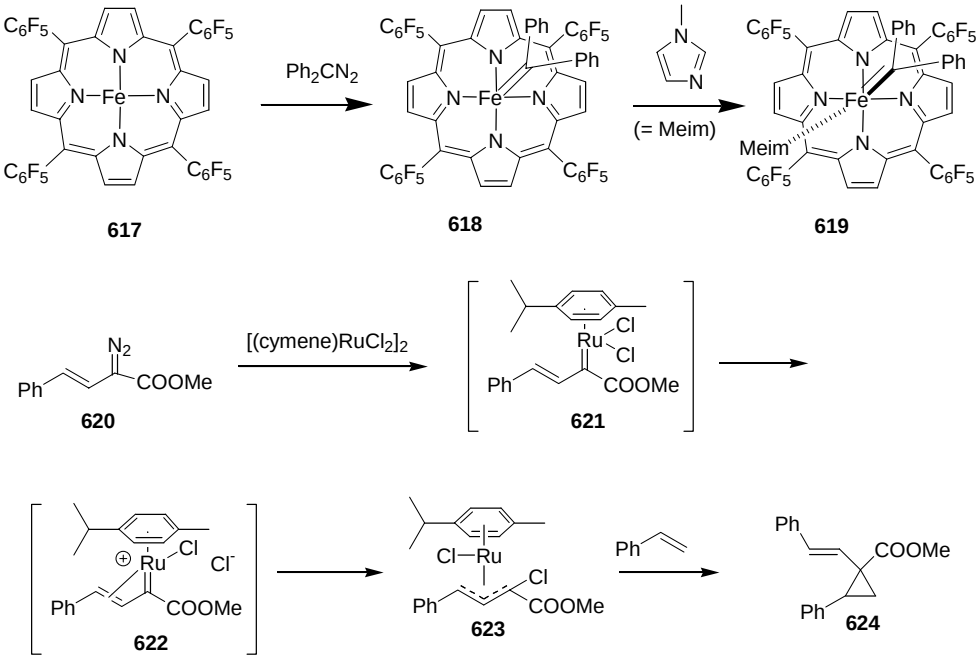
Several papers in 2002 reported on the direct formation of group VIII metal carbene complexes from the reaction of diazo compounds with metal complexes. Coupling of the iron porphyrin complex **617** (Scheme 67) with diazo compounds followed by *N*-methylimidazole led to isolable metal–carbene complexes (e.g. **619**) [564]. Complex **617** is also a catalyst for cyclopropanation of alkenes by diazo compounds. Other metal–carbene-porphyrin complexes were also synthesized from diazo compounds [565,566]. Preparation of ruthenium–carbene complexes through reaction of ruthenium complexes that feature an Arduengo-type carbene ligand with diazo compounds was reported [567]. These compounds could also be prepared through exchange of phosphine ligands of ruthenium–carbene–phosphine complexes. Allylruthenium complexes (e.g. **623**) were produced in the reaction of α,β-unsaturated diazoesters (e.g. **620**) with $[(p\text{-cymene})RuCl_2]_2$ complexes (e.g. **620**) [568]. Formation of a carbene complex (**621**) from the diazo compound followed by transfer of chloride to the carbene complex was proposed. The chloroallyl complexes can successfully cyclopropanate styrene, possibly through formation of a carbene complex by α-elimination.

Other studies of carbene complexes in this category are depicted in Scheme 68, and include: (1) formation of an aldol-like product (**626**) from the base-free coupling of triosmium carbene complex **625** with aldehydes [569]; and (2) [2+2]-cycloaddition reaction between ruthenium acetylides (e.g. **627**) and tetracyanoethylene followed by opening to give a dienylruthenium species (e.g. **628**) featuring contribution from zwitterionic carbene complex resonance form **629** [570].

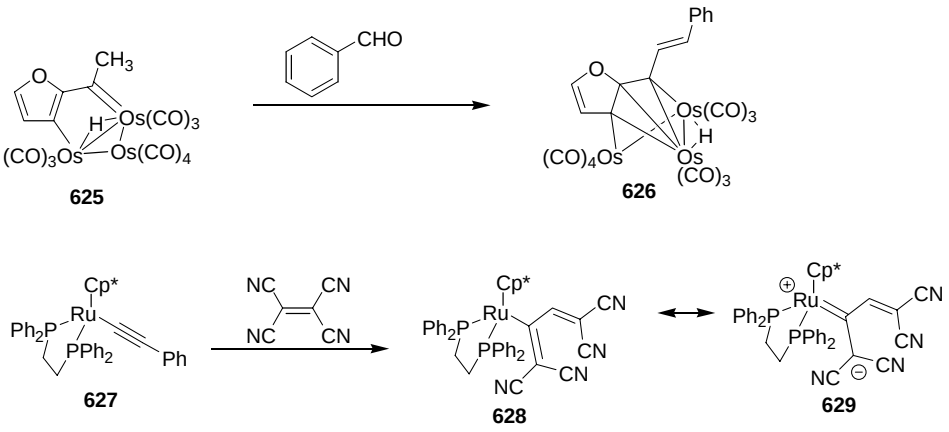
2.3.5.3. Heteroatom-substituted group VIII metal–carbene complexes. Coupling of ruthenium hydride complex **630** (Scheme 69) with cyclic ethers or cyclic amines led to alkoxycarbene complexes (e.g. **631**, **634**) or aminocarbene complexes (e.g. **633**) accompanied by ruthenium hydride **632** [571]. All of the ruthenium was converted to the carbene complex if 3,3-dimethyl-1-butene was added to absorb H_2. Similar reactions were noted for osmium analogs. Formation of chelating aminocarbene–ruthenium complexes (e.g. **636**) through triple C–H activation of amine-containing diphosphines (e.g. **635**) was also noted [572]. Analogous



Scheme 66.



Scheme 67.

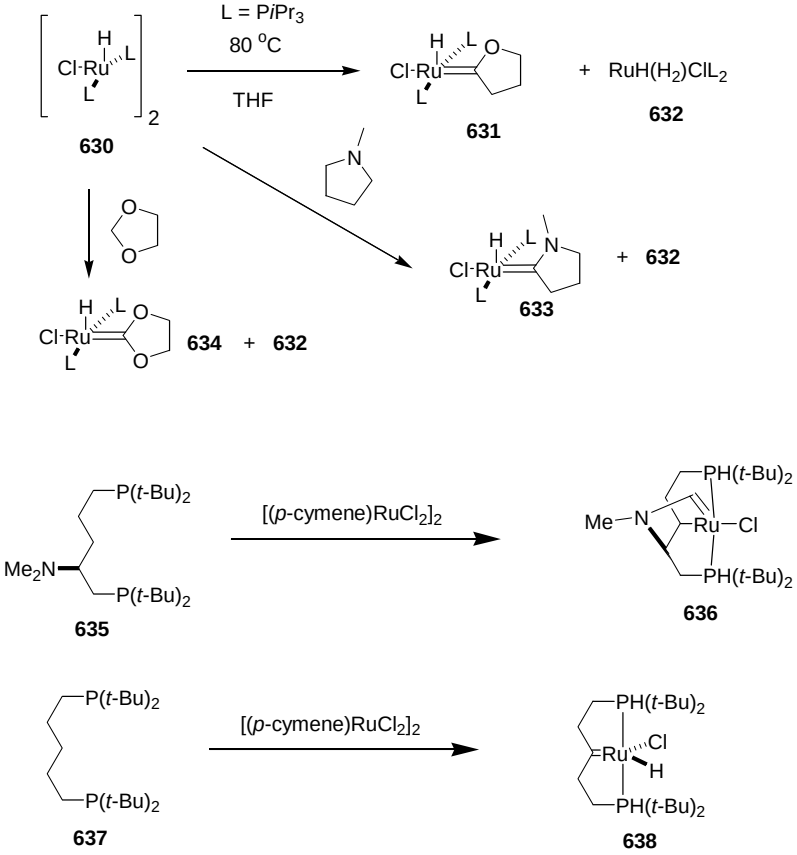


Scheme 68.

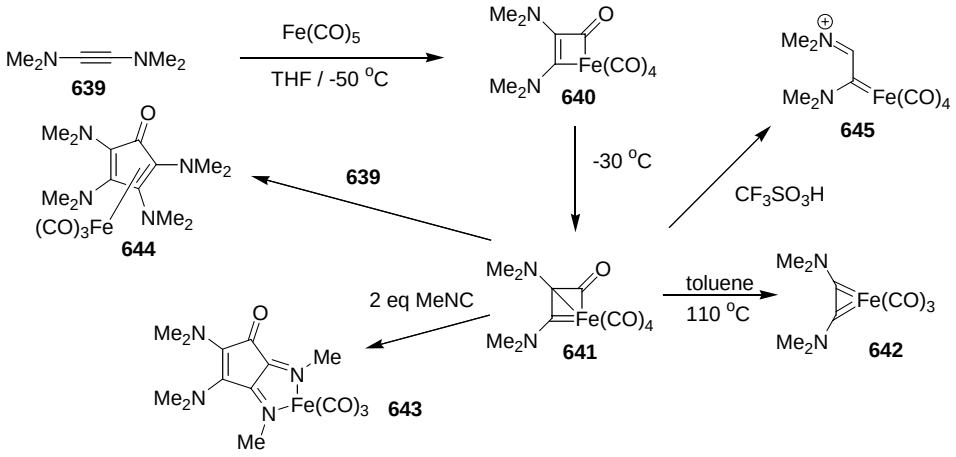
ruthenium and osmium carbene complexes (e.g. **638**) were prepared though double C–H activation on the ligands (e.g. **637**) [573].

A Fischer carbene iron complex (**641**, Scheme 70) was formed from the reaction of bis(amino)alkyne **639** and iron pentacarbonyl [574]. Simple thermolysis afforded the 4e-donor alkyne, or bis(carbene) complex **642**. Reaction with two moles of methyl isocyanide led to the cyclopentenone derivative **643**. Reaction with an additional equivalent of alkyne **639** led to the cyclopentadienone iron complex **644**. Protonation afforded the cationic iron carbene complex **645**.

The reaction of bridging thiocarbyne–diiron complexes (e.g. **647**, Scheme 71) with dithiocarbamate ligands was examined [575]. Coupling of complex **647** with dithiocarbamate **648** reaction led to formation of the bridging carbene–diiron adduct **649** and the diiron-bridged thiocarbyne adduct **650**. Photolysis effected the conversion of **649**



Scheme 69.

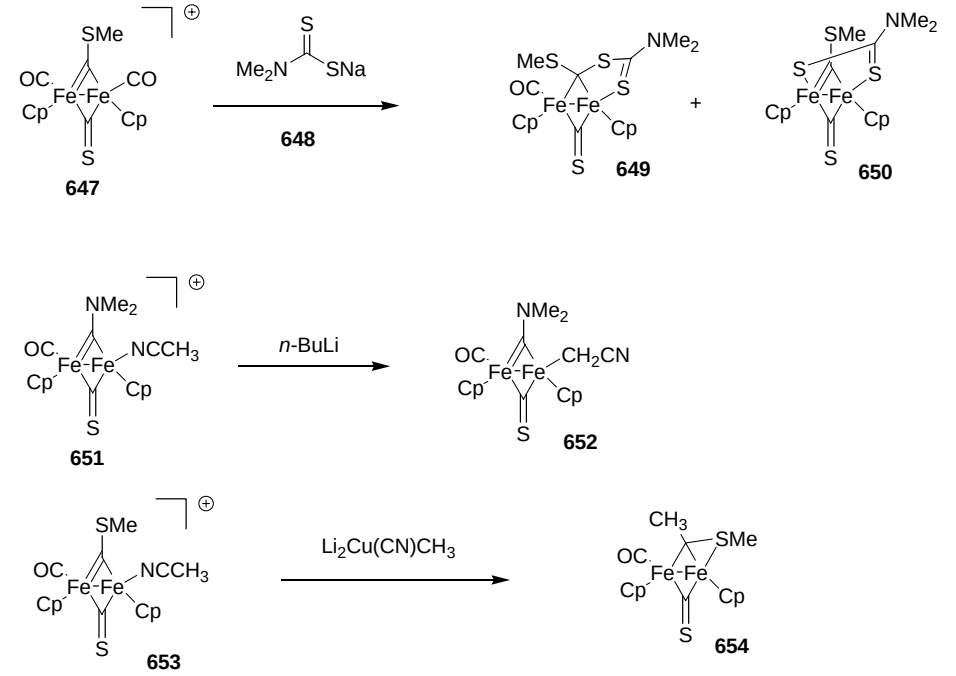


Scheme 70.

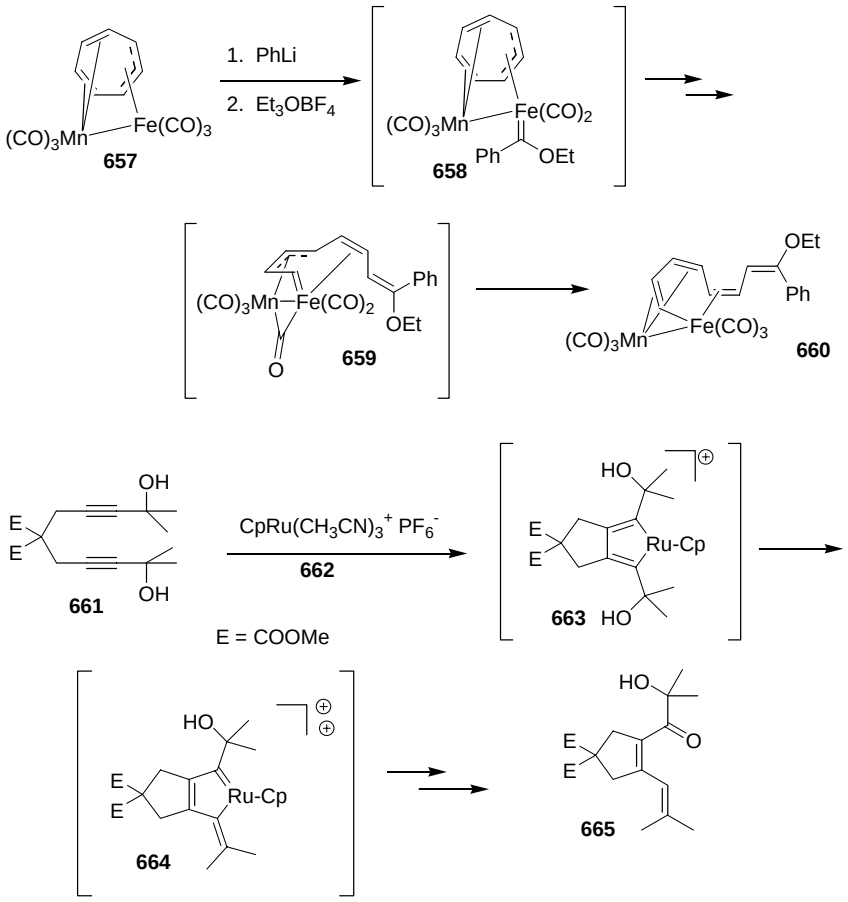
into **650**. Activation of the starting material by replacement of a CO with acetonitrile followed by reaction with the dithiocarbamate ligand led directly to the formation of **650**. The reaction of related diiron–carbyne complexes (e.g. **651**, **653**) with alkylmetal reagents was reported [576]. This reaction of aminocarbyne–diiron complex **651** with *n*-butyllithium led to conversion of the acetonitrile ligand to a $–CH_2CN$ ligand. Similar reactions were noted for the analogous thiocarbene complexes. Reaction of thiocarbyne complex **653** with cuprates however afforded compounds from addition to the carbene carbon (e.g.**654**).

Additional reports propose the intermediacy of carbene complexes in this class. These processes are depicted in Scheme 72, and include: (1) generation of an iron–carbene complex intermediate (e.g. **658**) as an intermediate in the transformation of iron–manganese complex **657** into polyene-ligated heterobimetallic systems (e.g. **660**) [577]; and (2) formation of a dicationic ruthenium–carbene complex (e.g. **664**) as an intermediate in the ruthenium-catalyzed conversion of bis(propargylic) alcohols (e.g. **661**) to cyclic dienones (e.g. **665**) [578].

2.3.5.4. Group VIII metal–vinylidene complexes. Many examples of the formation of metal–vinylidene complexes (**670**, Scheme 73) via coupling of coordinatively unsaturated group VIII metal complexes with terminal or silylated alkynes were reported in 2002. Representative examples are depicted in Fig. 13. Common reaction pathways for



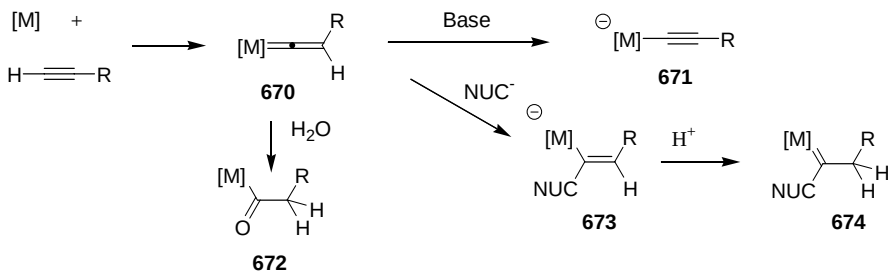
Scheme 71.



Scheme 72.

these complexes include reaction with nucleophiles to form vinylmetal species (**673**), reaction with alcohols (or amines) to form Fischer carbene complexes (**674**) or water to form metal acyls (**672**), and deprotonation at the β-position to form alkynylmetal complexes (**671**). Other common synthetic routes to metal–vinylidenes included addition of electrophiles to metal acetylide complexes (e.g. the reverse of the reaction synthesizing **671**), and treatment of acylmetal complexes with dehydrating agents (i.e. the reverse of the reaction synthesizing **672**).

Specific reports which highlight the reaction pathways of Scheme 73 are depicted in Fig. 13 and include: (1) preparation of cyclic Fischer carbene–ruthenium complexes (e.g. **675**) through reaction of alkynols with (η^5-indenyl)L_2RuCl complexes (L = phosphine) [579]; (2) reaction of neutral ruthenium vinylidene complexes (e.g. **676**) with thymine and uracil to form internally-ligated Fischer carbene complexes (e.g. **677**) [580]; and (3) generation of ruthenium vinylidene complexes featuring pincer ligands (e.g. **679**) from ruthenium complex **678** and terminal alkynes or silylated alkynes [581]. Many papers in 2002 invoke the processes in Scheme 73 for generation of vinylidene–metal complex reaction intermediates, including: (1) formation of Cp-chelates (e.g. **681**) from terminal alkynes and (acetylCp)-ruthenium halides (via intermediate cationic vinylidene complex **680**) [582]; (2) formation of alkynyl-iron complexes from terminal alkynes, iron iodides and base [583]; (3) formation of ruthenium dendrimers through



Scheme 73.

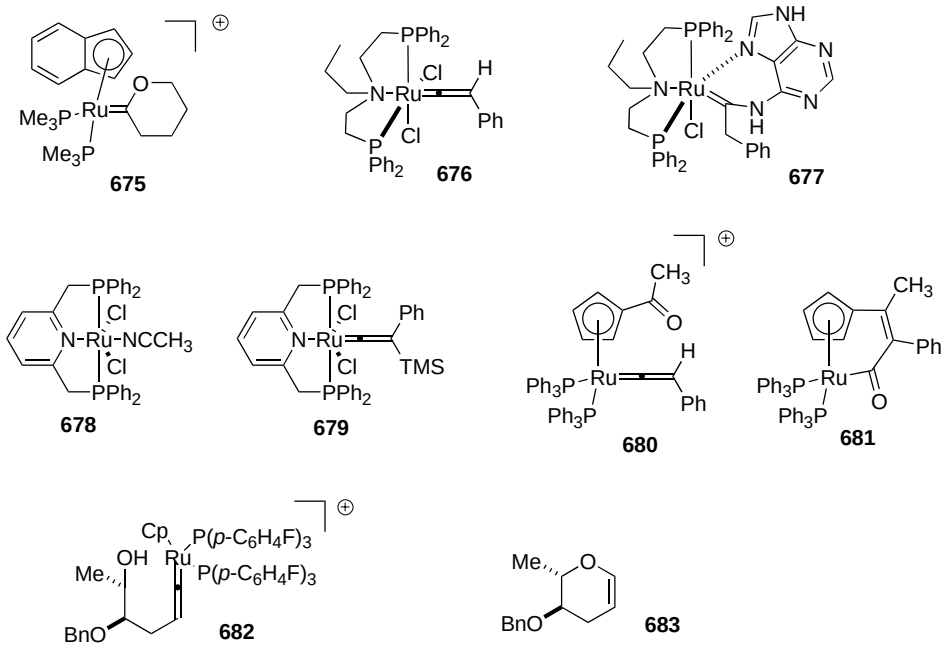


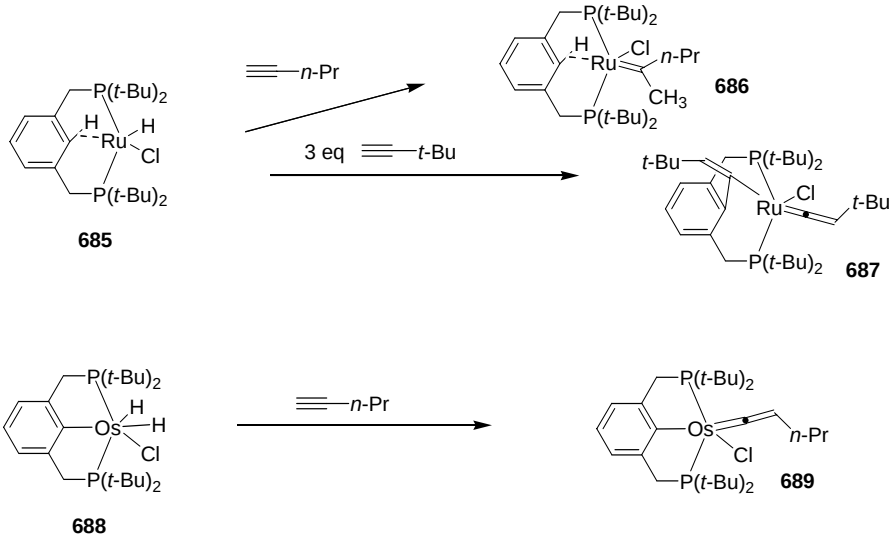
Fig. 13. Representative group VIII metal–vinylidene complexes reported in 2002.

reaction of trialkynyltriruthenium complexes with terminal alkynes in the presence of base [584]; and (4) formation of cyclic enol ethers (e.g. **683**) or cyclic esters from treatment of alkynols with (Cp)ClRu(PR_3)$_2$ complexes (via intermediate vinylidene complex **682**) [585].

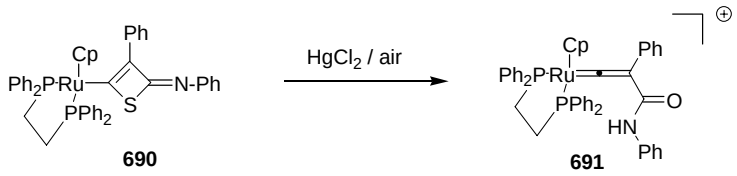
The coupling of ruthenium or osmium hydride complexes (e.g. **685**, **688**, Scheme 74) with terminal alkynes was reported [586]. Reaction of the ruthenium complex with one mole of 1-pentyne afforded the carbene complex **686**. A vinylidene complex (**687**) was formed from reaction with excess *t*-butylacetylene. A vinylidene complex was formed from coupling of osmium complex **688** with terminal alkynes. The progress of the reaction was monitored by low temperature NMR studies. Formation of the vinylidene complex appears to proceed through alkyne insertion to form an alkenylosmium monohydride, followed by β-hydride elimination and loss of hydrogen to afford the π-alkyne–osmium complex, followed by conversion to the vinylidene complex.

Ruthenium vinylidene complex **691** (Scheme 75) was produced by treatment of ruthenium sulfur heterocycle complexes (e.g. **690**) with $HgCl_2$ in the presence of air [587].

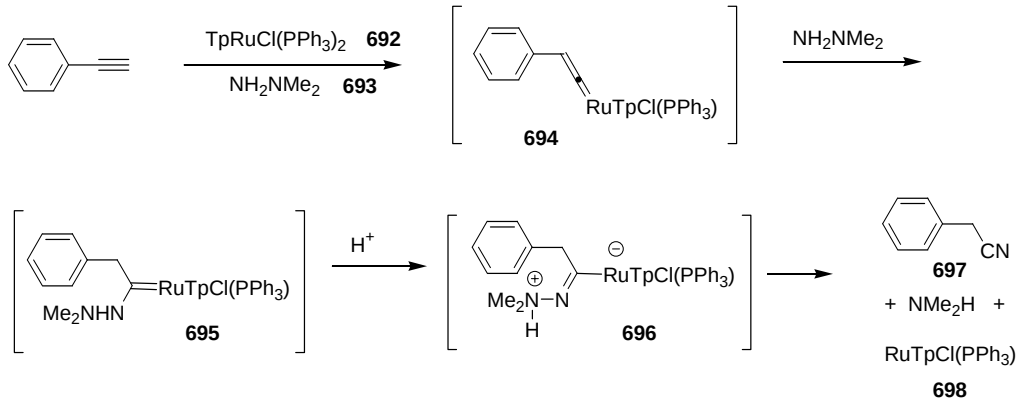
Ruthenium vinylidene (e.g. **694**, Scheme 76) and carbene complexes (e.g. **695**) have been proposed as intermediates in the ruthenium-catalyzed conversion of terminal alkynes and hydrazines to nitriles [588]. The proposed mechanism involves formation of the vinylidene complex followed by



Scheme 74.



Scheme 75.



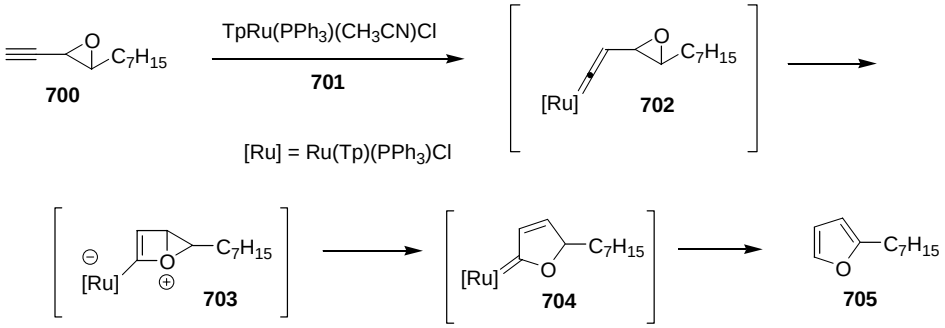
Scheme 76.

conversion to the hydrazinocarbene complex. Proton transfer to the distal nitrogen and elimination of amine affords the nitrile and regenerates the catalytically active species (**698**).

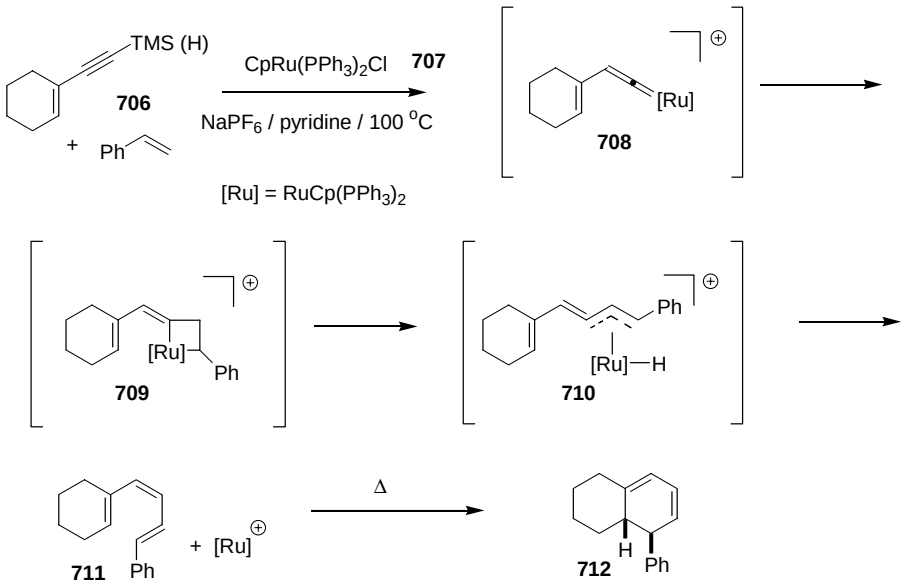
Ruthenium vinylidene complexes (e.g. **702**, Scheme 77) have been proposed as intermediates in the ruthenium-catalyzed isomerization of acetylenic epoxides (e.g. **700**) to furans (e.g. **705**) [589]. A mechanism involving initial formation of a ruthenium vinylidene complex (**702**), followed by nucleophilic attack of the epoxide oxygen at the carbene carbon, followed by ring opening to afford the Fischer carbene complex (**704**) was proposed, which undergoes demetallation to afford the furan. The proposed mechanism was supported by deuterium labeling studies.

Metal–vinylidenes (e.g. **708**, Scheme 78) were suggested as intermediates in the ruthenium-catalyzed cycloaddition of enynes (e.g. **706**) and simple alkenes to form cyclohexadienes (e.g. **712**) [590]. A mechanism involving formation of a vinylidene complex, followed by [2+2]-cycloaddition of the alkene to the ruthenium–carbon double bond, followed by β-hydride elimination, followed by reductive elimination to form triene **711** and thermal electrocyclic ring closure was proposed. In some cases, the triene intermediate could be isolated at short reaction times.

2.3.5.5. Group VIII metal complexes of higher cumulenes. Metal–higher cumulene complexes (**716**, **720**, Scheme 79) are produced from the coupling of coordinatively unsaturated group VIII metal complexes with propargyl alcohols that contain no hydrogens β- to the OH group, or by addition of electrophiles to the δ-carbon of alkenylethynyl–metal complexes (**719**). A variety of reaction processes of group VIII metal–cumulene complexes were reported in 2002. Common reaction pathways for these complexes include reaction with nucleophiles at the γ-position, resulting in alkynylmetal complexes (**717**), or attack at the α-position, resulting in allenylmetal complexes (**718**). Representative examples of this class of compounds are depicted in Fig. 14.



Scheme 77.

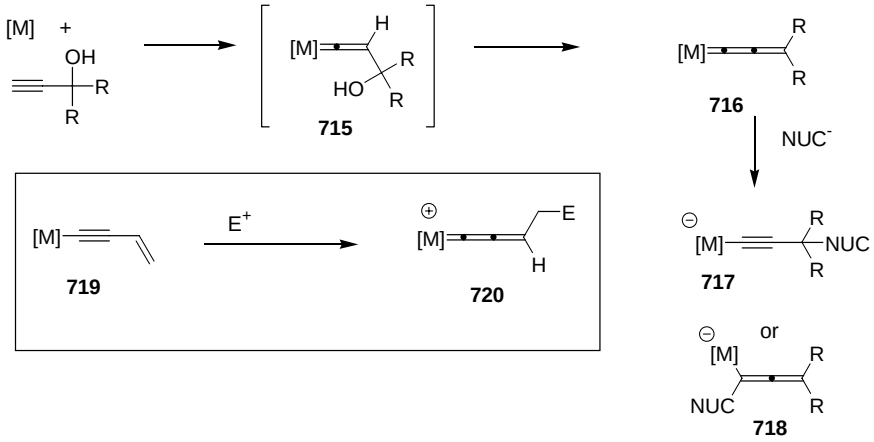


Scheme 78.

Specific reports which highlight the reaction pathways depicted in Scheme 79 are depicted in Fig. 14, and include: (1) synthesis of optically active cationic ruthenium allenylidene complexes (e.g. **720**), followed by moderately diastereoselective (2:1 with cyclopentenone enolate) reaction with ketone enolates to afford neutral acetylene complexes (e.g. **721**), followed by reaction with HBF_4 and acetonitrile to afford the free acetylenes [591] and related studies involving Grignard reagents as nucleophiles [592]; (2) formation of an equilibrium mixture of a cationic allenylidene complex (**722**) and alkenylvinylidene complex (**723**) from a steroidal-alkynol derivative and (η^5-indenylruthenium)$Ru(PPh_3)_2Cl$, and subsequent reactions with basic and nucleophilic reagents [593]; (3) formation of cationic osmium–allenylidene complexes (e.g. **724**), followed by reaction with methanol to form the α,β-unsaturated carbene complexes (e.g. **725**) or reaction with trimethylphosphine to form allenyl complexes (e.g. **726**) [594]; and (4) synthesis of cationic allenylidene–iron complexes from reaction of iron(II) chloride, triethylphosphite, triethylamine, and 1,1-diphenyl-2-pyropyn-1-ol [595].

Stepwise formation of ruthenium allenylidene complexes (e.g. **732**, Scheme 80) from propargyl alcohols was reported [596]. Subsequent reaction with nucleophiles (e.g. pyrrole) led to products resulting from attack at the γ-position (e.g. **733**). A dicationic alkenylcarbyne complex **734** could be produced upon protonation of the cationic allenylidene complex. Cationic allenylidene complexes (e.g. **736**) and vinylidene complexes were prepared from the corresponding ruthenium halide [597]. Vinylidenes (e.g. **738**) were also prepared from reaction of ruthenium–dihydrogen complex **737** with acetylene. Protonation of **738** afforded a cationic carbyne complex (**739**). The carbyne complex **739** is more active than Grubbs catalyst I for ROMP of cyclooctene.

Various cycloaddition processes were reported for allenylidene–metal complexes. Diels–Alder reactions were



Scheme 79.

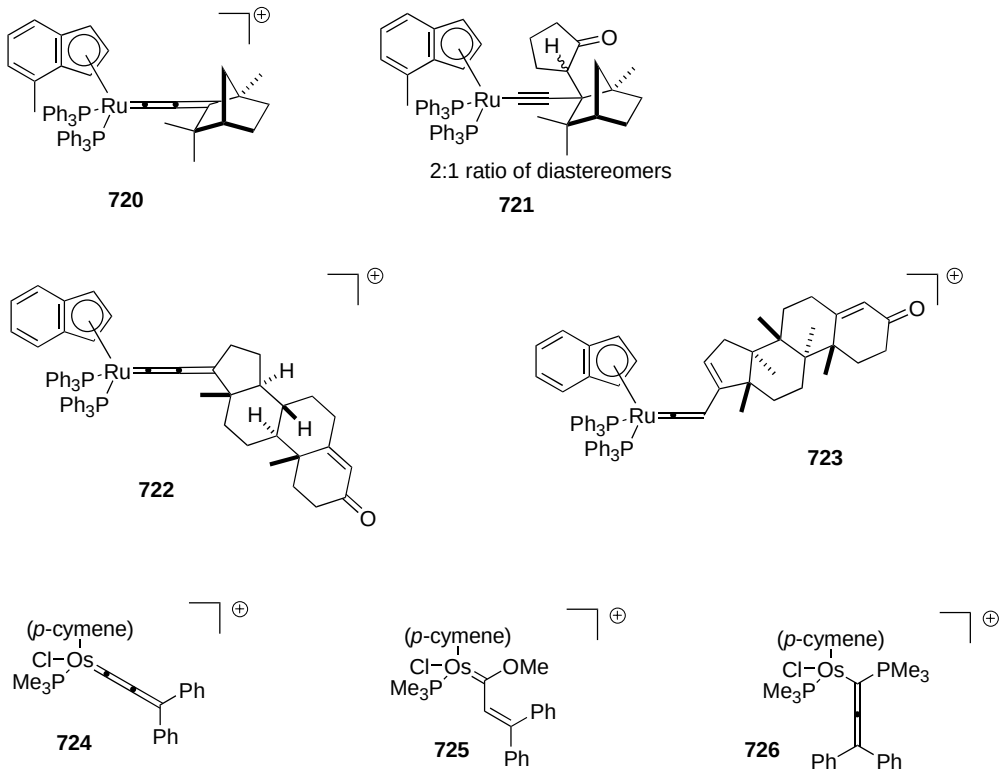
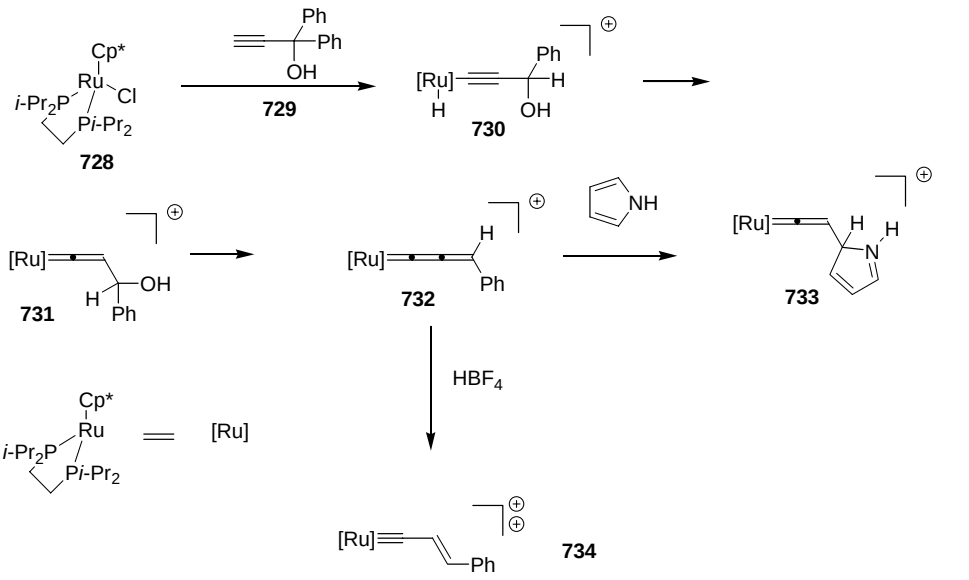


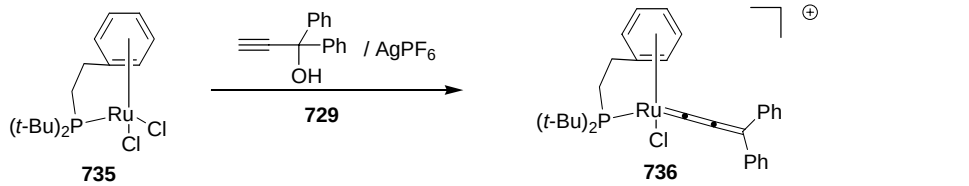
Fig. 14. Representative group VII metal–higher cumulene complexes reported in 2002.

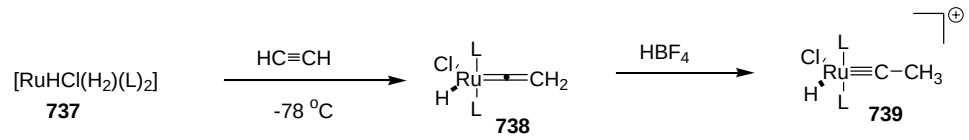
reported for cationic ruthenium allenylidene complexes (e.g. **742**, Scheme 81) [598]. Reaction occurs selectively at the β,γ-alkene to afford high yields of Diels–Alder adducts (e.g. **745**) using isoprene and 1,3-cyclohexadiene. Reaction of cationic allenylidene complexes (e.g. **746**) with ynamines (e.g. **747**) was reported [599]. Aminoallenylidene complexes (e.g. **749**) were produced via [2+2]-cycloaddition followed by ring opening. Hydride reduction of complex **749** occurred at the γ-position to afford an alkynylruthenium complex.

Coupling of allenylidene complex **750** (Scheme 82) and butadiynylruthenium complex **751** led to highly conjugated diruthenium complex **755** [600]. The observed coupling product was obtained through proton transfer to afford the simple butatrienylidene/enynylruthenium (**753**/**752**) pair followed by nucleophilic addition of the enynyl complex to the allenylidene complex to form **754**, followed by isomerization to the completely conjugated species **755**. Cyclic voltammetry studies were conducted for this compound. Similar complexes (e.g. **756**) were subjected to oxidation by ferrocenium ion [601]. The cationic allenylidene **757** and vinylidene complex **758** were produced from oxidation of complex **756**. Formation of a radical cation followed by disproportionative hydrogen atom abstraction was proposed. If the reaction was performed in the presence of tributyltin hydride, the vinylidene complexes were the exclusive products. Oxidation followed by treatment with cobaltocene afforded mostly the starting material accompanied by minor amounts of vinylidene complexes.

Group VIII metal complexes of higher cumulenes have been proposed as intermediates in several processes. Ruthenium–allenylidene complexes (e.g. **763**, Scheme 83) were suggested as intermediates in the propargylation of aromatic compounds (e.g. methylfuran, **761**) using propargyl alcohols (e.g. **760**) in the presence of $[Cp^*RuCl(\mu_2\text{-}SMe)]_2$ (**762**) [602]. A stoichiometric version of this reaction was also demonstrated. Naphthol derivatives were also propargylated using this catalyst [603], ultimately resulting in cyclic ether derivatives (e.g. **768**). Formation of a Fischer carbene complex (**766**) from allenylidene **763**, followed by a Cope-like rearrangement of the resulting alkynylcarbene complex to afford the vinylidene complex (**767**), followed by ring closure was proposed to account for formation of **768**. Cationic ruthenium allenylidene complexes were proposed as intermediates in the disproportionative formation of conjugated dienes and benzaldehydes from propargyl benzyl ethers [604]. Allenylidene complexes (e.g. **770**) are likely involved in the synthesis of a bis(carbene)ruthenium–tungsten complex (**771**) by coupling of (η^6-1,2,4,5-tetramethylbenzene)$Ru(Cl)_2(PMe_3)$ with tungsten–carbene complex **769** [605]. Complementary synthesis of **771** using a propargyl alcohol-containing ruthenium–carbene complex was also reported. Allenylidene complexes were proposed as intermediates in the ruthenium-catalyzed isomerization of propargyl alcohols to α,β-unsaturated aldehydes [606]. The importance of cumulenylidene-type resonance forms for various metal acetylide complexes was also noted [607]. Structural effects

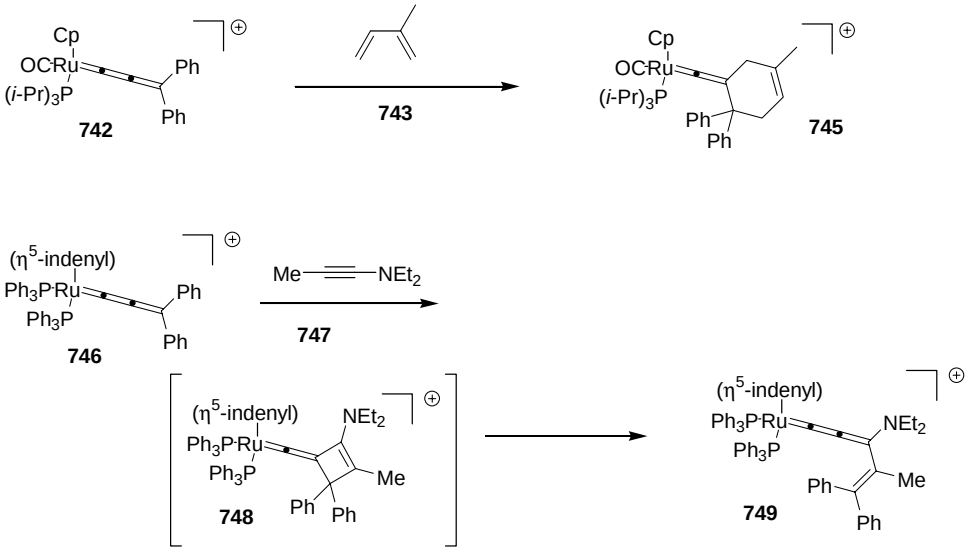




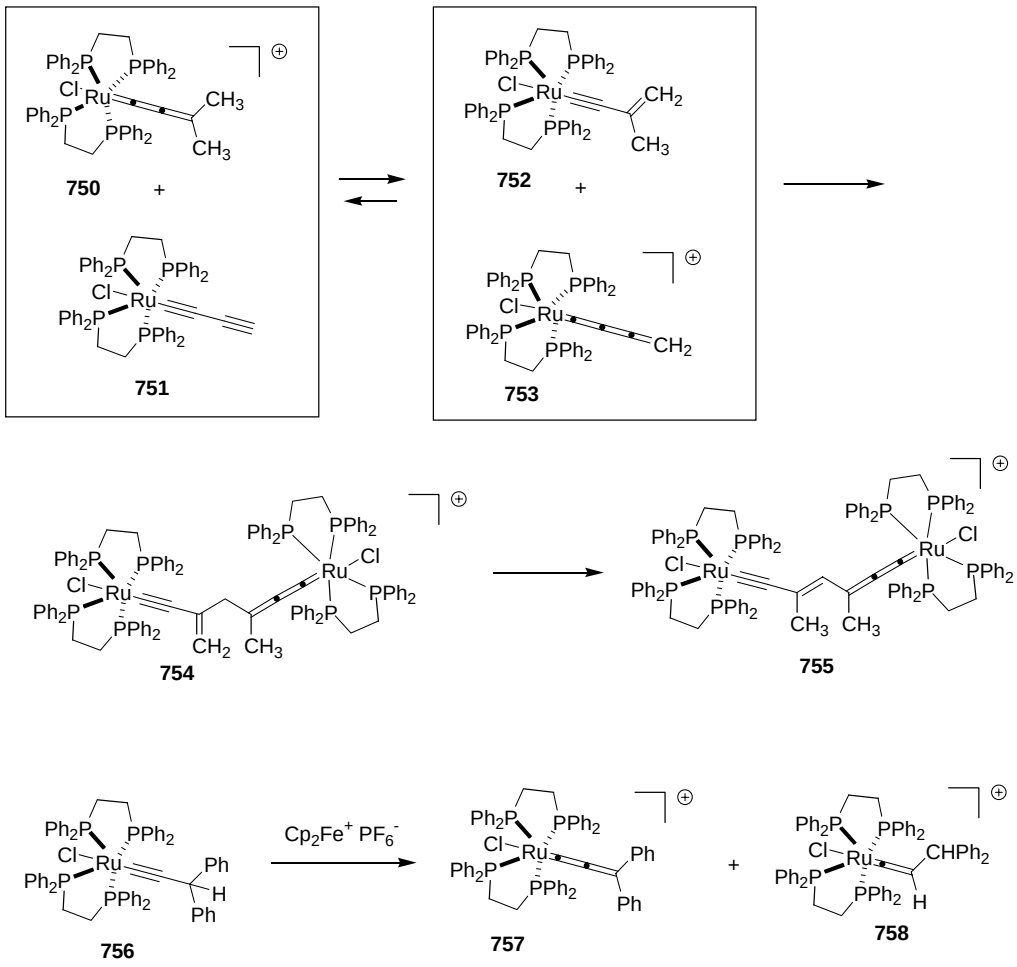


L = P(*t*Bu)$_2$CH$_2$CH$_2$Ph

Scheme 80.



Scheme 81.



Scheme 82.

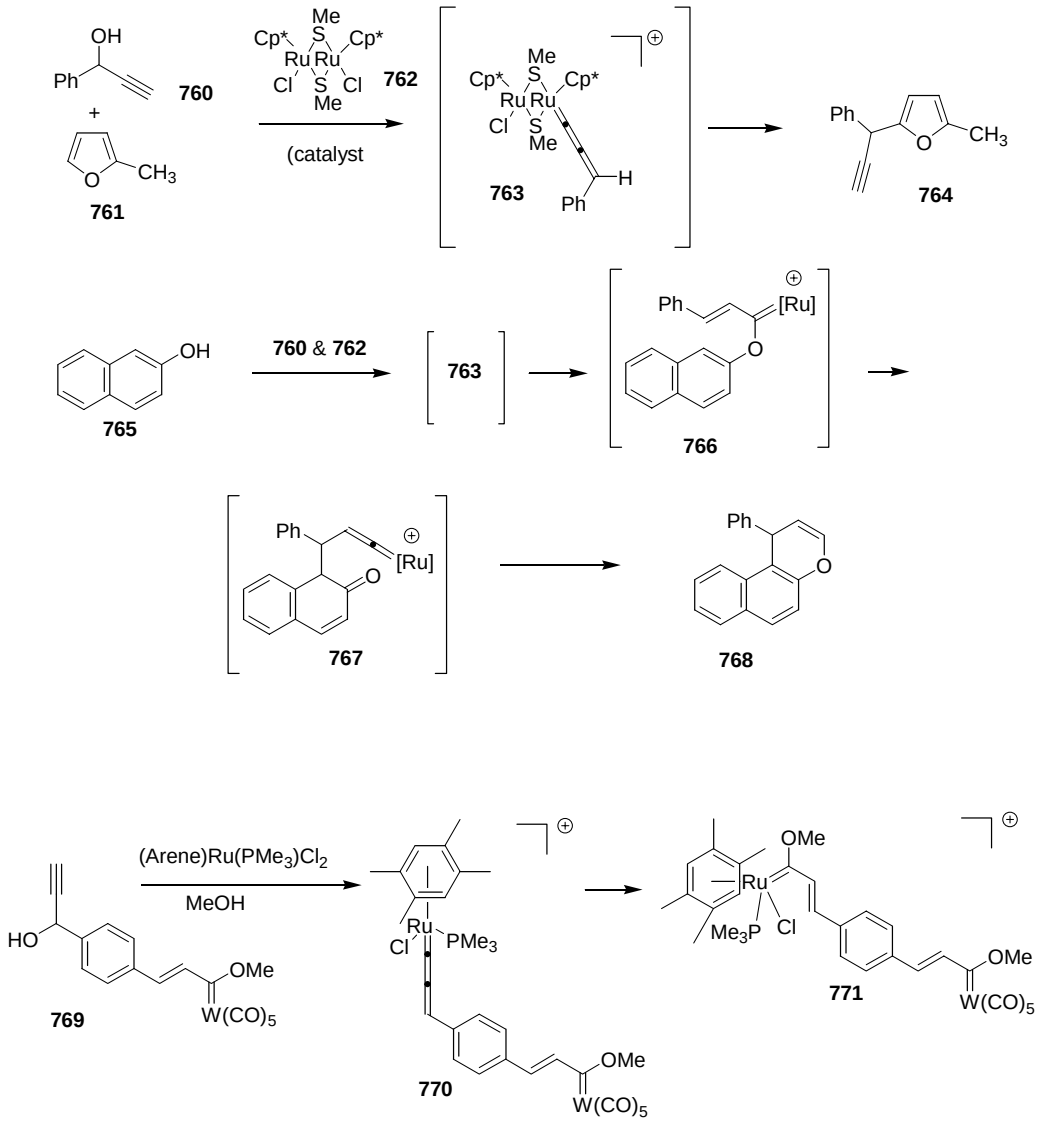
for cumulenylidene-linked metals were studied using DFT [608].

2.3.6. Group IX metal–carbene complexes

2.3.6.1. Simple carbene complexes. Several iridium complexes (e.g. **777**, Scheme 84) were prepared from the reaction of iridium ethylene complexes (e.g. **775**) with diaryl diazomethane derivatives [609]. These carbene complexes were transformed to other carbene complexes through ligand substitution processes. Protonation resulted in iridium hydrides (e.g. **778**). Reaction with diphenylacetylene resulted in alkyne insertion products (e.g. **779**). Diantimony–chloroiridium–carbene complex **780** was treated with base to afford the corresponding hydroxyiridium–carbene complex **781** [610]. Thermolysis of diantimony–rhodium analog **782** led to the triply bridged dirhodium species **783** [611]. Treatment of the triply-bridged rhodium–carbene complex with carboxylate anions led to ligand-substituted products (e.g. **784**). The bridge remains intact during substitution by carboxylate and acetylacetonate ligands. Chloro complex would undergo bridge cleavage upon treatment with an excess of bulky phosphines to afford the mononuclear carbene species **785**.

Several Bertrand-type carbene–rhodium complexes (e.g. **788**, Scheme 85) were synthesized directly from the stable carbene through ligand-substitution processes [612]. The rhodium–carbon bond length (2.096 Å) is suggestive of predominantly single bond character in the rhodium–carbene bond.

The coupling of iridium complex **791** (Scheme 86) with the organolithium reagent derived from iodide **790** led to a mixture of iridabenzvalene **792**, iridabenzene **794**, and Cp–iridium complex **795**. Thermolysis of iridabenzvalene **792** resulted in isomerization to iridabenzene derivative **796** [613], which provided the Cp–iridium complex **795** upon extended thermolysis. The enhanced reactivity of iridabenzene **796** compared to **795** was attributed to steric destabilization of this complex due to steric interaction between the bulky phenyl group and the ligands at iridium. Iridapyrroles (e.g. **797**) were produced in the thermolysis of alkyl(alkenyl)iridium complexes (e.g. **796**) [614]. Protonation of the irridapyrrole complex **797** afforded internally-coordinated β,γ-unsaturated imine complexes **799** and **800**. A stable cationic carbene complex (**802**)

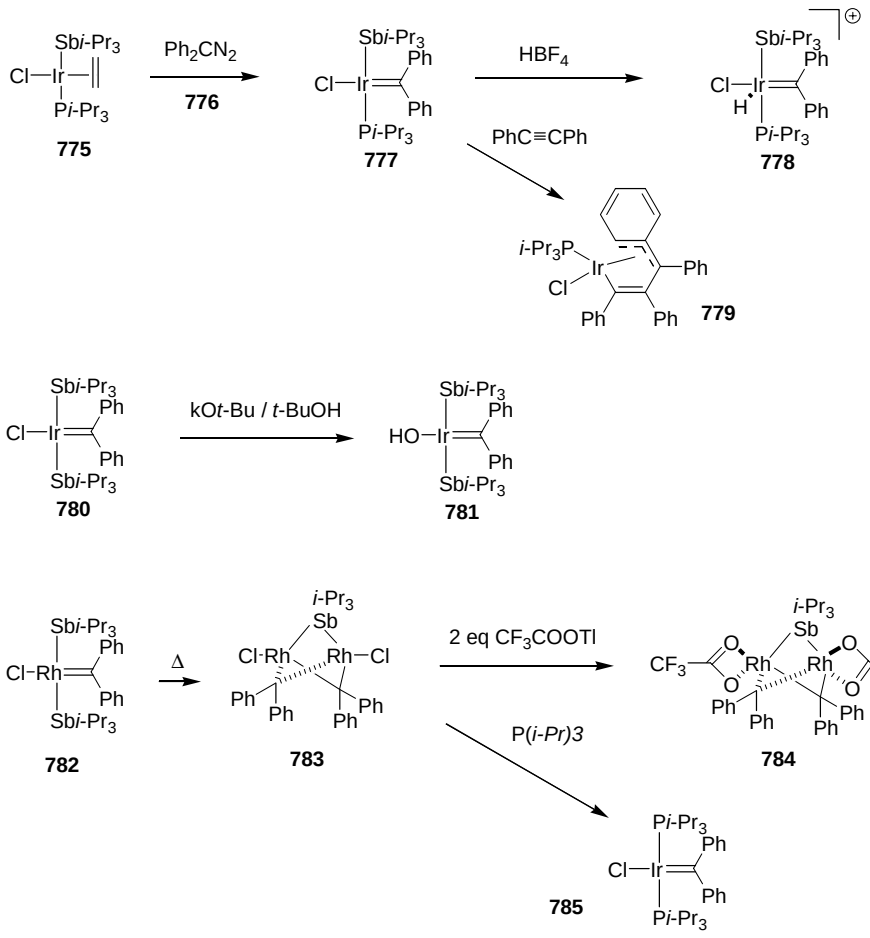


Scheme 83.

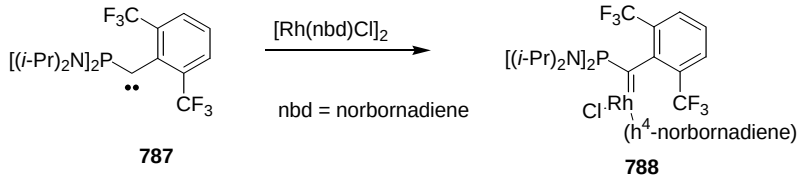
was obtained upon protonation of trimethyliridapyrrole **801**.

Other studies of group IX metal–carbene complexes (excluding cumulenes) include: (1) synthesis of bis(diisopropylamino)carbene–rhodium and iridium complexes and comparison with Arduengo-type metal–carbene complexes [615]; (2) formation of bridging carbyne complexes (e.g. **804**, Scheme 87) through reaction of bridging hydride complex **803** with isocyanides [616]; (3) formation of bis(heteroatom) cyclic carbene complexes (e.g. **806**) through aldol-like reactions of α-isocyano ester complexes (e.g. **805**); a low degree of diastereoselectivity favoring the depicted stereoisomer was observed [617]; and (4) proposed formation of iridium–carbene complex **808** as an intermediate in the transformation of trifluoroethyliridium complex **807** into the trihydride complex **809** and partially fluorinated ethane derivatives [618].

2.3.6.2. Cumulene complexes. Similar synthetic procedures and reactivity patterns were generally observed for groups IX and VIII (Schemes 73 and 79) metal–cumulene complexes. Formation of rhodium–vinylidene complexes (e.g. **813**, Scheme 88) through coupling of terminal alkynes with a rhodium-sulfonate complex (e.g. **812**) was reported [619]. Treatment with an excess of the alkyne leads to alkynyl(vinylidene)rhodium complexes (e.g. **814**). Treatment of these complexes with CO leads to enynyl–rhodium complexes (e.g. **815**) via migration of the alkynyl ligand. Rhodium–vinylidene complexes of general structure *trans*-[RhX(=C=CHPh)(P*i*-Pr$_3$)$_2$] were prepared and their vibrational spectra examined for a variety of different X substituents [620]. The vibrational spectra were also calculated by DFT. The trans influence of a series of ligands on the metal–carbon bond of vinylidene complexes was evaluated.



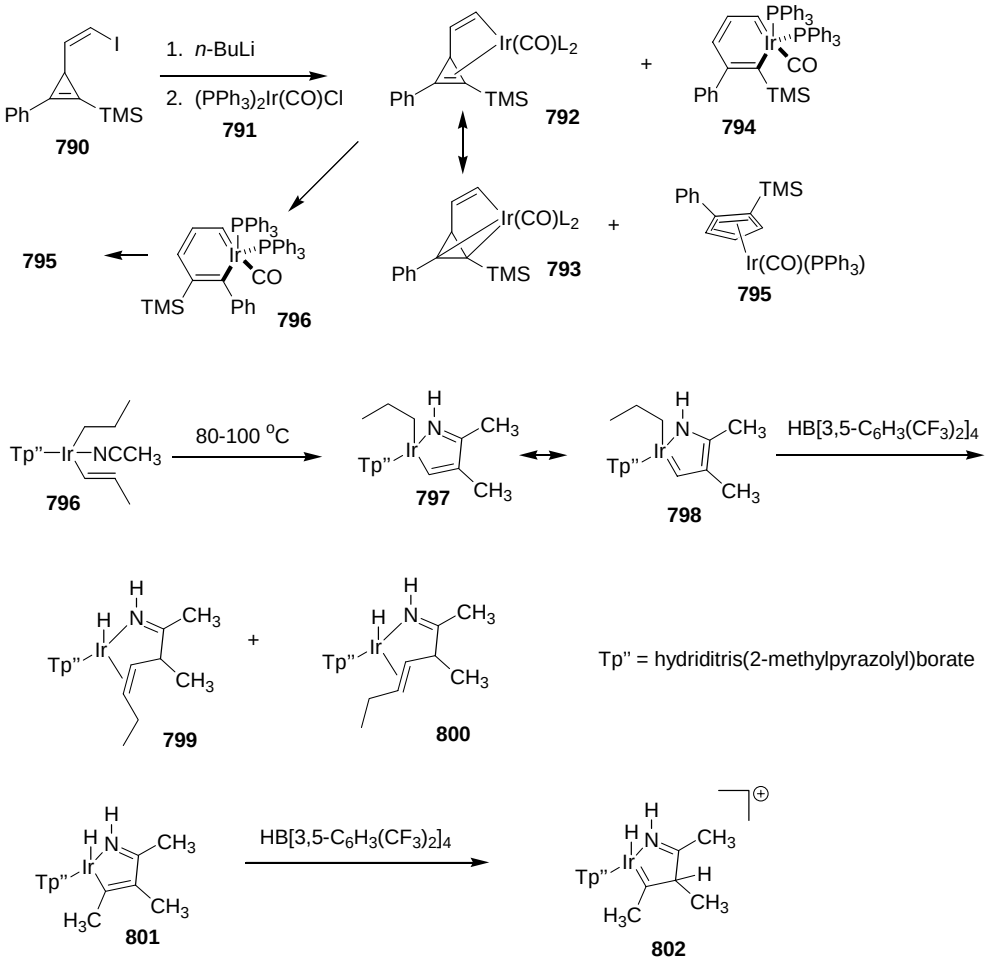
Scheme 84.



Scheme 85.

Several processes reported in 2002 proposed group IX metal–vinylidene complexes as intermediates. The coupling of rhodium/iridium dihalide **816** (Scheme 89) with terminal alkynes in water was reported [621]. Formation of the β-rhodium enone derivative **819** was observed from the rhodium system. A mechanism involving formation of the vinylidene (**817**), followed by hydration to afford the acyl complex (**818**), followed by alkyne insertion was proposed. The analogous acyliridium complex intermediate **818** undergoes deinsertion of CO followed by protonation of the benzyl ligand to afford iridium carbonyl complex **820** and toluene. A similar reaction process was noted for an iridium-arsine analog of complex **816** [622]. The formation of alkoxycarbene–iridium complexes from the reaction of iridium halides with terminal alkynes in the presence of methanol was reported [623]. Iridium vinylidene complexes (e.g. **823**) were proposed as intermediates in the synthesis of cross-conjugated alkenes (e.g. **825**) from alkynes and vinyliridium complex **821** [624]. Initial reaction in the presence of trimethylamine-*N*-oxide affords the alkynyliridium complex **822**, which affords the triene derivative upon treatment with HBF_4. A mechanism involving migration of a vinyl group to the carbene carbon followed by reductive elimination was proposed.

Reaction of rhodium–allenylidene complex **828** (Scheme 90) with various reagents was reported [625]. A simple ligand exchange resulting in complex **834** was observed upon reaction with NaCp. Reaction with HCl or Cl_2 led to the corresponding allenylrhodium–halide complexes (e.g. **831**). Reaction with vinylmagnesium bromide led to



Scheme 86.

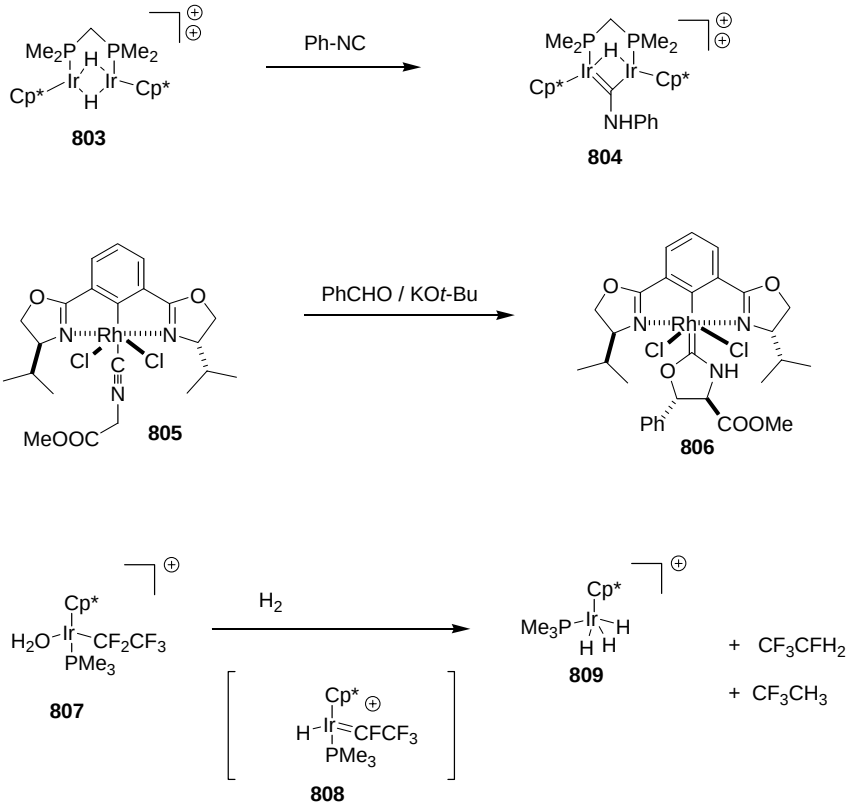
the π-allyl complex **829**, which afforded to allenyl complex upon treatment with CO. Reaction with diazomethane led to the η^2-tricumulene complex **832**; a related compound (**833**) was formed by treatment with iodomethane. Reaction with phenylacetylene led to a π-allyl complex, **836**. A mechanism involving [2+2]-cycloaddition to the Rh–C double bond followed by ring opening to afford carbene complex intermediate **835**, followed phosphine addition to the carbene ligand and η^3-coordination was proposed.

The synthesis of C4-cumulenylidene–iridium complex **838** (Scheme 91) was reported [626]. The most satisfactory synthetic route involved the addition of metal hydride **836** to the enynyl triflate **837** in the presence of triethylamine. The reactivity profile of this complex was determined. Reaction with CO afforded pentacoordinate complex **839**. Treatment with HCl or trifluoroacetic acid led to formation of the β,γ–π-bond addition products (e.g. **840**). Reaction with various nucleophilic reagents led to ligand substitution products (e.g. **841**). The methylirdium complex underwent migratory insertion by addition of CO, leading to compound **842** after a 1,3-shift of iridium.

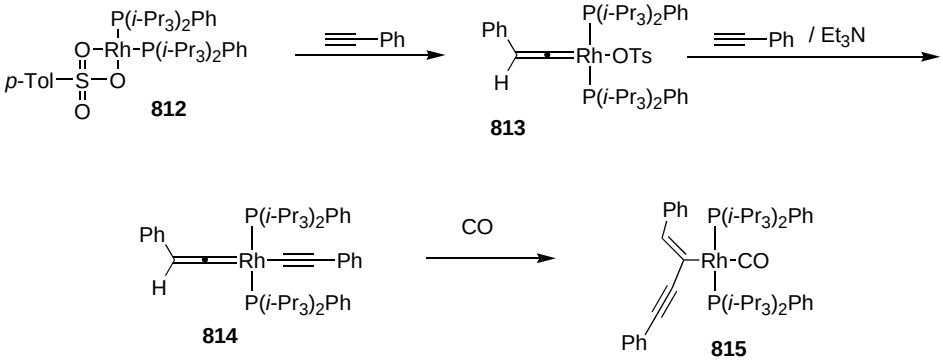
2.3.7. Group X metal–carbene complexes

The nickel–carbene complex **846** (Scheme 92) was prepared by treatment of nickel complex **845** with diphenyl diazomethane, followed by reaction with catalytic samarium(III) triflate to convert the diazo complex to a carbene complex [627]. The reactivity of the carbene complex with various substrates was reported. Malonate complex **847** was produced from reaction with CO_2. Formation of diphenylketene (**849**) and the dicarbonyl complex **848** was observed upon treatment with CO. Carbene addition products (**850**, **851**) were obtained upon treatment with diphenylketene or SO_2. Protonation led to the cationic nickel complex **852**.

Other studies leading to the formation of group X metal carbene complexes are depicted in Scheme 93, and include: (1) formation of a platinabenzene (**855**) by treatment of the organolithium reagent derived from alkenylcyclopropene **853** with $Pt(COD)Cl_2$ [628]; (2) formation of a palladium dicarbene complex (**857**) was formed from monocarbene complex **857** and the ligand **856** [629]; (3) generation of palladium- or platinum–carbene complexes (e.g. **860**) through intramolecular coupling alcohols with



Scheme 87.

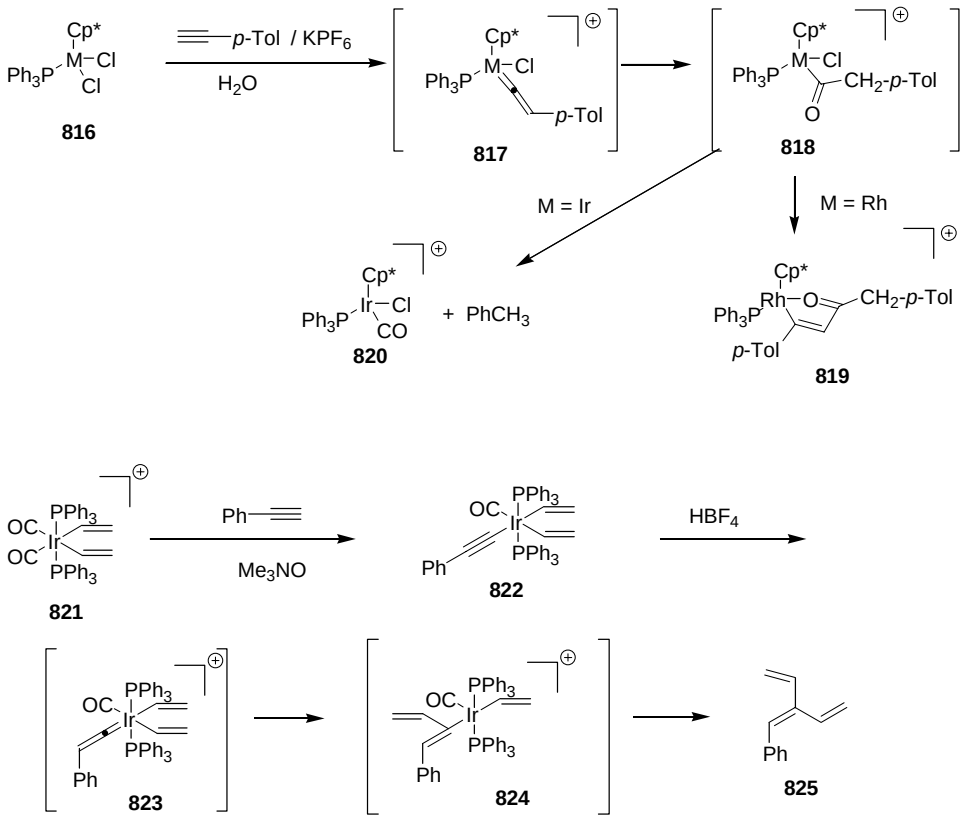


Scheme 88.

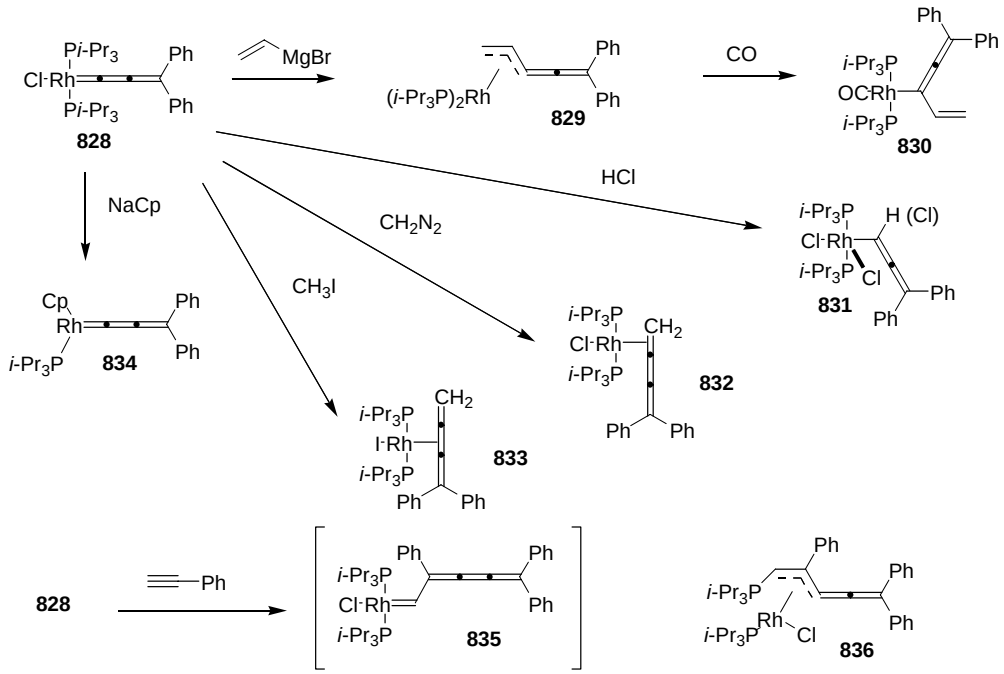
isocyanide ligands coordinated to palladium [630]; and (4) generation of platinum–carbene complexes from the reaction of diaryldiazo compounds with $[PtCl_2(PPh_3)_2]$ or $[Pt(PPh_3)_2(CH_3CN)_2][BF_4]_2$ and subsequent observation by FAB mass spectrometry [631].

Platinum–carbene complexes (e.g. **869–871**, Scheme 94) were proposed as intermediates in the isomerization of dienynes of general structure **861** to cyclic products **862–865** [632]. Compound **862** arises from platinum-catalyzed enyne-metathesis. Compound **863** arises from intramolecular cyclopropanation through carbenocarbene complex resonance form (**870**) of the platinum–alkyne complex resulting in intermediate **871**, which undergoes intramolecular cyclopropanation to afford **863**. Compounds **864** and **865** arise through a 1,2-shift of the oxygen in ylide resonance form (**867**) of the platinum alkyne complex resulting in intermediate carbene complex **869**, which undergoes intramolecular cyclopropanation with either alkene. The 1,2-shift process is unique to systems where X = acyl since this process can occur by carbonyl ylide formation followed by ring opening.

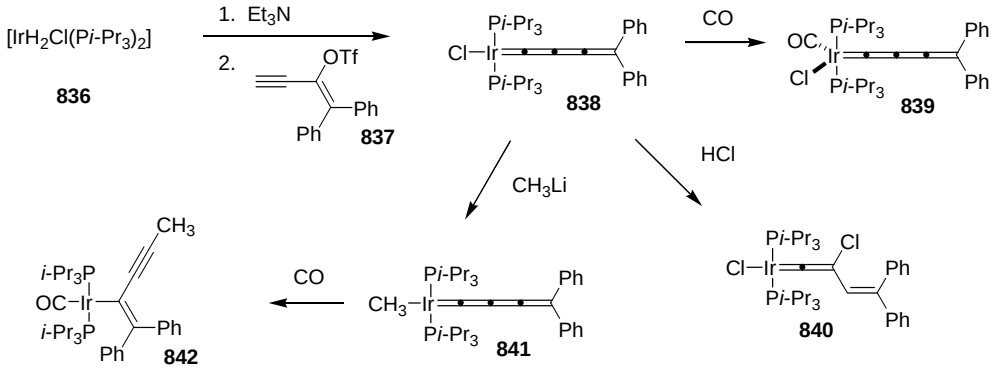
Palladium(II)-catalyzed cyclopropanation of alkenes by diazomethane was studied by DFT [633]. The calculations show that a catalytic cycle involving palladium(0) intermediates is energetically more reasonable. Elimination of nitrogen from a palladium diazomethane complex to form a palladium(0) carbene complex is the rate-determining step of the reaction. A DFT study of Simmons–Smith and



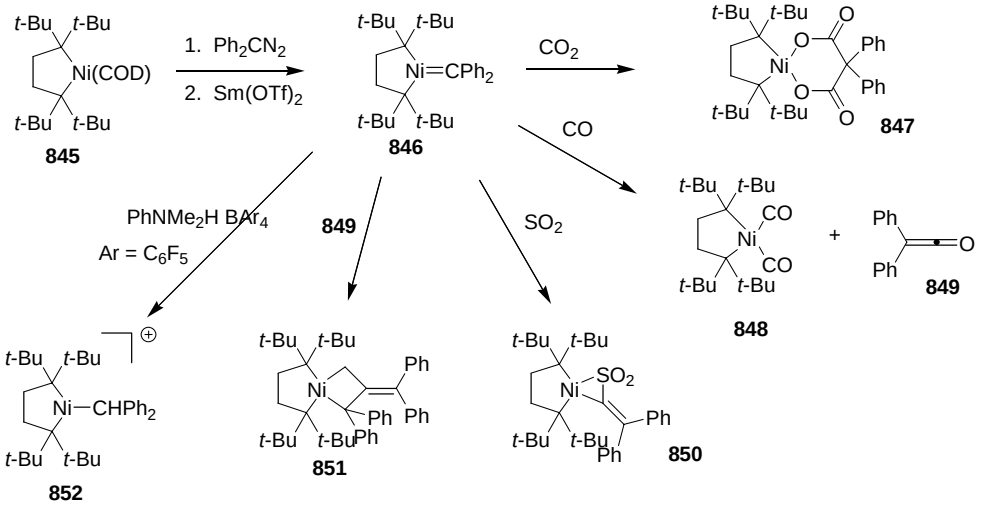
Scheme 89.



Scheme 90.



Scheme 91.



Scheme 92.

palladium-catalyzed cyclopropanation was also reported [634].

3. Metal–carbyne or metal-alkylidyne complexes

3.1. Review articles

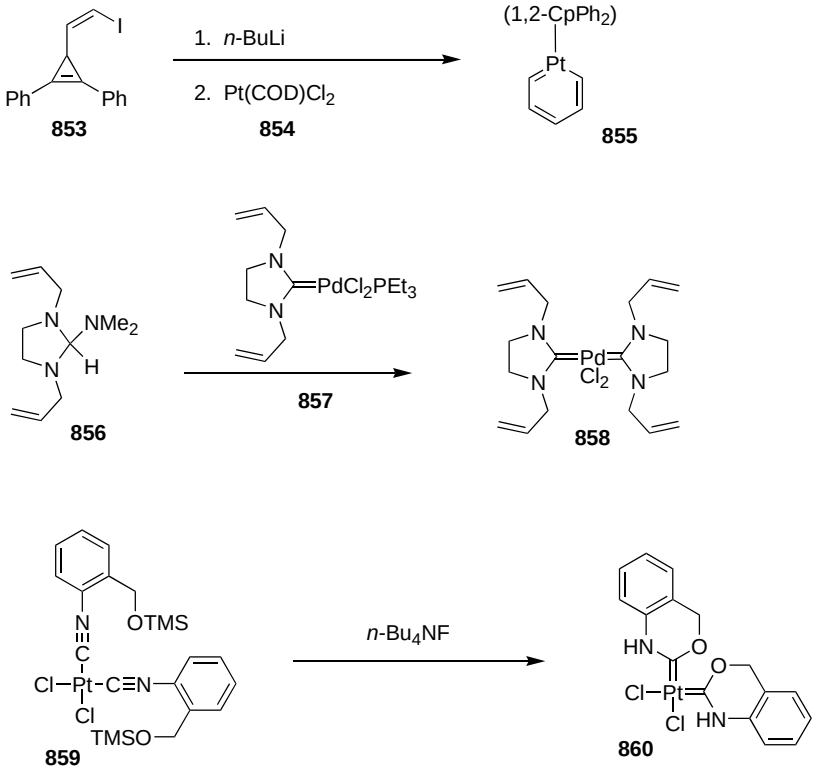
Review articles featuring metal–carbyne complexes which appeared in 2002 include: (1) reactions of manganese and ruthenium carbyne complexes with carbonylmetal anions [635]; and (2) high oxidation state carbon–metal multiple bonds [52].

3.2. Synthesis and/or generation

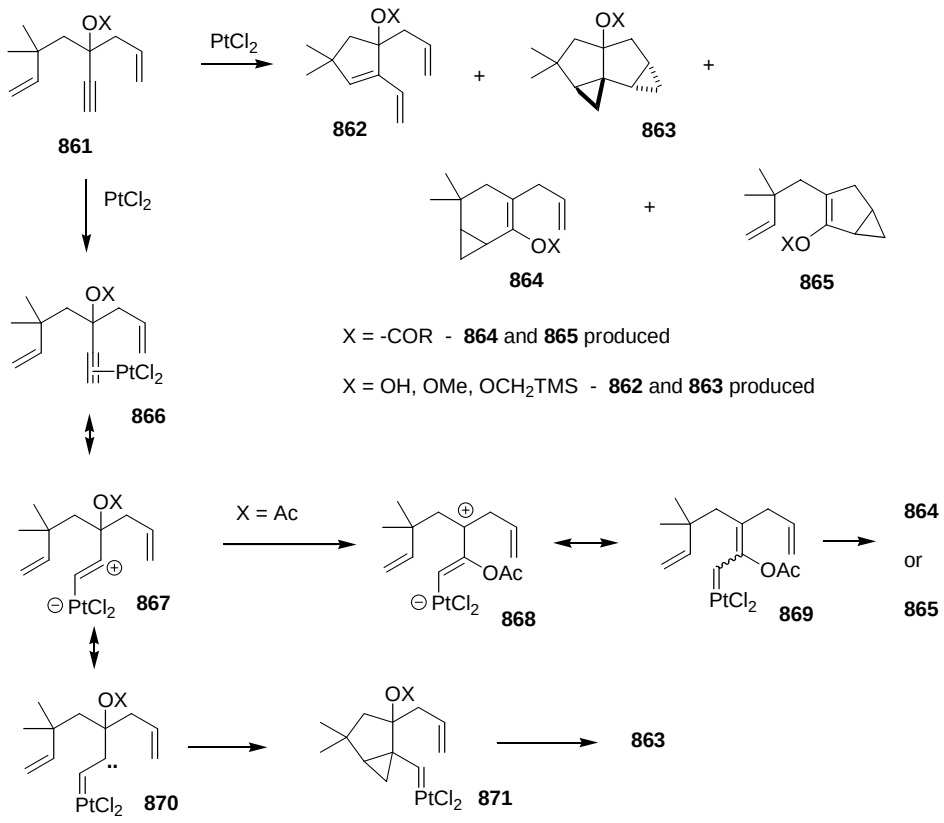
The cothermolysis of chromium complexes **875** (Scheme 95) and **876** led to the carbyne complex **877** in low yield, accompanied by numerous polynuclear chromium compounds [636]. Coupling of related compound **878** with **876** also afforded a carbyne complex (**879**), accompanied by mononuclear compounds **880–881** and a polynuclear chromium compound [637].

Synthesis of alkynylcarbyne–tungsten complexes (e.g. **884–887**, Scheme 96) was reported [638]. These complexes were most efficiently prepared through nucleophilic addition of an alkynyl anion to tungsten hexacarbonyl followed by treatment of the acylate complex (**883**) with triflic anhydride or oxalyl chloride. Ligand exchange reactions with NaCp, NaTp, NaTp', and TMEDA were reported.

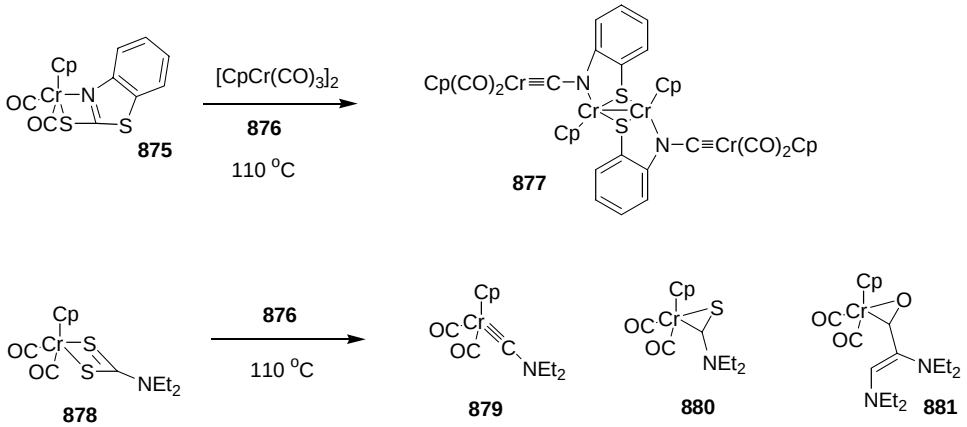
The formation and reactivity of tungsten–carbyne complexes (e.g. **890**, **891**, Scheme 97) was studied experimentally and theoretically [639]. DFT calculations predict that overall conversion of **888** and acetylene to the carbyne complex **890** is energetically favorable only for the tungsten–hydroxy complex. Reaction with molybdenum or sulfur analogs was endothermic. These calculations also predict that the tungsten–sulfur system would stop at the bridging alkyne complex (**889**) stage. This was verified experimentally by examination of the reaction between tungsten–carbyne complex **891** with thiol **892**. This



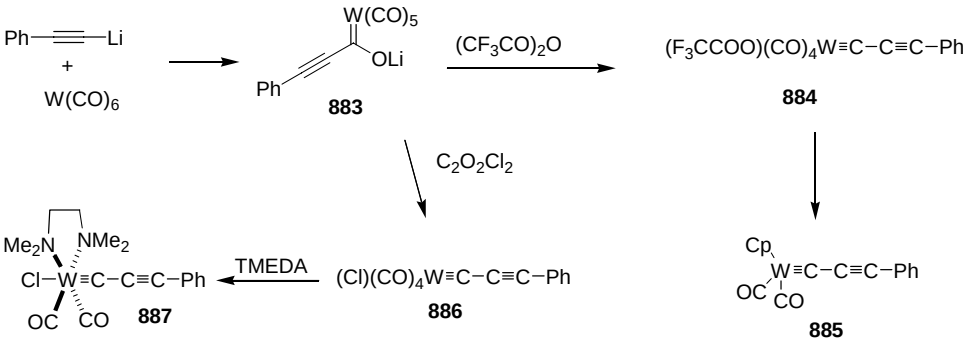
Scheme 93.



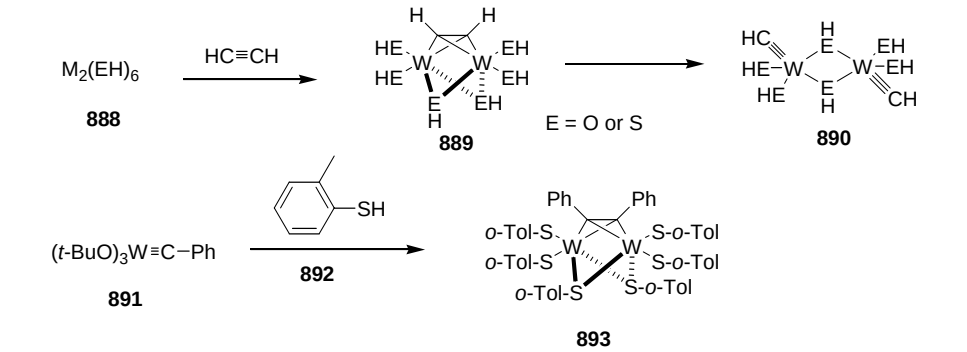
Scheme 94.



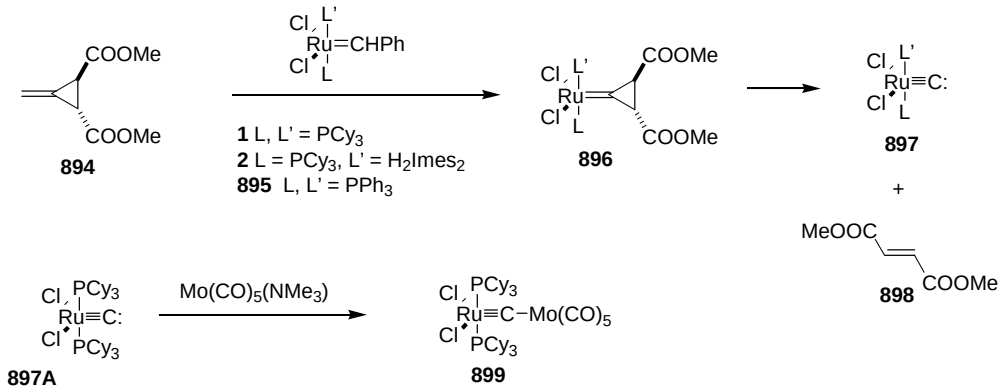
Scheme 95.



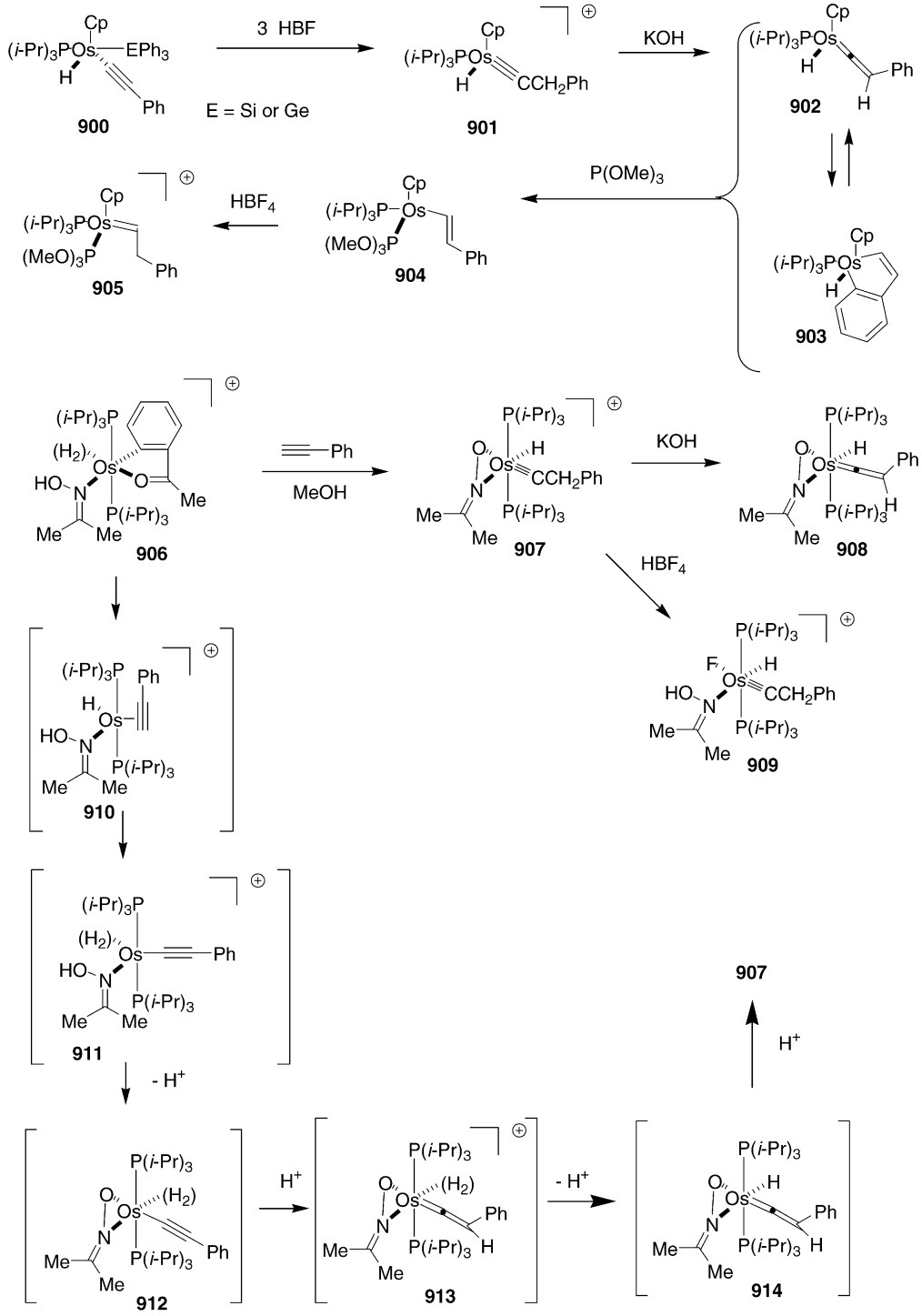
Scheme 96.



Scheme 97.



Scheme 98.



Scheme 99.

complex led to the stable alkyne-bridged complex **893** and did not convert to the dimeric carbyne complex.

A novel ruthenium–carbide complex **897** (Scheme 98) was prepared through reaction of Grubbs catylysts 1 or 2 with methylenecyclopropane derivative **894** [640]. Byproducts from this reaction are styrene and dimethyl fumarate. The corresponding bis(triphenylphosphine) complex **895** afforded stable cyclopropylidene complex **896** (L,L′ = PPh_3) as previously reported, however **896** converted to the carbide complex **897** (L,L′: PCy_3) upon treatment with tricyclohexylphosphine [641]. A molybdenum complex (**899**) and a palladium complex of the carbide ligand were also prepared.

Cationic osmium–carbyne complexes (e.g. **901**, Scheme 99) were prepared through triple protonation of osmium-hydride alkyne complex **900** [642]. Deprotonation led to the neutral vinylidene complex **902** in equilibrium with intramolecular C–H oxidative addition product **903**. Reaction of this equilibrium mixture with trimethyl phosphite followed by protonation led to the cationic carbene complex **905**. Osmium–carbyne complexes (e.g. **907**) were also prepared from chelating acetophenone complex **905** and terminal alkynes [643]. Deprotonation of the carbyne complex afforded the vinylidene complex **908**. Protonation transforms the oximate ligand to an oxime ligand (formation of complex **909**). Formation of the carbene complex occurs through the complex series of mechanistic events depicted in Scheme 99. This mechanism was supported through deuterium labeling studies.

Some papers in the carbene section feature minor segments on carbyne chemistry. These studies include reference [457] (Scheme 14), and [596,597] (Scheme 80).

3.3. Reactivity

3.3.1. Addition reactions of metal–carbyne complexes

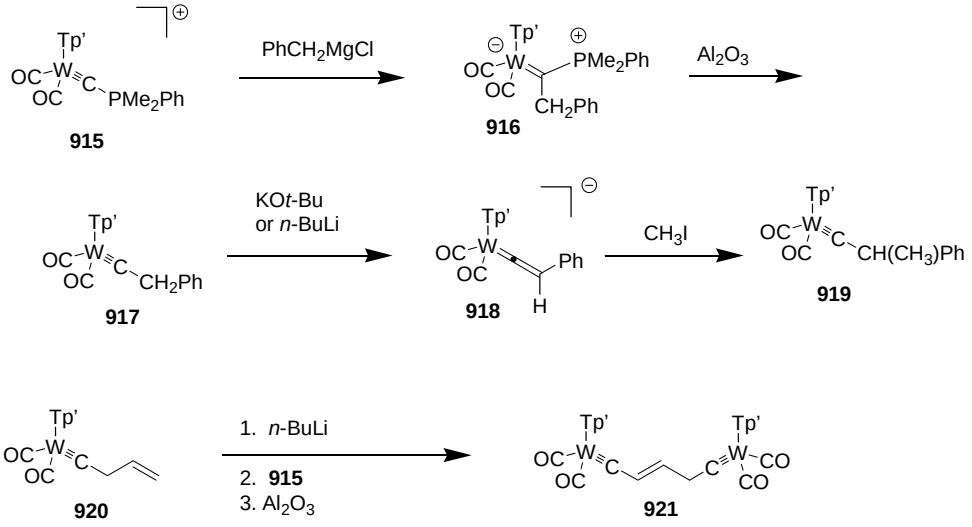
Cationic carbyne complex-phosphonium salt **915** (Scheme 100) was transformed to alkylcarbyne complexes (e.g. **917**) through reaction with Grignard reagents followed by treatment with alumina [644]. Further elaboration of carbyne complexes through deprotonation followed by alkylation was reported (e.g. conversion of **917** to **919**). A ditungsten complex (**921**) was prepared through reaction of the anion derived from allylcarbyne complex **920** with carbyne–phosphonium salt **915**. Coupling of complex **915** with various aryloxide nucleophiles was also reported, which affords either the simple substitution products or the subsequent CO insertion products, η^2-ketenyl complexes [645].

The addition of multinuclear group VIII metal carbonyl anions (e.g. **923**, Scheme 101) to manganese– and rhenium–carbyne complexes (e.g. **922**) was investigated [646]. Formation of heterotrimetallic compounds (e.g. **924**) was reported from these reactions. Reaction of complex **922** with molybdenum–manganese compound **925** led to manganese–carbene complex **926** and bimetallic species **927**.

3.3.2. Alkyne metathesis

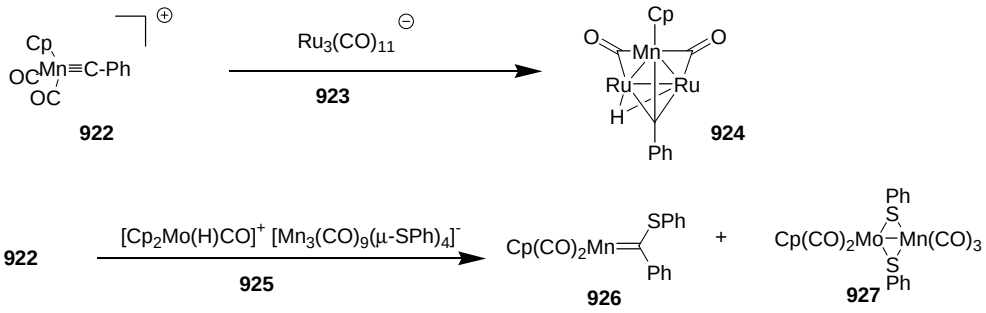
Alkyne metathesis, which involves metal–carbyne complexes as intermediates, has been covered comprehensively regardless of whether the initiator is a carbyne complex. General equations describing the mechanism and precedented modes are presented in Scheme 102. Several reports using alkyne metathesis for natural product synthesis and for polymer synthesis appeared in 2002; representative substrates and products are depicted in Fig. 15.

High molecular weight alkyne-containing polymers were prepared through ADIMET polymerization (see Scheme 102) of acyclic diynes (e.g. **928**, Fig. 15) and **929** [647–649]) using the molybdenum hexacarbonyl/2-chlorophenol system. This catalyst system also was effective at promoting the cross metathesis of enyne **930** and various alkynes [650]. RCAM (e.g. conversion of **930** to **931**) was also reported using a similar system that employs 2-fluorophenol as a substitute for 2-chlorophenol [651]. Compound **936** was made through either RCM or RCAM [652]. Use of RCM is complicated since both the E and Z alkene form, however the pure Z alkene can be obtained though alkyne metathesis followed by partial hydrogenation of alkyne metathesis product **934**. The alkyne

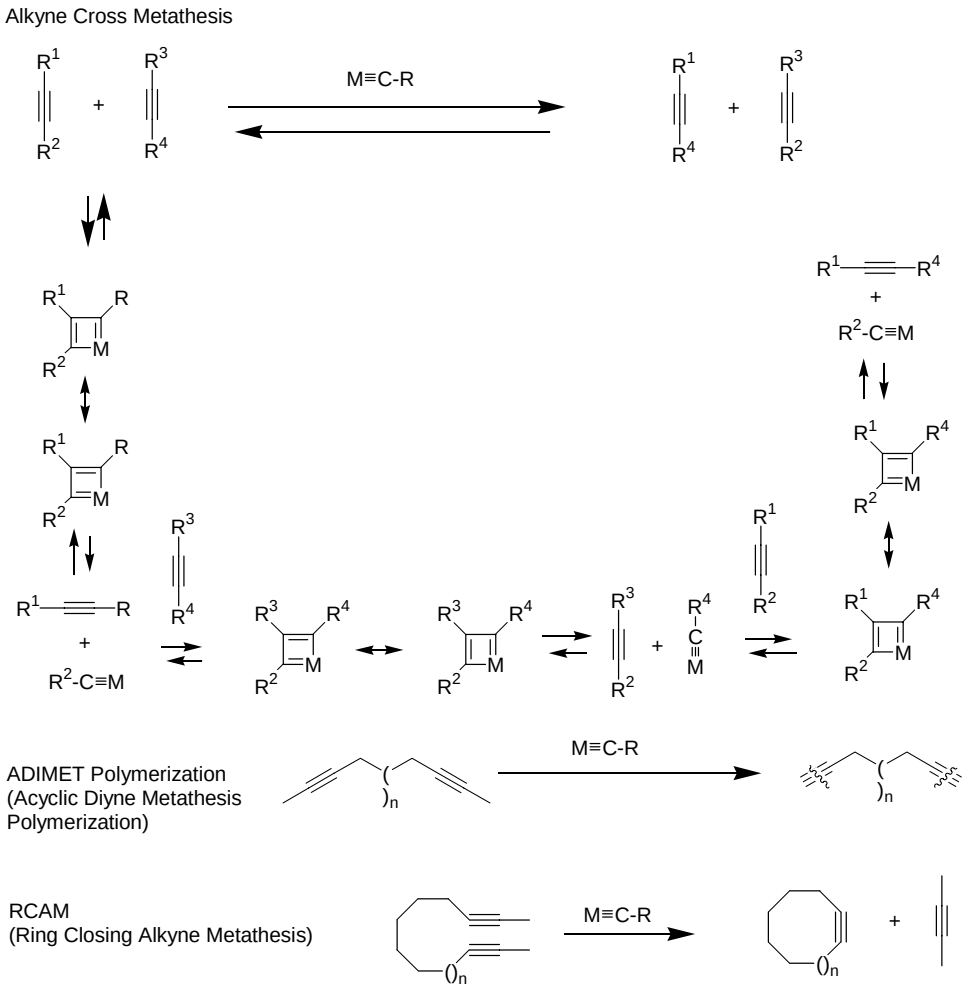


Tp' = hydridotris(3,5-dimethylpyrazoyl)borate)

Scheme 100.



Scheme 101.



Scheme 102.

metathesis was initiated using either the a tungsten–carbyne complex [(*t*-BuO)$_3$W≡C–C(CH$_3$)] or a molybdenum hexacarbonyl/phenolic compound system. Synthesis and use of [(*t*-BuO)$_3$W≡C–SnPh$_3$] as an alkyne metathesis catalyst was reported [653].

3.3.3. Other processes involving metal–carbyne complexes

Treatment of osmium–carbyne complex **937** (Scheme 103) with potassium bromide in THF led to the alkene complex **940** [654]. A mechanism involving conversion to the neutral hydrido vinylidene complex (**938**) by deprotonation, followed by hydride migration to form alkenylosmium complex **939**, followed by ligand attachment and reductive protonolysis of the alkenyl ligand and complexation was proposed. This mechanism was supported by deuterium-labeling studies. This result is in contrast to previously-reported reaction of **937** with trimethyl phosphite, which leads to the carbene complex **941**.

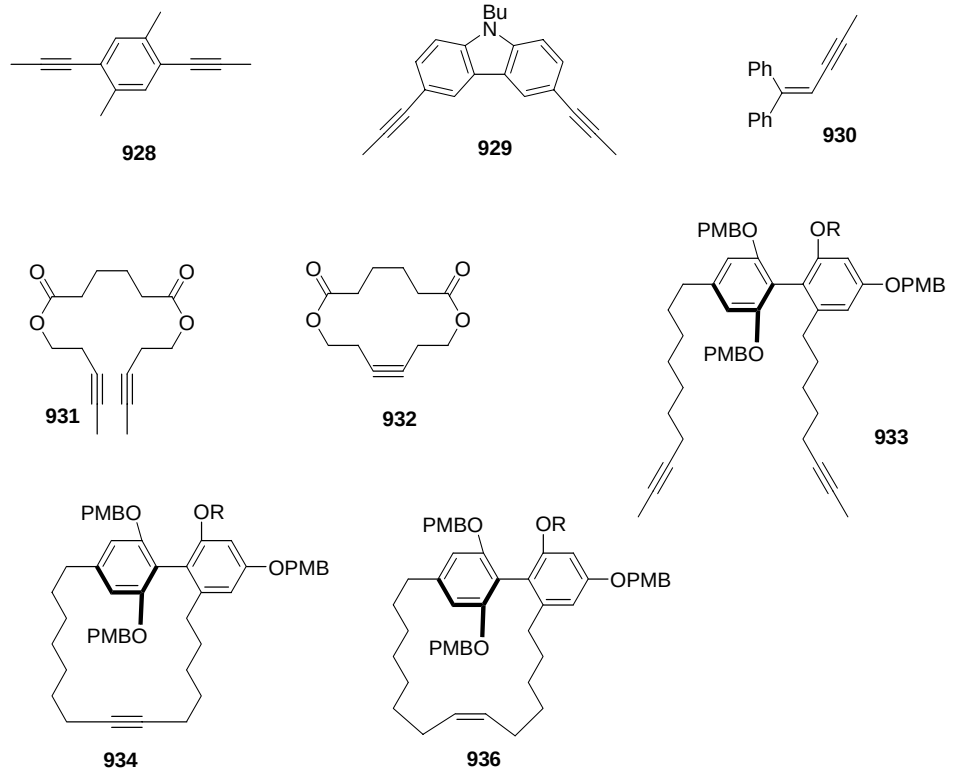
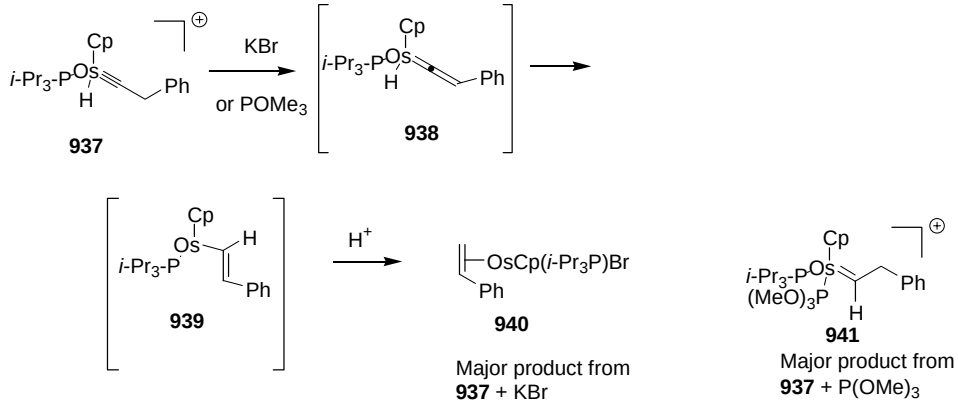


Fig. 15. Alkyne metathesis substrates and products.

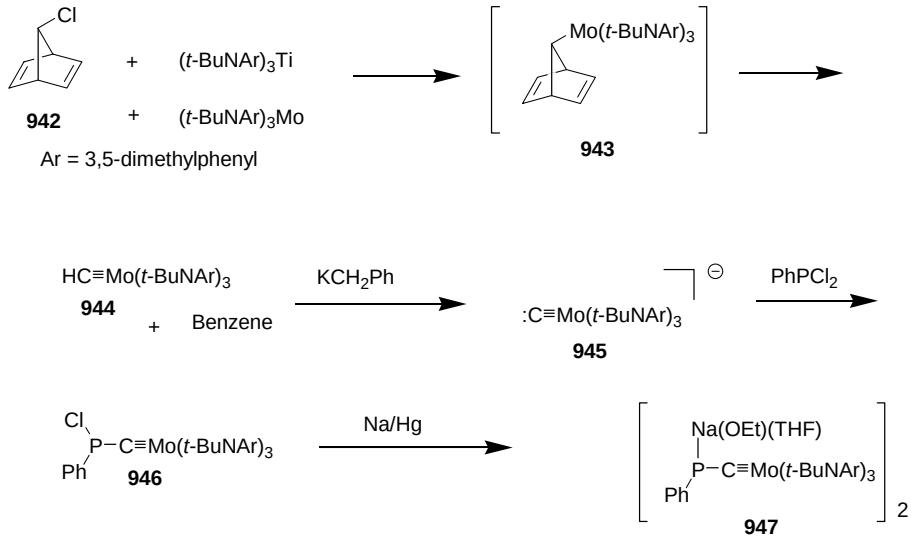


Scheme 103.

Synthesis and elaboration of molybdenum–carbyne complex **944** (Scheme 104) was reported [655]. Synthesis of **944** was accomplished through benzene elimination of intermediate norbornadiene derivative **943**. Initially formed carbyne complex **944** was converted to the anionic carbide complex **945** through reaction with benzylpotassium. Phosphorylation of **945** afforded carbyne complex **946**, which was transformed to the anionic dimeric structure **947** by sodium amalgam reduction.

3.4. Mechanistic/structural studies

Several mechanistically/structurally-oriented studies of the reactions of metal–carbyne complexes were reported in 2002. The linearity of the W≡C–H bond was verified by single crystal neutron diffraction analysis [656]. The effect of trans carbyne (and nitrosyl, nitride) ligands on W–H bond strength and polarizability was studied by DFT [657]. The W–H bond strength and polarizability was in the order H–W–N≡O > H–W≡C–R > H–W≡N. Multinuclear tungsten–carbyne complexes linked to the other metal through an isocyanide ligand of general structure W≡C–C_6H_4–N≡C–metal were prepared [658]. The focus of the manuscript was the vibrational spectra of these complexes. The C≡N, C≡O, and C≡M of these complexes were studied by IR and Raman spectroscopy. The effect of pressure on the vibrational spectra of these complexes was also determined. Carbyne complexes and vinylidene



Scheme 104.

complexes were identified by inelastic neutron scattering during methane decomposition over ruthenium and alumina [659]. Silica-bound rhenium carbene–carbyne complexes were characterized by 2-D J resolved NMR [660].

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