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Review

The chemistry of the carbon-transition metal double and triple bond: Annual survey covering the year 2014☆

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Contents

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ABSTRACT

This is a review of papers published in the year 2014 that focus on the synthesis, reactivity, or properties of compounds containing a carbon-transition metal double or triple bond.

☆ For 2013, see J.W. Herndon, Coord. Chem. Rev. 286 (2015) 30.

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1. Introduction

This survey is intended to be a comprehensive synopsis 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 using conventional catalysts are not covered, unless there is some effort to characterize the carbene complex intermediate or a non-traditional reaction pathway is noted. Several reviews in this area appeared in 2014 [1–8]. Although a determined effort has been made to include patents, in general, only patents listed in the sections "Organometallics and Organometallic Compounds" or "Catalysis, Reaction Kinetics, and Inorganic Reaction Mechanisms" of *Chemical Abstracts* have been included. Patents that appeared in 2014 editions of *Chemical Abstracts* have been included. Only compounds that feature a multiple bond between a single carbon atom and a single transition metal are discussed in this survey, thus bridging carbene and carbyne complexes are not covered unless there is a multiple bond to at least one transition metal. The complexes of N-heterocyclic (or Arduengo) carbenes with transition metals have not been included since the π-acceptor component of these complexes is usually minimal, and thus there is no formal carbon–metal multiple bond [9]. The chemistry of NHC complexes was reviewed several times in 2014 [10–21], and several in languages other than English [22–24]. Every effort has been made to include NHC complexes where significant π-acceptor ability of the NHC ligand is noted. 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 [25] 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 instructions for authors in the *Journal of Organic Chemistry* [26] and the list of ligand acronyms in the Strem Catalog [27] (Fig. 1)).

NHC	N-heterocyclic carbene
Grubbs catalyst I	Structure **1** (Fig. 1)
Grubbs catalyst II	Structure **2** (Fig. 1)
Grubbs catalyst III	Structure **3** (Fig. 1)
Hoveyda–Grubbs catalyst	Structure **4** (Fig. 1)
Zhan catalyst	Structure **5** (Fig. 1)
Schrock catalyst	Structure **6** (Fig. 1)
Tp'	Tris(3,5-dimethylpyrazolyl)borate
Dipp	2,6-diisopropylphenyl
Tipp	2,4,6-triisopropylphenyl
E (as a substituent)	COOMe

Unless otherwise indicated, all alkanes and alkyl groups are assumed to be the straight-chain (*n*) isomer.

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

2. Metal–carbene or metal–alkylidene complexes

2.1. Review articles, highlights, and comments

Several reviews/highlights/comments covering aspects of metal–carbene complex chemistry appeared in 2014. Many articles focusing on some aspect of carbene complex-initiated olefin metathesis were published, including the following specific subjects: (1) the evolution of catalytic stereoselective olefin metathesis [28]; (2) development of cleaner olefin metathesis catalysts [29]; (3) key processes in ruthenium catalyzed olefin metathesis [30]; (4) olefin metathesis in the preparation of active pharmaceutical substances [31]; (5) industrially relevant olefin metathesis catalysts [32]; (6) olefin metathesis in the synthesis of natural products [33]; (7) multi-reaction processes involving Overman rearrangements, metathesis cyclizations, and Diels–Alder reactions [34]; (8) metathesis and polymerization [35]; (9) ROMP of eight-membered ring cyclic olefins [36]; (10) preparation of stereoregular polymers via ROMP [37]; (11) preparation of self-assembled supramolecular polymers [38]; (12) combining ROMP and thiol–ene coupling chemistry for preparation of linear and nonlinear macromolecules [39]; (13) synthesis of cyclo-polyolefins through ring expanding metathesis polymerization [40]; (14) precision polymers through ADMET polymerization [41,42]; (15) systematic studies of morphological changes of ADMET-derived precision polyethylene [43]; (16) concurrent cross-metathesis and enzymatic oxidation reactions [44]; (17) rhenium oxide-based olefin metathesis [45]; and (18) olefin metathesis over molybdenum-exchanged zeolites [46]. Additional reviews in languages other than English include: (1) olefin metathesis in complex synthesis [47]; (2) Z-selective olefin metathesis catalysts and their applications [48]; (3) modification of biodiesel using olefin metathesis [49]; (4) cyclic aminocarbene complexes (Bertrand carbene complexes) in olefin metathesis reactions [50]; (5) progress in ROMP of dicyclopentadiene [51]; and (6) the role MgO in WO_3/SiO_2 catalyzed olefin metathesis [52].

Several review articles report on synthesis of various compounds or compound classes where carbene complex initiated olefin metathesis is a commonly-employed synthetic route. Specific compounds or compound classes represented include: (1) tetrahydropyrans [53]; (2) cyclopentenones [54]; (3) 3,4,5-trisubstituted isoxazolines [55]; (4) carbocyclic nucleosides [56]; (5) lycopodium alkaloids [57,58]; (6) cyclic hydrazines and azo compounds [59]; (7) tropone and tropolone natural products [60]; (8) seven-membered ring natural products [61,62]; (9) tetrahydroisoquinoline-3-carboxylic acid derivatives [63]; (10) chalcones and their heterocyclic derivatives [64]; (11) marine-derived cyclic ethers [65]; (12) pericosine and related marine-derived carbasugar natural products [66]; (13) carbohydrate derived macrocyclic compounds [67]; (14) neurotrophic natural products [68]; (15) isodon diterpenes [69]; (16) non-isoprenoid polyene natural products [70]; (17) heterophosphacyclanes [71];

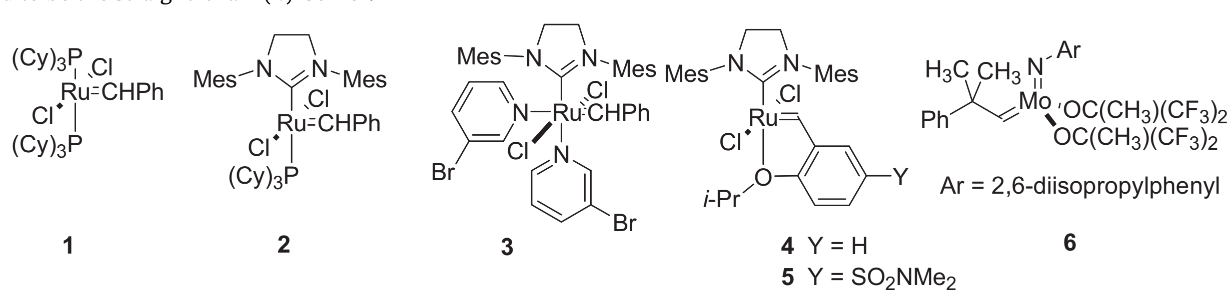

Fig. 1. Structures of alkene metathesis catalysts 1–6.